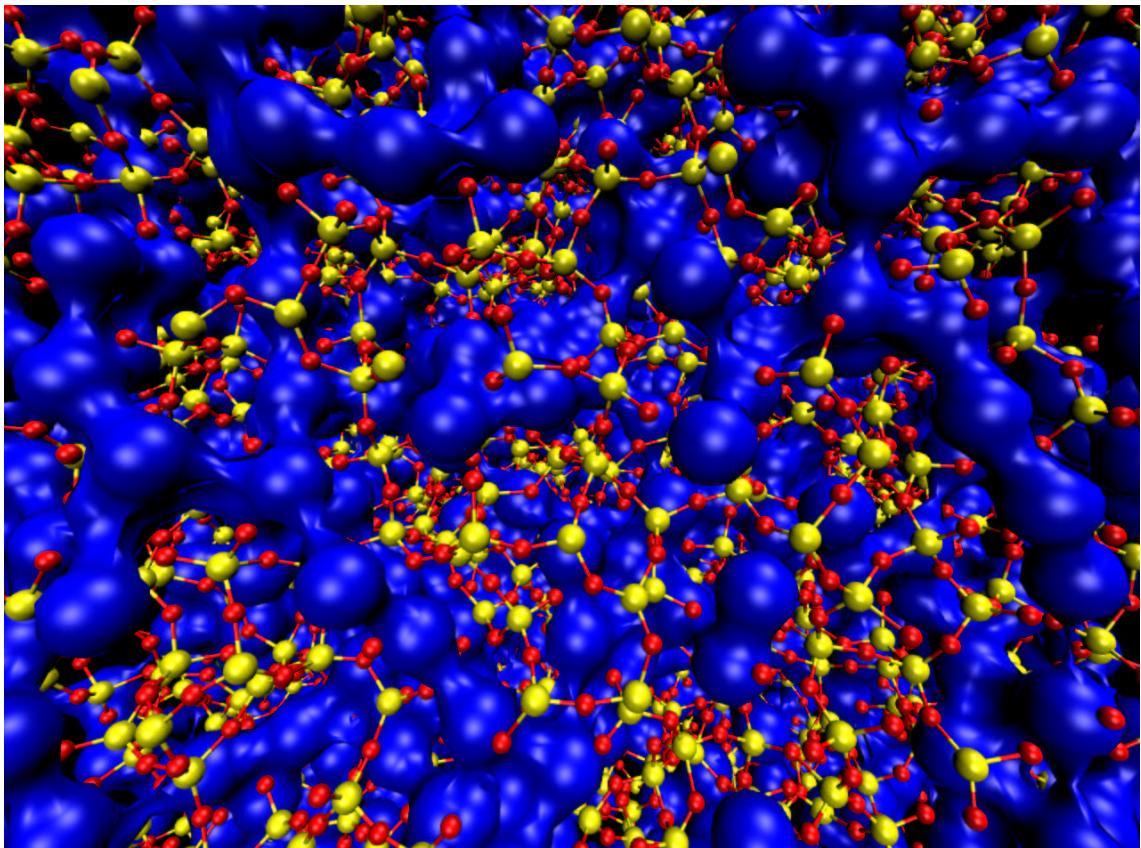


Jahresbericht 2003

des Lehrstuhls von Prof. Dr. Winfried Petry

Physik Department E13



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Titelbild:

Natriumsilikate stellen ein einfaches Analogon von komplexen geologisch und technisch relevanten Silikaten dar. Bis dato konnte jedoch nicht einmal in diesen Schmelzen geklärt werden, wie die Natriumatome in die Si-O-Struktur eingebaut sind und welche Prozesse im Detail zu der relativ schnellen Diffusion der Natriumionen und der nur schwachen Abhängigkeit der Viskosität von der Natriumkonzentration führen. In Zusammenarbeit mit Kollegen von der Universität Mainz und der Université Montpellier konnte in einer kombinierten Studie aus inelastischer Neutronenstreuung und klassischer Molekulardynamiksimulation die Ausbildung einer Natrium-Kanalstruktur auf intermediären Längenskalen nachgewiesen werden. Die Abbildung zeigt einen MD-snapshot der Natriumatome (blau) in einer Natriumtrisilikatschmelze bei 2100 K. Die Silizium- (gelb) und Sauerstoffatome (rot) sind verkleinert dargestellt: Die Natriumatome bilden ein perkolierendes Netzwerk aus Kanälen in der statischen Struktur eines stark gestörten Si-O-Tetraedernetzwerkes aus.

A. Meyer, J. Horbach, W. Kob, F. Kargl, H. Schober, Phys. Rev. Lett. (eingereicht)

Dezember 2003
Andreas Meyer

Vorwort

Mit dem Jahr 2003 blicken wir auf ein durchwachsesenes Jahr am Lehrstuhl E13 zurück. Nunmehr im vierten Jahr in Folge wurden am Physik Department die Landesmittel für die Lehrstühle drastisch gekürzt. Mittlerweile erreicht die Zuweisung gerade einmal die Hälfte der Summe aus dem Jahr 1999. Diese Reduzierung der Landesmittel hat unter anderem unmittelbar zur Folge, dass die notwendigen grösseren Reparaturen und Wartungsarbeiten an der Röntgenanlage und an einigen Lichtstreuapparaturen auf nicht absehbare Zeit verschoben werden müssen, so dass diese Apparaturen nur eingeschränkt für unsere Forschungsarbeiten eingesetzt werden können.

Erfreulich ist demgegenüber die kontinuierlich steigende Zahl der Drittmittelprojekte und der eingeworbenen Drittmittel an E13. Mit den so erzielten Mitteln hat das wissenschaftliche Personal heute den höchsten Stand seit der Neubesetzung des Lehrstuhls erreicht. Der internationale Charakter unserer Forschung spiegelt sich nicht nur in der intensiven Zusammenarbeit mit Wissenschaftlern ausländischer Universitäten und Großforschungseinrichtungen wider, sondern auch durch die internationale Besetzung unserer Arbeitsgruppen mit Postdoktoranden aus Japan, China, Russland, Italien und Frankreich sowie Doktoranden aus Dänemark, Indien und Algerien. Auch pendelt sich die Anzahl der Diplomanden und Doktoranden auf hohem Niveau ein.

Zu Beginn des Jahres erhielten nach abgeschlossenem Habilitationsverfahren Peter Müller-Buschbaum und Andreas Meyer ihre Lehrbefugnis und ihre Ernennung zum Privatdozenten. Mit nunmehr sechs Dozenten engagiert sich der Lehrstuhl am Vorlesungsbetrieb des Physik Departments. Der interne wissenschaftliche Austausch konnte im Juli bei einer Klausurtagung der wissenschaftlichen Mitarbeiter und Studenten von E13, E21 (Lehrstuhl Prof. Peter Böni) und dem FRM-II auf der Burg Rothenfels mit einem Workshop zum Thema *Neutron Scattering on Advanced Materials* sehr erfolgreich gestaltet werden. Mit der Ernennung von Christine Papadakis auf die bei E13 angesiedelte Universitätsprofessur auf Zeit wird die Forschung auf dem Gebiet der Polymerfilme und -grenzflächen im Department weiter intensiviert. Im Dezember wurde der diesjährige Promotionspreis des Bundes der Freunde der Technischen Universität München an Sabine Wiebel für ihre Arbeiten zur Dynamik zäher, molekularer Flüssigkeiten verliehen.

Sehr positiv zu vermelden ist die Genehmigung für den Betrieb des FRM-II. Nach einer konstruktiven Aufbauphase und der zweijährigen Begutachtung des letzten Genehmigungsschrittes durch den Bund sehen wir alle dem Routinebetrieb der Anlage und der Instrumente im kommenden Jahr erwartungsfroh entgegen. Winfried Petry wird sich auch im akademischen Jahr 2003/2004 am Lehrstuhl vertreten lassen, um die Inbetriebnahme des FRM-II vorzubereiten. Er hat einen Ruf als wissenschaftlicher Direktor an das Forschungszentrum Rossendorf erhalten. E13 wünscht sich eine erfolgreiche Rufabwehrverhandlung.

Ich danke Winfried Petry für das Vertrauen, das er mir durch die Übertragung der kommissarischen Leitung des Lehrstuhls entgegen gebracht hat, und ich wünsche mir weiterhin eine gute Zusammenarbeit mit den Mitarbeitern von E13.

Andreas Meyer

Dezember 2003

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1 Instrumentelle und methodische Entwicklungen

Time of flight spectrometer at FRM-II near completion

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2003 has been a successful year for the group of the time-of-flight spectrometer TOFTOF at FRM-II. Several milestones could be reached on the way to the completion of the spectrometer: The chopper system has been installed and tested successfully. The 605 detectors were tested individually including the preamplifiers. The detectors and the preamplifiers were mounted on the racks and wired with the time-of-flight electronics. Last but not least a stage with the measuring cabin for the users of the instrument has been built up. The last main components of the spectrometer have now been delivered: The radial collimator, the focussing neutron guide and the shielding for the primary spectrometer. These components will finally be assembled in spring of 2004.

A picture of the instrument is displayed in Fig. 1.1. The shielding of the primary spectrometer is



Abbildung 1.1:
Front view of the time-of-flight spectrometer at FRM-II with disassembled shielding of the primary spectrometer (see text)

disassembled. Thus the view is free to the four vessels containing a total of the 7 chopper discs. It provides synchronous and asynchronous operation of each disc (diameter: 600 mm) with speeds from 100 rpm up to 22000 rpm. The phase shift of the discs can be adjusted with an accuracy of about 0.05 degree.

The flight chamber of the secondary spectrometer is positioned at the end of the primary spectrometer and is partly visible behind the chopper vessels in Fig. 1.1. This chamber also houses the racks with the 605 detectors and preamplifiers. On top of the flight chamber the electronics rack can be seen which includes the time-of-flight electronics and some hardware for instrument control. The cabling has been finished for the whole detector system which is currently being tested.

On the left hand side in Fig. 1.1 two measuring cabins are visible. The first one is for the neighbouring REFSANS instrument and the second one is for the time-of-flight spectrometer. The TOF group is looking forward to furnish the cabin and to control the first TOF experiments from there next year.

Coherent X-ray Scattering from Ultrathin Probe Layers

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X-ray standing waves are an established tool for the analysis of adsorbates and ultrathin films on surfaces of single crystals. The standing wave that forms upon the interference between the incident and the reflected wave has a period of $2\pi/q_z$ where q_z is the momentum transfer along the surface normal. Thus, in grazing incidence geometry, x-ray standing waves can be used for the investigation of thin films with a thickness of several nm. If the film thickness matches an integer multiple of the period of the standing-wave field, the intensity of the electric field inside the layer is resonantly enhanced due to multi-beam interference. This wavefield can be used as primary wave for structural analysis of the film [1]. The highest intensity enhancement is achieved when the layer under study is sandwiched between two layers of higher electron density, thus forming an x-ray waveguide structure. This approach was systematically investigated by Sinha and coworkers [2]. In particular, the intensity of the radiation that is *coherently* scattered from any kind of matter within the wavefield is strongly amplified. For that reason, this technique is very sensitive to smallest amounts of material like ultrathin films in the monolayer regime. Here we investigate coherent x-ray scattering from an ultrathin probe layer that is located in a standing wave field. The remarkable result is that the reflected amplitude from the probe layer is proportional to the *square* of the field amplitude $a(z_p)$ at its position z_p in the layer system [3]:

$$\mathbf{R}_p = id a(z_p)^2 \mathbf{f}_p(\omega), \quad (1.1)$$

where d is the thickness of the probe layer and $\mathbf{f}_p(\omega)$ is the energy-dependent forward scattering amplitude of the layer material. A similar relation was suggested recently by Andreeva *et al.*, for the special case of an ultrathin film on the surface of a layer system [4]. We have shown recently, that this result is valid for an ultrathin film that is embedded anywhere in an arbitrary layer system [3].

For an experimental verification of this relation, we have performed nuclear resonant scattering from ultrathin isotopic layers consisting of ^{57}Fe . While isotopic probe layers have been used in conventional Mössbauer spectroscopy for a long time, coherent scattering from ultrathin layers became feasible only after the advent of high-brilliance synchrotron radiation sources [5,6,7]. The

sample used in this experiment is sketched in the inset of fig. 1.2a. It was deposited by rf magnetron sputtering on a superpolished Si wafer. A 0.7 nm thick probe layer of ^{57}Fe was embedded in the center of the Fe layer. The preparation of these layer systems was motivated by the investigation of the in-depth spin structure in a soft-magnetic layer (Fe) that is exchange-coupled to a hard-magnetic layer (FePt) [7]

The experiments were performed at the Nuclear Resonance beamline (ID18) of the ESRF. Figure 1.2a displays the angular dependence of the electronic reflectivity. The first-order guided mode shows up at 4.3 mrad as a pronounced dip in the electronic reflectivity. Figure 1.2b shows the resonant signal $|\mathbf{R}_p|^2$ from the ^{57}Fe probe layer as obtained by taking the time-integrated delayed signal within a time window ranging from 12 ns to 160 ns after excitation. Its angular dependence shows a strong peak at the angular position where the waveguide mode is excited. One observes a 36-fold enhancement of the intensity relative to the value obtained at large angles of incidence. For better illustration of the relative intensities, the same data are shown in the inset on a logarithmic scale. The dashed line displays the normalized intensity of the electric field at the position of the ^{57}Fe layer. In the antinode of this TE_0 mode the intensity exhibits a 6-fold enhancement relative to the intensity of the incident beam. Correspondingly, the coherently scattered signal displays a 36-fold enhancement [3]. The solid line in both graphs is obtained by squaring the values of the dashed curve and scaling them to the measured data. The very good agreement verifies the quadratic dependence on the intensity at the probe layer position as established in eq. (1.1). It should be noted that in the *incoherent* scattering channels, the signal scales only linearly with the intensity at the probe layer position [1].

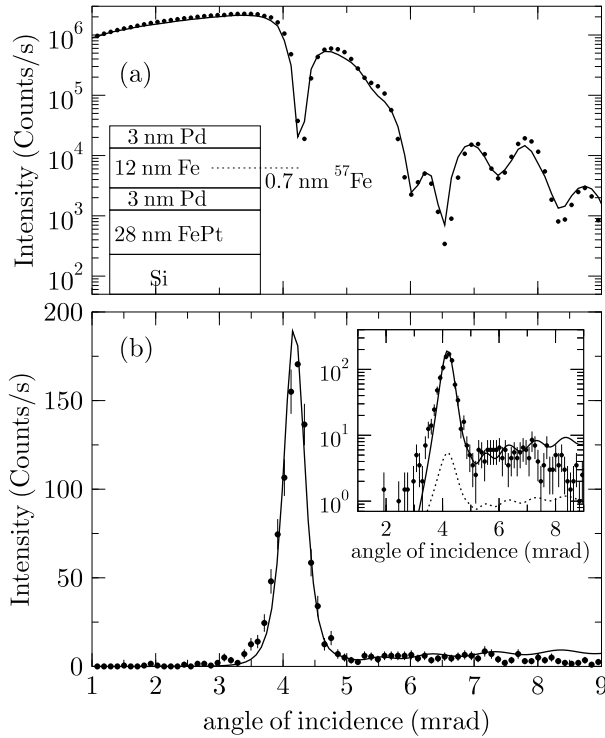


Figure 1.2:

a) Measured electronic reflectivity from the layer system, shown in the inset, at a photon energy of 14.4 keV. In the center of the Fe layer an ultra-thin film of 0.7 nm ^{57}Fe is deposited. At $\varphi = 4.3$ mrad, the radiation couples into the first-order guided mode. b) Time-integrated delayed intensity from the layer system, recorded within a time window from 20 - 160 ns after excitation. The inset shows the same data on a logarithmic scale. The dashed line is the normalized intensity of the electric field at the position of the ^{57}Fe layer. The solid lines are the square of this curve, scaled to the measured data.

The coherent enhancement described here leads to a very strong amplification of the signal in the coherent scattering channels. In combination with x-ray waveguide structures, this technique can be employed for signal amplification from smallest amounts of material. Thus, probe layers

of monolayer thickness can be used to investigate the in-depth properties of thin films with unprecedented spatial resolution. It is obvious that this method can be applied to other Mössbauer isotopes as well. Moreover, this coherent enhancement effect is of course not restricted to nuclear resonant x-ray scattering. It can be exploited in many other areas where coherent scattering from stratified media is used. The technique can be applied, for example, to investigate the properties of clusters or nanoparticles that are embedded in the center of the guiding layer of an x-ray waveguide. If the photoabsorption in the guiding layer material is sufficiently low, as for elements like B, C, Al, coherent enhancement factors greater than 10^3 can be expected. This method is also very attractive for off-specular methods that probe the in-plane structure of thin films and surfaces like grazing-incidence small-angle x-ray scattering (GISAXS). Moreover, it can be very beneficial also for spectroscopic methods that probe dynamical properties of condensed matter like IXS (inelastic x-ray spectroscopy) and XPCS (x-ray photon correlation spectroscopy).

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2 Polymergrenzflächen

Nanostructured polymer films build-up of diblock copolymers: A GISAXS study

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Future generations of microelectronic devices will require both, ever-decreasing critical dimensions and shrinking tolerance on those dimensions. The rising costs and complexity associated with lithographically created structures at nanometer length scale opened opportunities for alternative techniques. Following this track, self-assembly in physical systems might play a key role in future technological applications. Self-assembling materials are characterized by spontaneous formation of nanometer-scale structures.

One extremely promising candidate are nanostructured polymer films built-up from diblock copolymers [1]. In literature various diblock copolymer thin films have been explored. Due to the chemical connection between the two immiscible polymeric blocks, a microphase separation structure is naturally installed to minimize the free energy density of the system. Instead of micrometer sized domains in case of phase separating polymer blends, the typical dimensions of the microphase separation structure are in the nanometer regime, yielding the desired nanostructured films. These dimensions are determined by the fundamental properties of the diblock copolymer, and can be adjusted by changing the total copolymer molecular weight while keeping the molecular weight ratio between the blocks constant. In case of a thin film, the solid support is completely covered by the nanostructured polymeric layer. Alternatively, a super-structure can be imposed, replacing the thin film geometry. As a typical example, the initially continuous polymer film is replaced by an assembly of isolated polymer droplets. The droplet arrangement usually results from a dewetting process of the initially continuous film. Inside the host structure of these droplets, the microphase separation structure is present. Consequently, this type of systems exhibits two characteristic lateral lengths, the first given by the microphase separation structure and the second resulting from the spacing of the droplets assembled upon the solid support. As compared to the thin film geometry, the possibilities of installing length scales matching the underlying nanofabrication problem are increased. The self-assembly based nanofabrication process is especially attractive because of its simplicity. The basic preparation procedures involve only a few preparation steps: Substrate cleaning, thin film creation, nanostructure creation. Based on the example of dewetted poly(styrene(deuterated) -block- paramethylstyrene) diblock copolymer P(Sd-b-pMS) films the possibilities and limitations of GISAXS are enlightened within this investigation. Research is directed towards the host structure created by dewetting, because this enables a direct comparison with real space analysis techniques such as AFM or SEM. The development of the internal arrangement of the diblock copolymer molecules was under investigation in previous work [2, 3] and is not revisited here.

The grazing incidence small angle x-ray scattering (GISAXS) measurements were performed at the BW4 USAX beamline of the DORIS III storage ring at HASYLAB/DESY in Hamburg. The selected wavelength was 0.138 nm. The scattered intensity was recorded with a two dimensional detector which consists of a 512x512 pixel array. Due to the sample-detector distance of 12.1 m a high resolution was achieved. The beam divergence in and out of the plane of reflection was set by

two entrance cross-slits. At one fixed angle of incident the two-dimensional intensity distribution can be cut in several vertical and horizontal slices with respect to the sample surface. Vertical slices mainly contain scattering information from structures perpendicular to the sample surface, whereas horizontal slices contain only scattering contributions with an in-plane information. Thus for the investigation of surface morphologies we restrict ourselves to horizontal slices, which are frequently called out-of plane-scans.

Because the host structure resulting from the destabilization of an initially continuous P(S-b-pMS) layer is expected to exhibit characteristic lateral lengths above the resolution limit of a conventional small angle scattering distance the GISAXS experiments were performed with a very large sample-detector distance. Figure 2.1 shows six typical two-dimensional GISAXS scattering pattern. Since an incident angle $\alpha_i = 0.534^\circ$ larger than the critical angle of the polymeric material was chosen, the specular and the diffuse scattering contributions are well separated.

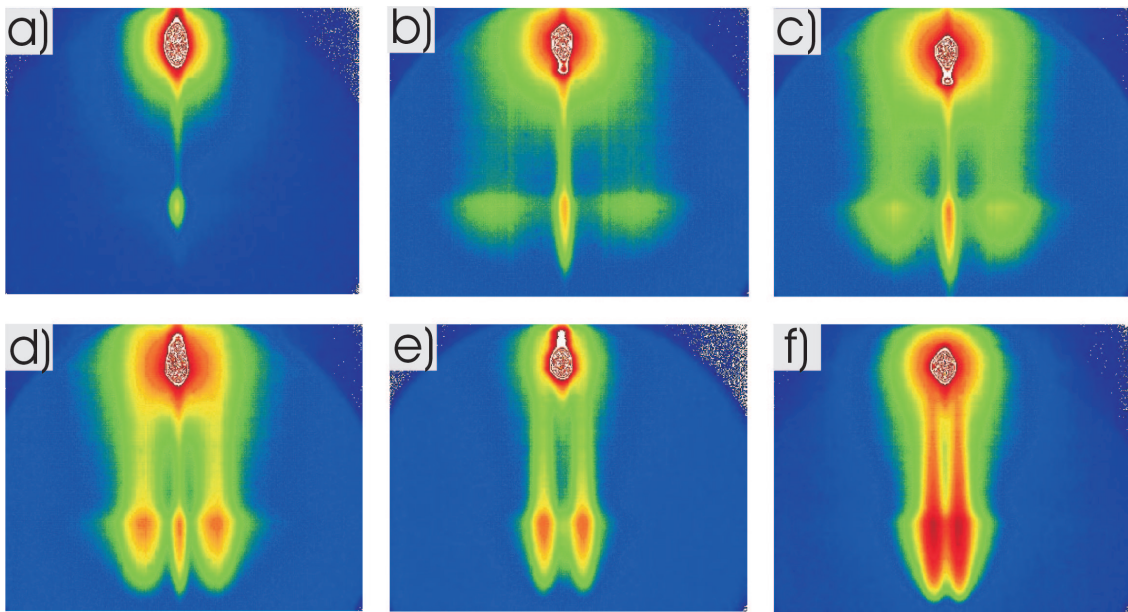


Figure 2.1:

Typical two-dimensional GISAXS scattering pattern measured at BW4: a) bare silicon substrate, b) after 0.5 h, c) 1 h, d) 2 h, e) 3 h and f) 4 h storage under toluene vapor atmosphere. Each two-dimensional intensity mapping covers a range of $-0.48^\circ < \psi < 0.48^\circ$ in horizontal direction and $0.0^\circ < \alpha_f < 0.55^\circ$ in vertical direction. The intensity is shown on a logarithmic scale. The color coding was chosen to emphasize on the features in the diffuse scattering (blue=low and red=high intensity). As a consequence, the specular peak in the top region of each two-dimensional intensity mapping appears with a staggered intensity. [4]

GISAXS data of the base silicon surface (figure 2.1a) differ markedly from the ones of the substrates with polymeric material on top (figure 2.1b-f) [4]. Due to the extremely small surface roughness of the silicon substrates on the order of a few Angstroms only, the two-dimensional intensity mapping is dominated by the specular peak (in the top region). With increasing storage time under toluene vapor, the intensity of the Yoneda peak increases. In addition the marked shape of the Yoneda peak changes during ongoing storage. The initially central Yoneda peak exhibits two side maxima after 0.5 h storage. After the doubled storage time (figure 2.1c) the position of the side maxima slightly shifted as well as the maxima got more pronounced in the two-dimensional

intensity mapping. After a again doubled storage time these processes proceed (figure 2.1d), whereas after 3 h of total storage time the Yoneda intensity distribution again changes (figure 2.1e). The central peak vanishes and only both side maxima remain.

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GISAXS characterization of particle track etched polycarbonate membranes onto glass substrates

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It is well known that nanoporous polymer membranes provide an ideal surface to grow cells. Nanoporous gold electrodes can be prepared on the surface of track-etched membranes and immobilize the enzyme glutamate oxidized onto them. The use of nanowire surfaces instead of planar ones gives a higher sensitivity due to their larger surface area. This is of special interest for sensor applications. The nanowire surfaces can be prepared directly from nanoporous particle track etched membranes.

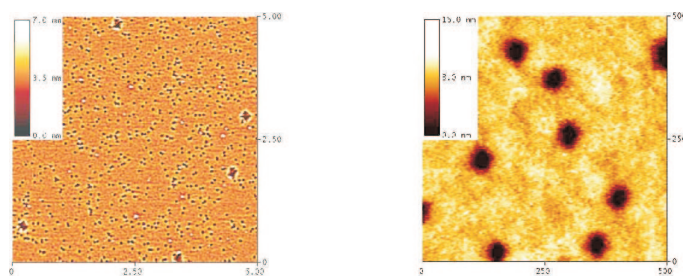


Figure 2.2:

Pore size and pore density are controlled by using an atomic force microscope. The examples show SFM data of a glass supported polycarbonate template with a homogenous pore size of approximately 36 nm on top.

Commercially available polycarbonate was solvent casted from chloroform onto cleaned glass substrates. The samples were annealed at 190° for 4h. The energetic heavy ion irradiation of polycarbonate films with Ar Ions with 4.8 MeV/amu at 109 cm⁻² was carried out at the Cyclotron Research Centre of Louvain-la-Neuve in the vacuum chamber commonly used by Whatman for

their own industrial production [1]. Etching conditions are similar to those described in [2]. We obtained polycarbonate films on glass substrates with good adhesion and a smooth surface (surface roughness RMS ~ 2 nm). Real space pictures of the sample surfaces are obtained from scanning force microscopy measurements (SFM) using an atomic force microscope (DI3000). Tapping operation mode was chosen and all measurements were performed in air at room temperature. Figure 2.2 shows two typical examples of SFM data. Statistical information parallel to the surface is obtained from the power spectral density function (PSD) [3-4]. The PSD data is equivalent to a scattering signal and thus pictures the existence of a most prominent in plane length scale, which might be present within the resolvable range. We found pore diameters of ~ 36 nm.

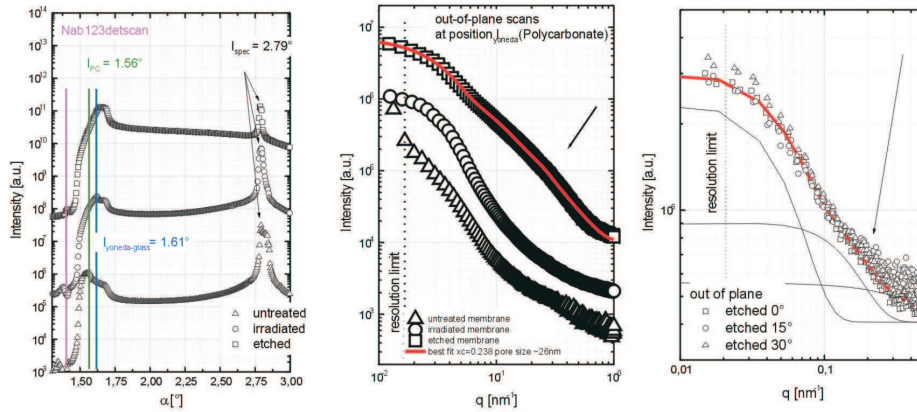


Figure 2.3:

Left) Detector scans of untreated, irradiated and etched polycarbonate films (from the bottom to the top) measured at the A2 beamline. Middle) Corresponding out-of-plane scans. The shape of the curve is well described by a broad shoulder located at the position $q = 0.12 \text{ nm}^{-1}$ which originates from a dominant length of $\sim 52 \text{ nm}$. This proves the existence of nanopores with a mean size of 52 nm . Right) Influence of sample orientation with respect to the incoming x-ray beam checked with 3 out-of-plane scans of the etched polycarbonate film. The sample was rotated around the z-axis for 0° (squares), 15° (circles) and 30° (triangles). No significant change in the scattering intensity indicates a parallel (to each other) and perpendicular (to the surface) orientation of the pores.

At the synchrotron HASYLAB (DESY Hamburg) at the BW4 beamline and A2 beamline the diffuse scattering of virgin and irradiated/etched PC films was measured [5]. The samples were placed horizontally on a two-circle goniometer with a z-translation table. We used a set up of high-quality entrance slits and a completely evacuated pathway. At the selected wavelength $\lambda = 0.138 \text{ nm}$ (BW4)/ 0.154 nm (A2) due to the sample-detector distance of 2211 mm (BW4)/ 1964 mm (A2) with the two-dimensional detector (Gabriel Detector BW4/MarCCD A2) one detector scan and several off-detector scans were measured simultaneously. At a fixed incident angle of $\alpha_i = 1.514^\circ$ (BW4)/ 1.395° (A2) the prominent features in a detector scan, the specular as well as the Yoneda Peak are well-separated (see figure 2.3).

From out-of-plane scans the dominant length scales in the sample surface (topography) or inside the nanostructured film are accessible. In the double-logarithmic plot the intensity axis was arbitrarily chosen and the resolution limit is shown by the dashed line. The curve is well described by a broad shoulder located at the position $q = 0.12 \text{ nm}^{-1}$ which corresponds to a dominant length

of $\sim 52\text{nm}$ (see figure 2.3 middle). This proves the existence of nanopores with a size of $\sim 52\text{nm}$. There are at least three possibilities for the broadening of the structure peak in the GISAXS data. First of all, the pores are probably not cylindrical but conically formed. After treatment with the etching solution the pores are rinsed with pure water. The exchange of these two liquids is too slow to stop the etching process immediately which results in a conical pore shape. Another possibility could be a reflection of Argon ions from the substrate. As a consequence, the pore diameters decrease to the substrate side evermore. A third possibility is an imperfect alignment of the pores with respect to the substrate surface. To get more information about the orientation of the pores, the sample was rotated around the z-axis. We found no significant change in scattering intensity of the GISAXS. Thus the pores are nearly perpendicularly arranged with respect to the substrate surface with a tilt angle smaller than 1.5° and parallel to each other.

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Influence of surface cleaning on the stability of thin polymer films

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The stability of thin polymer films is of major interest in numerous technical applications such as dielectrics or coatings, as well as in basic research. Instable films dewet from the substrate underneath and the initially homogeneous film is destroyed giving rise to an assembly of drops instead. Since the cleaning is the first step in every dewetting experiment to guarantee equal starting conditions we investigated the influence of the cleaning on the stability of thin polystyrene films.

In literature a large variety of different cleaning procedures were reported [1, 2, 3, 4, 5]. Many of them are based on single step cleans. Within our investigation we restricted to particular examples: Four different cleaning procedures such as rubbing with a toluene soaked KIMMWIPE, 24 hours of storage in Milli-Q-water, cleaning in an acid bath [6, 7, 8, 9] as well as in a leach bath have been compared. As model system we picked up silicon (100) substrates and the polymer polystyrene (PS) ($M_W = 27500\text{g/mol}$, $M_W/M_N = 1.04$) which is frequently used in many investigations related to dewetting. Ultrathin PS films were prepared by spin-coating (2000 rpm) immediately after the applied cleaning. As the final preparation step the samples were exposed to heat load modelled via a temper plate at 130°C and quenched down to room temperature after a given time interval. Series of different time intervals were performed for each applied cleaning procedure to check for stability and dewetting. A stable film is defined by the presence of a homogeneous film and the presence of first holes growing with longer heating times and ending up with droplets on the surface is taken as a signature of the instability.

The real space analysis of the resulting surfaces was performed with scanning force microscopy (SFM) in non-contact mode. Because only one polymer component is present on top of the substrate, in principle SFM is well suited to detect signs of the instability as a function of the exposure time to the heat load. However, SFM had to be performed within small scan ranges on the order

of a few micrometers, because the expected surface features (either holes or droplets) are small due to the ultra-thin film thickness regime addressed in this investigation. As a consequence only very small surface areas are checked with SFM and the related statistical significance is rather limited. To overcome these problems of limited statistical relevance grazing incidence small angle x-ray scattering (GISAXS) measurements were performed. With GISAXS surface structures of the expected size are well resolvable [3] and due to the large illuminated surface area which is on the order of several centimetres, originated by the grazing incidence conditions, a statistical significant information is available.

The grazing incidence small angle x-ray scattering (GISAXS) measurements were performed at the BW4 USAX beamline of the DORIS III storage ring at HASYLAB/DESY in Hamburg. The scattered intensity was recorded with a two dimensional detector which consists of a 512×512 pixel array. The beam divergence in and out of the plane of reflection was set by two entrance cross-slits. The samples were placed horizontally at 12.56 m from the 2D detector (Gabriel) and the wavelength of the incident beam was 0.138 nm, the incident angle $\alpha = 0.325^\circ$. At one fixed angle of incidence the two-dimensional intensity distribution can be cut in several vertical and horizontal slices with respect to the sample surface. Vertical slices contain mainly scattering information from structures perpendicular to the sample surface, whereas horizontal slices contain only scattering contributions with an in-plane information. Thus for the investigation of surface morphologies we restrict ourselves to horizontal slices, which are frequently called out-of plane-scans.

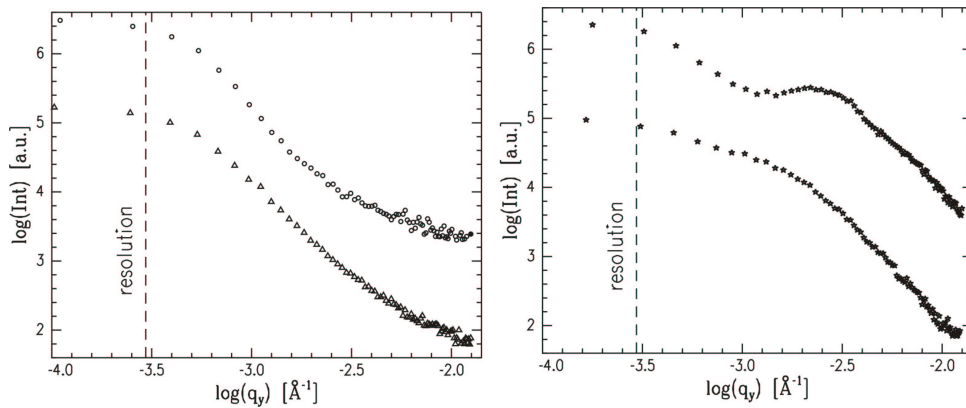


Figure 2.4:

GISAXS data shown as logarithm of the intensity versus logarithm of the wave vector component parallel to the surface and perpendicular to the scattering plane q_y . The data are shifted vertically for clarity. The broken line indicates the resolution limit. a) Samples before exposure to heat load, cleaned by the water storage (bottom) and by the toluene clean (top), b) Samples after three hours of exposure to heat load at 130°C , again the lower one shows the sample stored in water, the upper one is the toluene cleaned sample, showing up a clear peak.

It was observed that the cleaning strongly alters the stability of the PS-film. For comparison data of the toluene cleaned and the water stored samples are shown in figure 2.4. In figure 2.4a the samples without heat load are compared. The GISAXS data are shifted vertically for clarity. No dominant lateral structure is detectable which corresponds to a uniform PS surface in both cleaning procedures. This means a homogeneous thin films is the starting point of our experiment. In figure 2.4b the samples were exposed to heat load for three hours. Clearly a difference shows up. A strong peak appears in the GISAXS data of the top curve at a wave vector $\log(q)_y = -2.68$

$\text{\AA}^{-1}$, which corresponds to a dominant length scale of $0.3\mu\text{m}$. This structure resulted from the toluene cleaning. By comparison with SFM pictures this may correspond to the diameter of the droplets on the silicon surface. In the GISAXS data obtained by water storage cleaning (bottom curve) such a structure is not present after three hours of heating at 130°C . Thus the wetting behavior of these two films is modified due to the applied cleaning. This is in agreement with results shown in [6].

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Polymer films with linear thickness gradients: A new class of heterogeneous films

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Thin polymer films are used in many high-tech applications like functional coatings. In general homogenous films with uniform structures are used for these applications. The creation process of structures by self-assembly of polymers is part of numerous investigations. One major aim of this research is the customized design of thin film morphologies. In general, the structures of thin films depend on the used polymers and their physical properties as well as on external parameters such as film thickness and the preparation process. In common investigations this demands to prepare a large number of samples for mapping-out the parameter space. Polymer gradient samples are a new class of samples which are characterized by the change of external variables in different directions along the sample surface [1, 2]. This drastically reduces the number of samples necessary to investigate structure creation. In the case of crossed gradients (two different variables changed perpendicularly to each other) only one sample is sufficient. However, with respect to scattering investigations these crossed gradients are rather inconvenient and single gradients are preferable. This results basically from the big footprint area of the x-ray beam in a reflection geometry.

In our investigation we used a polystyrene-block-polyisoprene diblock copolymer with a molecular weight of 13000 g/mol, a polydispersity index of 1.06 and a symmetric block ratio of 0.5. Diblock-copolymers are a class of polymers in which two chemically different polymers are linked via one covalent bond. Different polymers are typically immiscible and phase separate from each other. The two polymer blocks can only phase separate on a microscopic scale due to the

covalent binding. The used polymer system shows a lamellar order of the polymers in the case of an equilibrium structure in the bulk as well as in thin films on top of solid supports.

A one dimensional film thickness gradient was prepared by solution casting on an inclined substrate. The substrate was pre-cleaned in a standard cleaning solution (RCA-1 clean). Along the thickness gradient the film thickness increases from 30 nm to more than 300 nm over a distance of 50 mm. Thus it is a rather smooth gradient. The prepared film is homogenous perpendicular to the thickness gradient to allow for scattering experiments such as reflectivity and grating incidence small angle x-ray scattering (GISAXS) [3]. From x-ray reflectivity measurements the density profile was determined exhibiting a lamellar order of the polymers inside the film parallel to the substrate surface. The total film thickness is given by either nL or $nL/2$, depending on the position along the gradient where n is an integer number and L is the bulk lamellar period [4]. The numbers determined from x-ray reflectivity agree well with data from additional ellipsometry measurements.

Figure 2.5A shows a typical surface structure obtained by atomic force microscopy (AFM) measurements on an arbitrary position along the gradient. The film surface shows an island like surface structure independent of the film thickness. With AFM a typical lateral size of the islands between 250 and 300 nm is determined. To get a statistically significant information verifying the local information from AFM measurements GISAXS measurements were performed. In addition these GISAXS data allow for a detection of internal lateral structures. GISAXS data were probed at selected positions along the gradient, which had been pre-characterized by the use of AFM and x-ray reflectivity.

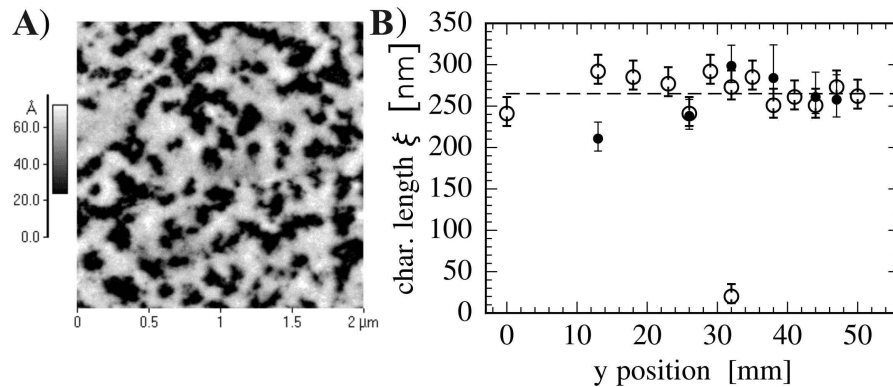


Figure 2.5:

A) Typical AFM picture of the surface structure present on top of the polymeric gradient irrespective of the sample position. B) Comparison of the lateral in-plane length scale ξ measured with GISAXS (open circles) and AFM (filled circles) as a function of the position y along the gradient [5].

Since a rather large range of lateral structures possibly is present, in a simultaneous beamtime at both, the A2 und the BW4 beamline, GISAXS measurements with two different resolutions were performed at the DORIS III storage ring at HASYLAB/DESY in Hamburg. This enabled the investigation of exactly the same samples, without any time delay with two set-ups which differ in resolvable the real space length scales (BW4: high, A2: relaxed resolution). Because the diblock copolymer under investigation contains one fluid-like blocks, this will improve the results with respect to the influence of aging of the samples. The common transmission geometry was replaced by a reflection geometry and the sample was placed horizontally on a two-circle

goniometer with a z-translation table. The selected wavelength was 0.154 nm at A2 and 0.138 nm at BW4. At both beamlines the scattered intensity was recorded with a two dimensional detector. The beam divergence in and out of the plane of reflection was set by two entrance cross-slits. Due to the different collimations possible at A2 and BW4, at the A2 beamline a rather relaxed resolution was chosen, which in combination with a sample to detector distance of 2.1 m enabled for a detection of length scales between 5 nm and 350 nm. In contrast at the BW4 beamline at 12.8 m distance between sample and detector this interval is shifted to 39 nm and 2500 nm.

At one fixed angle of incidence the two-dimensional intensity distribution can be cut in several vertical and horizontal slices with respect to the sample surface. Vertical slices contain mainly scattering information from structures perpendicular to the sample surface, whereas horizontal slices contain only scattering contributions with an in-plane information. Thus for the investigation of surface morphologies we restrict ourselves to horizontal slices, which are frequently called out-of plane-scans.

In both GISAXS data, measured at A2 as well as BW4, the surface structure gives rise to a structure factor-like contribution. Whereas due to the lateral length of ξ between 250 nm and 300 nm it is located close to the resolution limit in the A2 data, but in the BW4 data easily resolved. Additional marked lateral lengths were not detected. Figure 2.5B shows a comparison of the lateral length scales of both methods AFM and GISAXS. Within the range of error the determined values are in good agreement independent of the measurement position along the film thickness gradient [5].

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A new versatile sample chamber for high-resolution scattering experiments at BW4

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In the last years BW4 established as a powerful beamline for ultra-small angle x-ray scattering (USAX) as well as for grazing incidence small angle x-ray scattering (GISAXS) [1]. Driven by the extremely time demanding set-up for GISAXS a new versatile sample chamber for high resolution scattering experiments at BW4 was constructed. The new sample chamber combines ideas of a common reflection sample chamber such as available at the beamline A2 with special demands due to GISAXS. In addition a high degree of flexibility was implemented to ensure versatility.

The heart of the sample chamber is a HUBER goniometer enabling vertical and horizontal positioning via linear positioning devices in x-, y- and z-direction and angular positioning with two circle segments (see figure 2.6). The series 5204.1 goniometer head is intended for experimental setups, which require the capability of carrying heavy loads. The slides are guided by dovetails, which

provide precise and smooth positioning. Most important details concerning this head are [2]: Mounting area $100 \times 100 \text{ mm}^2$, angle positioning range $\pm 15^\circ$, linear positioning range $\pm 12 \text{ mm}$, sphere of confusion single axis (R_x, R_y) $< \pm 15 \text{ }\mu\text{m}$, both axes ($R_x + R_y$) $< \pm 20 \text{ }\mu\text{m}$, position accuracy (X, Y) $< \pm 20 \text{ }\mu\text{m}$, reproducibility (X, Y) $< \pm 5 \text{ }\mu\text{m}$, reversal error (X, Y) $< \pm 10 \text{ }\mu\text{m}$, maximum load 500 N and spindle slope $1^\circ/\text{rev}$.

The series 5204.1 goniometer head is placed on a high-precision Z positioner HUBER series 5103.1 with a range of 15 mm in height. It limits the maximum load down to 300 N and effective 250 N (25 kg). Most important details concerning this positioner are [2]: Accuracy $< \pm 6 \text{ }\mu\text{m}$, reproducibility $< \pm 4 \text{ }\mu\text{m}$ and resolution 0.02 mm/rev . Underneath the positioner a one-circle goniometer HUBER series 410 enabling a 360° rotation is present.

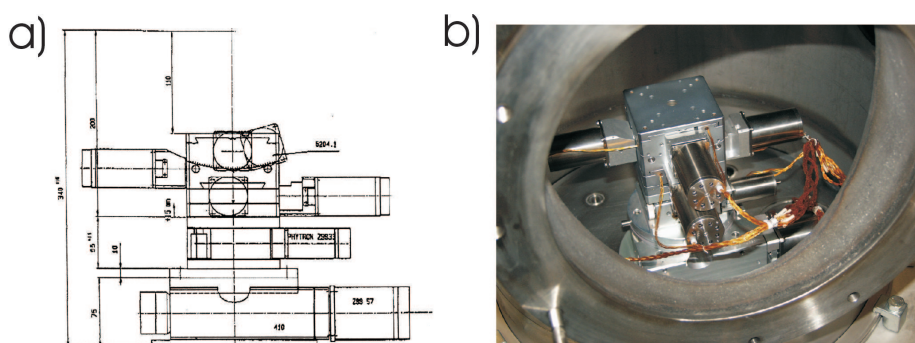


Figure 2.6:

a) Schematic sketch of the HUBER goniometer of the new BW4 sample chamber enabling vertical and horizontal positioning as well as angular positioning with two circle motions. b) Photograph of the goniometer placed inside the sample chamber.

The complete goniometer sits inside a vacuum chamber dominating the outer appearance as visible in figure 2.7. The vacuum chamber is equipped with two entrance flanges, which are connected to the flight tubes of the BW4 beamline. In principle this enables a full-vacuum set-up with a completely evacuated pathway from the separation window towards the synchrotron ring down to the detector. In a first test experiment with the new sample chamber an implemented ionization chamber interrupted this completely evacuated pathway (see figure 2.7 to the right). To the rear a small flange opening and to the front a large flange opening are present. The front penning allows an easy sample changing. In the present version a PMMA window was utilized which offers the possibility of a visual inspection of the sample and its surrounding without breaking of the vacuum. In addition the window of the top flange is build from PMMA as well to ensure sufficient light inside the chamber. During realistic usage of the sample chamber this choice of the window material enables a pressure of $3.9 \times 10^{-5} \text{ mbar}$ inside the chamber. The complete sample chamber is fixed on a moveable base plate. By the help of the crane at BW4 it is easily placed on top of the optical bench. As compared to previous GISAXS set-ups at BW4 the total build-up time is reducible by more than 5 hours due to this technique.

For GISAXS experiments different types of sample holders are designed. These sample holders cover the distance of 110 mm between the top of the goniometer head and the point of rotation of the two circular motions. First scientific examples are presented in this annual yearbook by P. Panagiotou and P. Müller-Buschbaum. In addition sample holders for USAX experiments will be available on request.

Several small flanges in the bottom of the sample chamber will enable the installation of additional devices such as heating tables or environmental boxes.

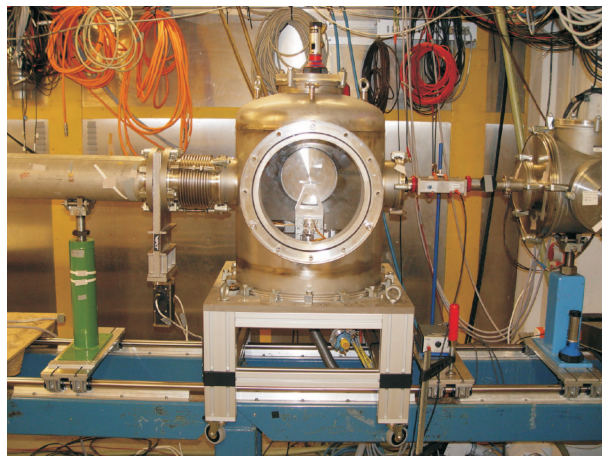


Figure 2.7:

Photograph of the new versatile sample chamber for high-resolution scattering experiments at BW4 during the first testing under realistic conditions. To the left it is connected directly via its flange with the flight tube without adding a window towards the detector side. To the right an introduced ionization chamber demands two additional windows separating sample chamber and flight tube. Inside the GISAXS sample holder is visible.

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Surface morphology of thin immiscible ternary polymer blend films investigated with GISAXS

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For developing high performance materials their properties and parameters which are responsible for a creation of the structures are of fundamental importance. Since it is known that thin polymer films exhibit different physical characteristics compared to their bulk materials, the interest increased rapidly. Considering the fact that by blending of different polymers the required properties can be achieved more competitive than synthesizing new types of polymers, they became increasingly interesting for research as well as for technological application.

In the present investigation we used three different polymers, namely polystyrene (PS), poly(α -methylstyrene) (P α MS) and polyisoprene (PI), with different glass transition temperatures T_g and different molecular weights M_w . Each polymer was solved at a given mass concentration in toluene and blended together at a weight fraction of PS:P α MS:PI = 5:1:4 to get the polymer blend.

The silicon substrates with a native oxide surface were cut into pieces and cleaned in a piranha bath to remove impurities. Afterwards the substrates were rinsed several times with deionized water and dried with compressed nitrogen. Subsequently the substrates were spin-coated at 2000 rpm for 33 sec using the ternary blend solution. Afterwards the samples were annealed at different times to investigate the mechanism of phase separation of thin films [1, 2]. This leads to a relaxation of the individual substance towards equilibrium of the morphology.

Due to the chosen temperature, which is above the glass transition temperature of PS and of PI but below the one of P α MS the domain structures vary as a function of the annealing time, which results in different dominant length scale ξ . Basic origin is an immobility of P α MS, while PI and PS stay mobile.

Scanning the sample with atomic force microscopy (AFM) gives information about the surface structure of the polymer film. Marked lateral structures are visible with multiple length scales. Applying the technique of grazing incidence small-angle x-ray scattering (GISAXS) gives in addition a statistical information the morphology of inside the film [3].

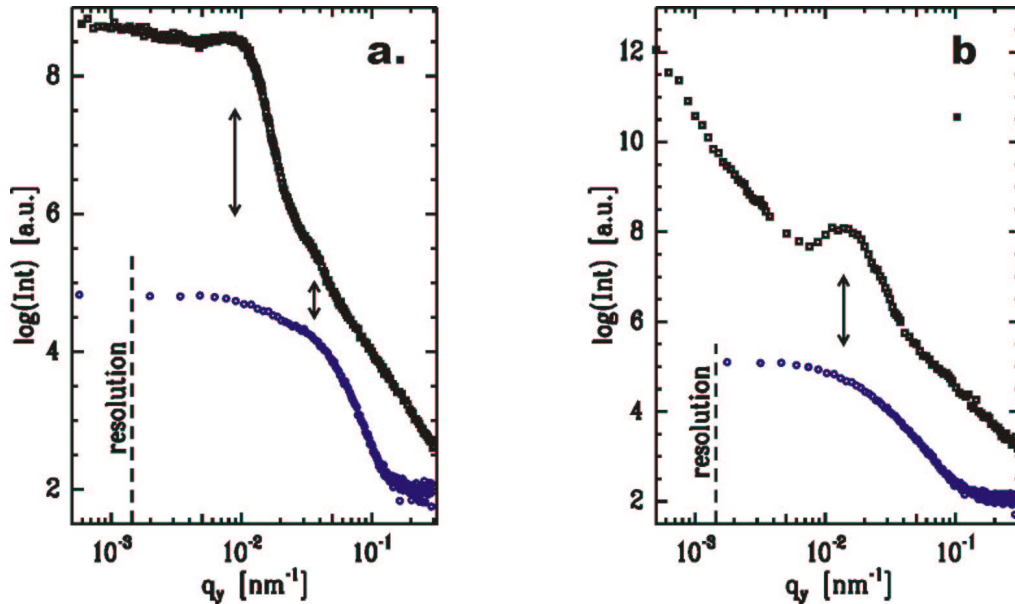


Figure 2.8:

Typical GISAXS cuts (blue circle) compared with the power spectral density (PSD) of the AFM scans (black squares). The dominant in-plane length scales are indicated by arrows and the resolution limit by a dashed line. The figure a) exhibits the measured sample as prepared, while the right b) shows a sample annealed for 500 min

The GISAXS measurements were realized at the BW4 beamline of the storage ring at the synchrotron radiation facility HASYLAB/DESY at Hamburg, Germany. The selected wavelength was $\lambda = 0.138$ nm and the sample-detector distance was 12782 mm. Within the utilised reflection geometry, the sample was placed horizontally on a two circle-goniometer attached on a z-translation table with a fixed angle to the incident beam. The complete pathway of the beam was evacuated and a beam stop was installed. The Gabriel detector with an array of 512x512 pixel was used to record the specular intensity as well as the Yoneda peak. From this two-dimensional intensity distribution typical vertical (so-called detector) and horizontal (so-called out-of-plane) cuts were sliced. The position of the out-of plane cuts were according to the critical angle of the immobile

polymer P α MS and of the mobile one, PS. From this data the dominant in-plane length scale ξ as a function of the annealing time was compared with the 2d-Fourier analysis of the topography scanned with the AFM.

As an example data of two samples at different annealing times are shown in figure 2.8. In figure 2.8a the dominant length scales of the as prepared sample (corresponds to an annealing time 0) are marked by arrows which point out the obtained structures at 689 nm and 228 nm. The structure of the sample which was annealed for 500 min is displayed in figure 2.8b and shows only one peak at 455 nm.

Preparing the samples by spin-coating, the solvent evaporates and leaves the polymer components in a non-equilibrium state which is indicated by a frozen morphology with varying length scale. Due to the annealing procedure the mobile components can relax as a function of the annealing time towards an equilibrium [4, 5].

By comparison of the AFM images and the related Fourier transformed with the GISAXS data an understanding of the kinetic phase separation process can be achieved as follows: In the PSD curve of the not annealed sample (figure 2.8a) the dominant length scale at 689 nm indicates a pronounced in-plane surface structure of the mobile polymers. From the shape of the GISAXS curve the length scales (228 nm) formed by the immobile component P α MS can be extracted. It is only very weakly visible in the surface data. The dominant length scale induced by the mobile components parallel to the surface shifts to smaller structures (455 nm). This shift is due to relaxation of PI and PS towards an equilibrium structure by the annealing applied. It is observable in the PSD curve of the annealed sample (figure 2.8b). The shape of the GISAXS curve remains nearly unchanged after annealing. This indicates that the immobile component lays mainly in the volume region and is not detected with AFM. Such a behavior is quit typical for complex blend systems like ternary ones.

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GISAXS investigation of ultra thin films of adhesive polymers

S. Loi, E. Maurer, A. Götzendorfer, P. Müller-Buschbaum

The adhesion between different polymers as well as between polymer and non polymer surfaces is important for a wide range of applications. In many cases a high adhesion is required, like in the glue industries or coating and paint techniques. On the other hand, some adhesives combine the high tackiness with the ability to be removable. The pressure sensitive adhesives (PSA) belong to this class of adhesives and allow the bond formation by simple contact with the surface [1]. Examples from the everyday life are stick-on-notes or adhesives stickers. The peculiarity of the

PSA is that the tackiness depends strongly on the bond history, which means on parameters like contact pressure, contact time, temperature and debonding rate [2]. It has been observed that the surface roughness and topology greatly affect the tack energy as well [3]. In order to vary the roughness and morphology of the adhesive film, we investigate blends of adhesive and non adhesive polymers. In the bulk, the immiscibility of the two blend components yields a phase separation process. As a function of blend composition and polymer-polymer interaction parameter different phase separation morphologies have been observed [4]. For polymer blend films on different substrates, attention must be paid at the interplay between phase separation and dewetting processes [5]. On reducing the film thickness to values below the radius of gyration (R_g) of the unperturbed molecule, the ultra thin film regime is entered. This regime yields a special conformation of the polymer chains and changes in their thermodynamical behavior. The combination of atomic force microscope (AFM) and grazing incidence small angle X-ray scattering (GISAXS) measurements allows the investigation of lateral structure and in-plane composition of the ultra thin film. The investigated films consist of polystyrene (PS) and poly(n-butylacrylat) (PnBA) blended in different concentrations. They are prepared by spin coating a toluene solution on a glass substrate. The real space surface topography of the samples was investigated with a PARK Autoprobe CP AFM. All the measurements were performed at different scan ranges in non-contact mode in order to minimize the tip induced sample degradation (Figure 2.9A).

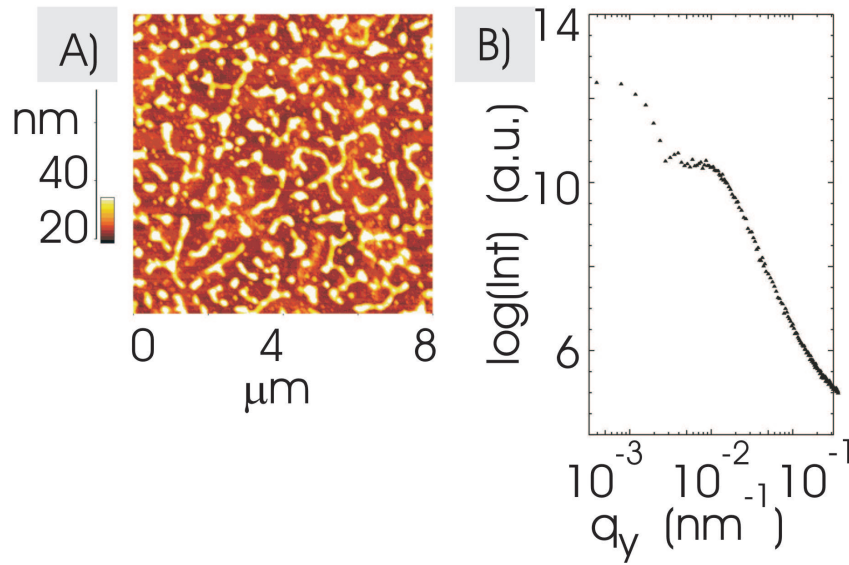


Figure 2.9:

A) AFM image (scan range $8 \times 8 \mu\text{m}^2$) of a PS and PnBA blend film for a fixed blend ratio. B) Master curve corresponding to the same sample as calculated from the AFM data of different scan range.

From the surface data of the different scan range and samples, the two-dimensional power spectral density (PSD) function was calculated and radially averaged. Combining the data of different scan ranges yields a master curve and thus enlarges the range covered by one individual PSD function. The resulting master curve (Figure 2.14B) is comparable with the scattering data. Despite the non-contact mode utilized for the AFM measurements, it was quite tricky to image the film surface since the tip sticks to the surface and can modify the structures. This problem is avoided in the

GISAXS measurements. In addition GISAXS provides informations about buried structures [6]. The GISAXS measurements were performed at the BW4 beamline of the DORIS III storage ring at HASYLAB/DESY in Hamburg. Due to the sample-detector distance of 12.7 m a high resolution was achieved. The selected energy was 8.979 keV. The scattered intensity was recorded with a two dimensional detector which consists of a 512x512 pixel array. For a fixed angle of incidence the two-dimensional intensity distribution can be cut in several vertical and horizontal slices with respect to the sample surface. Vertical slices contain only information from structures perpendicular to the sample surface, whereas horizontal slices contain only scattering contributions from lateral structures parallel to the sample surface. Thus for the morphology investigation we focused on the horizontal cuts. Figure 2.10 shows the horizontal cuts for samples at different PS/PnBA concentrations. Comparing the master curves from the AFM measurements and the GISAXS cuts for each sample, the curves show different features. In most of the GISAXS cuts a shoulder is visible that is not present in the corresponding master curves. This suggests the presence of an internal structure with regular distances.

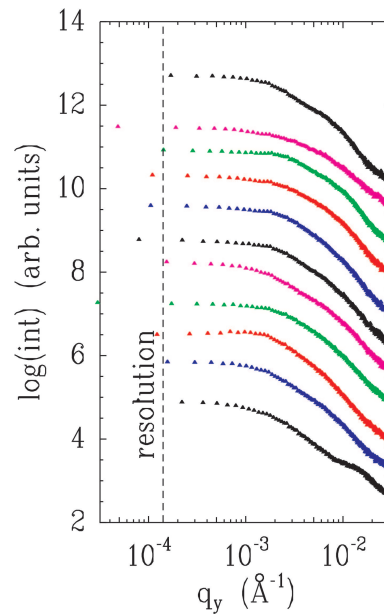


Figure 2.10:

Scattering data measured at the BW4 beamline. Instead of the full two-dimensional scattering data cuts from the two-dimensional intensity distribution, taken at the exit angle equal to the critical angle of one component of the blend polymer (PnBA), are displayed. Each curve refers to a sample with a different PnBA percentage. For clarity, the curves are shifted along the y-axis.

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Microscopic properties of adhesive polymer films

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Pressure sensitive adhesive (PSA) form an important class in polymer adhesive technology. Typical examples in daily life are adhesive stickers, Scotch tape or stick-on notes. Symptomatic for this kind of adhesives is the dependence of adhesions quality of the bonding history. Important parameters are contact pressure and contact time. In most applications of PSA a controlled debonding of the glued devices at an assigned time is desired. Despite high technological relevance the physical mechanism of adhesion are still not fully understood. A macroscopic understanding of adhesion is provided by the so called tack test [1-4]. A cylindrical punch is pressed under defined conditions (contact force, contact time) onto an adhesive film. While redrawing the punch with a constant velocity the adhesion force is measured (see figure 2.11C). The shape of the force distance curve is highly non-linear. First a sharp force maximum appears introducing major debonding. After the peak the force drastically drops down to a finite-dimensional value, the so called plateau value. By further retracting the punch from the polymer film the force remains, dependant on the PSA type, more or less constant at this plateau value. During this debonding stage fibrillation can be optically detected. The glue forms filaments which perpetuate a certain degree of connection in between punch and polymer film. The force recorded in this regime is attributed to the fibrils. This macroscopic fibrillation, a feature at large length scales, is part of a general structure forming process during debonding. The structures pursue in microscopic length scales, too. Theoretical work was done on structure forming during debonding on PSA [5,6]. In a more overall attempt structure forming has also been investigated in a lifting Hele-Shaw Cell on high viscous liquids [7]. Microscopic structures of the adhesive can be investigated by scattering experiments. We performed small angle x-ray scattering (SAXS) in transmission during the tack test. For this purpose a special home designed tack apparatus has been installed at the scattering facility. This apparatus meets the requirements of both mechanical tack testing and scattering (convenient goniometer handling possible and free path for in- and outgoing beam). Thereby the fibrils are in-situ created during the scattering experiment. As polymer adhesive basic components of industrially used glues are investigated. Former scattering experiments were done on a statistical copolymer of 80% ethylhexylacrylate and 20% methylmethacrylate. A well ordered microscopic structure was found. The reported experiments were performed on a modified statistical polymer consisting of 79% ethylhexylacrylate, 20% methylmethacrylate and 1% acrylic acid. The polymer was dissolved in solution of iso-butanol and solution casted on glass slides. In order to create fibrils for the scattering experiment a glass cylinder of 2 mm diameter was pressed with 6 N onto the PSA film. The pressure was maintained for 10 s. While the subsequent retracting of the punch the fibrils were in-situ provided for the scattering experiment.

The scattering measurements were performed at the BW4 beamline of the DORIS III storage ring at HASYLAB/DESY in Hamburg. The energy selected by a monochromator was 8.979 keV. Two entrance cross-slits set the beam divergence. With a sample-detector distance of 12.5 meters and an active detector diameter of roughly 20 cm (angles lower than 0.46°), we performed ultra small angle x-ray scattering (USAX). A centered beam stop avoided oversaturation of the detector due to the primary beam. The exact position of the primary beam was alternatively determined by a lupolen measurement. The polymer film was placed horizontally (see figure 2.11A). The incoming

angle was aligned to be zero with respect to the film. The punch was moved vertically, resulting in likewise vertical fibrils, being perpendicular to the incoming beam. In order to detect momentum transfers in the horizontal plane, we are mainly interested in horizontal cuts of the detector signal. The measurements were repeated for several distances between the polymer film and the punch (see figure 2.11B). The scattering signals show well pronounced fringes. The analysis of the fringes provides information on prominent microscopic length scales during fibrillation.

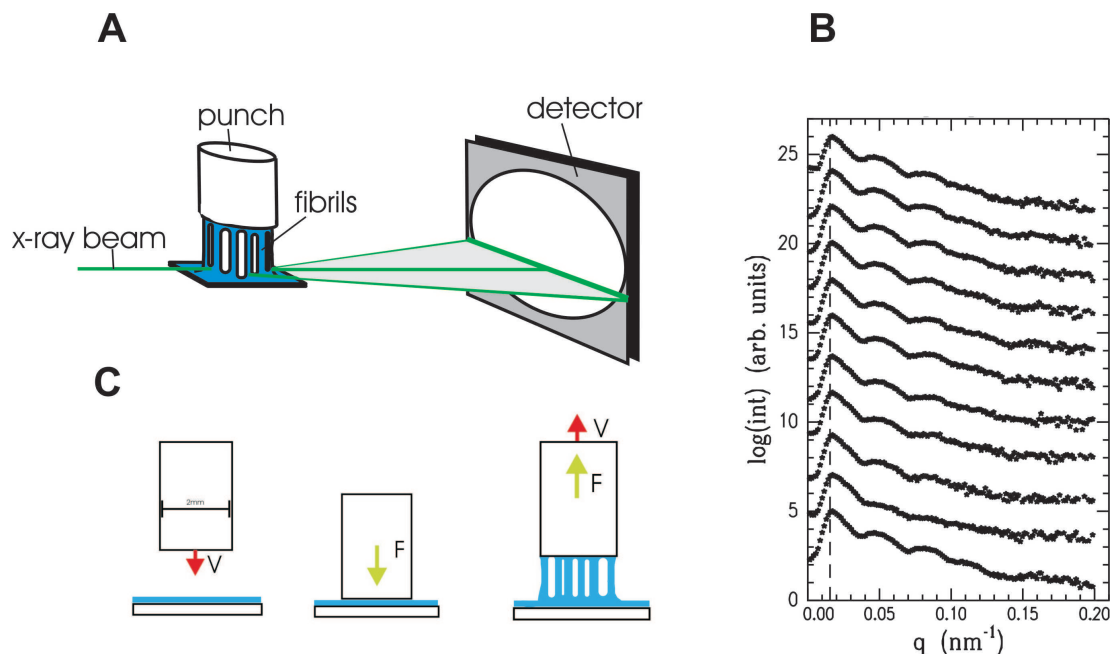


Figure 2.11:

A) Scattering geometry: The fibrils created in the debonding process are perpendicular to the scattering plane (grey plan). The transmission signal is detected. Horizontal cuts including the primary beam position yield information about the microscopic structures during debonding. B) Horizontal cuts of the detector signal. The position at the detector is converted into a horizontal momentum transfer. The intensity is displayed in a logarithmic scale. The cuts are shown for several punch polymer distances. For clarity all curves are shifted in the y-direction. C) The tack test is proceeded in three steps: 1. A glass cylinder (probe) is pressed onto a PSA film. 2. The applied force is maintained. 3. The probe is retracted from the film.

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Scanning Microfocus Small-Angle X-ray Scattering: A New Tool to Investigate Defects at Polymer-Polymer interfaces

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The adhesion at polymer-polymer interfaces has been an important subject of both experimental and theoretical investigations. During the generation of an interface (welding) the diffusion of polymer chains across this interface is the most important process.

Mechanical testing has been applied to characterize the fracture toughness between welded polymer slabs. A simple and effective way to test the strength of an interface was established with the Double Cantilever Beam test (DCB) [1]. During this test a starter crack is created at the polymer-polymer interface. Next this crack is forced to propagate by pushing a razor blade between both polymer slabs. The relatively slow velocity of the razor blade (some $\mu\text{m}/\text{s}$) ensures that the crack propagates steadily at the same rate as compared to the blade [2]. Thus the elastic energy release rate matches exactly the energy dissipation near the crack tip. The fracture toughness is calculated directly from the length of the crack. This method provides a quantitative measure of the strength of an interface. Although it has been applied successfully in many investigations it does not provide details about the nature of the energy dissipation process during crack propagation. If the interface is weak almost all the energy put in the system is dissipated very closely to the crack. The tougher the interface becomes, the more energy is dissipated in the formation of a plastic zone around the crack tip. The spatial distribution of defects in the plastic zone is mainly addressed in the present investigation: How far does the energy dissipation in form of defects reach into the bulk material? What are distribution, orientation and structural properties of these defects? In previous work, spatially resolved structural investigations of failure in the bulk or at interfaces were limited to experimental techniques like optical microscopy or transmission electron microscopy (TEM). Information obtained from optical microscopy is limited towards small structures by the optical resolution (typically $1\mu\text{m}$) irrespective of the geometry used (reflection or transmission mode). With TEM much smaller structures are observable. However, the disadvantage of this technique is the need to cut the samples into small slices or to use very thin samples from the beginning. Thus, an unknown amount of defects might be related to this preparation or the geometry is not typical for bulk applications. A suitable way to probe bulk structures on the nanometer scale with no additional mechanical stresses imposed to the sample is small angle X-ray scattering (SAXS). Anyhow, with a conventional setup this method does not provide information with resolution in real space across the sample because it averages over the complete sample volume illuminated by the X-ray beam (typically $> 300\mu\text{m}$). With decreasing beam diameter ($< 10\mu\text{m}$) combined with a scanning over the sample an image of structures at different positions in the samples is obtained.

Nowadays, the use of synchrotron radiation and an improvement in collimation techniques allows beam diameters in the micrometer range still having a high flux. Thus scanning of large sample areas with a high spatial resolution in two directions perpendicular to the beam is possible. We used this new option to investigate interface failure and crack propagation between two welded poly(methyl methacrylate) (PMMA) slabs for the first time.

The scanning micro focus-small angle X-ray scattering (SM-SAXS) experiments were performed

at the micro focus beam-line ID13 at the ESRF in Grenoble. With a collimator the beam diameter was reduced to $10\ \mu\text{m}$.

Figure 2.12 shows an example of a crack tip as investigated with optical microscopy and SM-SAXS. This sample exhibits a very pronounced defect pattern. The crack enters from the bottom.

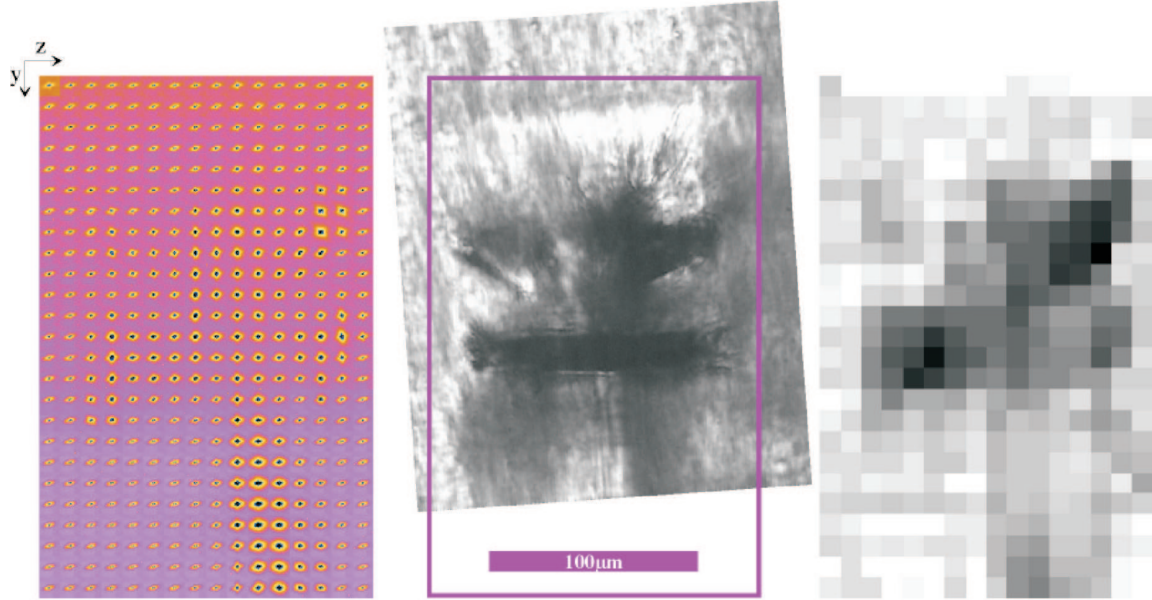


Figure 2.12:

Left) Scattering pattern corresponding to each measurement position composed to a map of the complete scan field (size of each image 400×400 pixels, $q \leq 1.935\ \text{nm}^{-1}$). Center) Micrograph of the scan zone (bordered by the rectangular). The actual scan zone has been slightly larger than the micrograph and the microscope camera had a slight tilt of 4° . Right) Map of slopes for each measurement position in the corresponding cut direction with respect to the horizon. The color coding covers $\alpha = -1.5$ (white = largest slope) down to $\alpha = -5$ (black = lowest slope) with a step width of $\Delta\alpha = 0.1$ in grey levels.

The optical microscope is a video microscope without special equipment. Thus the dark areas in the image reflect defects and voids that scatter light in the optical regime. The left part of figure 2.12 exhibits the 400 scattering pattern gained from each measurement position composed into one map. The distance between the neighboring measurement positions of these SAXS images is $10\ \mu\text{m}$. To gain more information on the origin of the scattering it is not enough to evaluate the integrated intensity but one also has to consider the slope of the scattering curves. As shown in reference [4] in the entire q -range no further unaccounted scattering is present. Thus the observed scattering intensity (I_{obs}) obeys a scaling law over the full accessible q -range $I_{obs} \propto q^\alpha$ (see right part of figure 2.12).

Thus estimating integrated scattering intensity and the decline of the scattering curves together yield information about the condition of the defect structures in the probed scattering volume: High integral scattering intensities combined with steep slopes in the observed scattering volume mean the presence of a wide region with a diffuse transition in electron density between polymer and air/vacuum and not a higher amount of single scattering features with sharp boundaries.

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Metallic nanoparticles in thin diblock copolymer films: Influence of nanoparticle concentration

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Composite materials are important in several technical applications and as model systems for basic research. Composites are formed from a matrix (polymer) and a filler which may be metallic (e.g. metal, metal oxide or alloy) or nonmetallic (e.g. silicon nitride, silicon carbide, carbon fibers). The great potential of composites derives from the substantial modification of the thermal, mechanical and electrical characteristics of polymers that result from the combination of the polymer with a filler. The interest to lamellar composite materials and successful attempts to create copolymer-nanoparticles organized structures were reported by several groups [1-4].

To overcome problems related to high nanoparticle concentrations we applied a new approach in the thin film preparation. Instead of a single spin-coating step a two-step procedure based on spin-coating and solution casting, as explained elsewhere [5], was utilized. The diblock copolymer was polyisoprene-block-polyethyleneoxide P(I-b-EO) with a molecular weight of 9.3 k and a narrow molecular weight distribution 1.09. A rather symmetric block ratio of $f_{PI}=0.55$ was chosen, resulting in a lamellar structure. The magnetite Fe_3O_4 nanoparticles were hydrophilically coated and have a mean diameter of 10 nm. Films with different amount of nanoparticles were prepared and investigated with grazing incidence small angle x-ray scattering (GISAXS).

The GISAXS measurements were performed at the beamline A2 of the DORIS III storage ring at HASYLAB/DESY in Hamburg. The selected wavelength was 0.154 nm. The scattered intensity was recorded with a two dimensional detector (MARCCD) which consists of a 1024x1024 pixel array due to a binning factor of 2. Due to the sample-detector distance of 1.1 m a relaxed resolution was achieved which enabled the detection of lateral structures between 2 and 340 nm. This fits well to the typical regime expected for polymeric lamellae as well as for the nanoparticles. The beam divergence in and out of the plane of reflection was set by two entrance cross-slits. At one fixed angle of incidence the two-dimensional intensity distribution can be cut into several vertical and horizontal slices with respect to the sample surface. Vertical slices contain mainly scattering information from structures perpendicular to the sample surface, whereas horizontal slices contain only scattering contributions with an in-plane information.

Figure 2.13 shows the example of 6 different nanoparticle concentrations inside the polymeric matrix. From figure 2.13a to e the concentration decreases and figure 2.13f shows the pure diblock copolymer film for comparison. On first sight it is visible that the GISAXS pattern is strongly changed by a variation of the nanoparticle concentration. Without nanoparticles (figure 2.13f) the GISAXS pattern exhibits the common features of thin diblock copolymer films, namely the specular peak (top part) and a broadened Yoneda peak (bottom part of figure 2.13f). Bragg peaks

are absent due to the small film thickness. With increasing nanoparticle concentration the diffuse scattering increases and spreads out in its angular range. At the highest nanoparticle concentration shown (figure 2.13a) only a very weak specular peak sits on top of a huge hump of diffuse intensity. Irrespective of the nanoparticle concentration distinct peaks in the GISAXS pattern, for example originated by a structure factor of the polymer lamellar, are missing. This indicates the absence of high degree of lateral order of the host matrix. Instead a sign of nanoparticle diameter is present in the GISAXS pattern matching with the magnetite diameter of 10 nm. From the amplitude of this contribution the amount of nanoparticles inside the polymeric matrix will be calculated. A detailed data analysis is in progress.

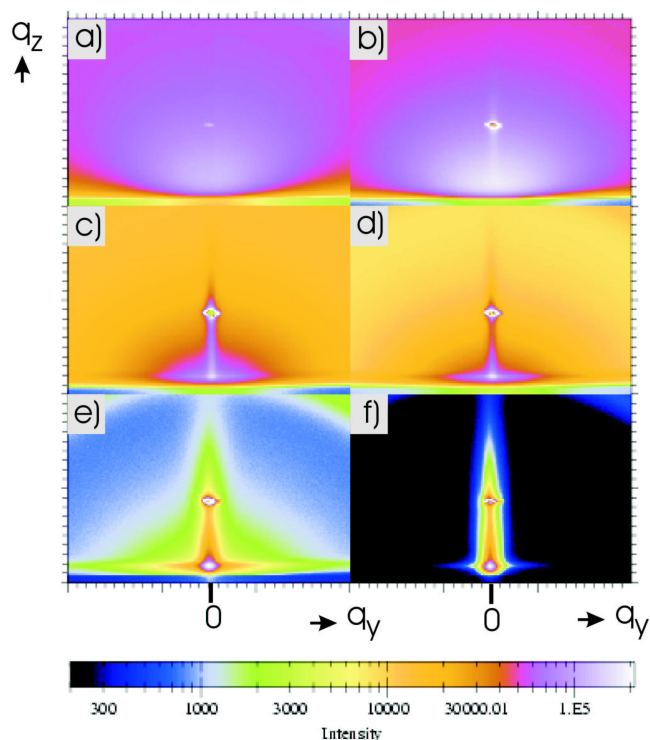


Figure 2.13:

Typical two-dimensional GISAXS scattering pattern measured at beamline A2: a-e) nanoparticle diblock copolymer composite thin films and f) thin diblock copolymer film without additional nanoparticles. The intensity is shown on a logarithmic scale. The color-coding was chosen to emphasize on the features in the diffuse scattering (black=low and white=high intensity).

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Parallel and perpendicular lamellar phases in copolymer-nanoparticle multilayer structures

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Recent results in the development of novel nanocomposite multilayer structures are presented. We used symmetric polystyrene-block-polymethylmethacrylate (deuterated) P(S-b-MMA_d8) lamellar thin films as a self-assembling matrix for the lamellar arrangement of Fe₃O₄ nanoparticles. In the surface near part of the film pure copolymer films showed an unusual structure of a perpendicular orientation of the lamellae with respect to the surface. This is a new phenomena because up to now this orientation was obtained only on specially prepared substrates. After the incorporation of nanoparticles into the copolymer matrix the system switched to a lamellar structure parallel to the surface. Further increasing of the nanoparticles concentration leads to a more perfect lamellar structure, which shows that the upper limit for the maximum concentration of nanoparticles inside the polymer matrix is not yet reached.

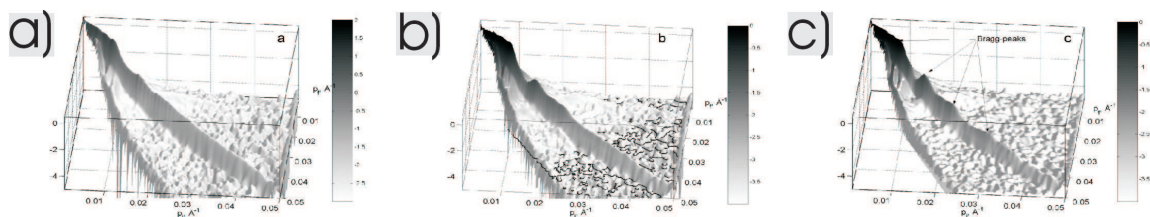


Figure 2.14:

Experimental 3-dimensional intensity maps from P(S-b-MMA_d8) films with incorporated Fe₃O₄ nanoparticles with the volume fraction of 0% (a), 2% (b) and 4% (c). p_i and p_f are the perpendicular to the surface of incoming and outgoing wavevector, respectively.

The symmetric diblock copolymer P(S-b-MMA_d8) was prepared anionically (Polymer Standard Service, Mainz). Magnetite (Fe₃O₄) superparamagnetic nanoparticles covered with polystyrene hairs were synthesized from α -lithium polystyrene sulfonate. The mean size of the coated particles as determined with light scattering is 10 nm. P(S-b-MMA_d8) and coated nanoparticles were blended in a toluene solution. The volume fraction of the nanoparticles was varied between 1% and 9%. After the spin coating homogeneous P(S-b-MMA_d8) films with magnetite nanoparticles were obtained. The samples were annealed during 72 h at a temperature $T = 190^\circ \text{C}$. The neutron reflection experiments were performed on reflectometers REMUR (JINR, Dubna) and D17 (ILL, Grenoble).

In our previous experiments nanoparticles were incorporated in P(Sd-b-BMA) copolymer films [1] and the distortion of the lamellar structure and of the interfaces increased with increasing concentration of nanoparticles.

A remarkably different behaviour of P(S-b-MMA_d8) nanocomposite films was observed in the present experiment. Figure 2.14 shows 2-dimensional intensity maps from 3 samples with 0%

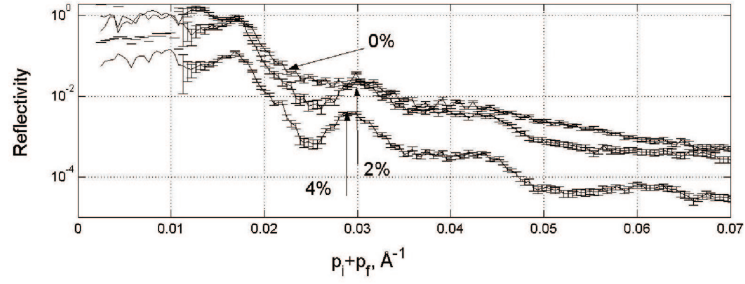


Figure 2.15:

Experimental reflectivity curves for P(S-b-MMAd) films with different volume fractions of the Fe_3O_4 nanoparticles. Positions of the Bragg peaks are indicated with arrows. $p_i + p_f = Q_z$ denotes the momentum transfer perpendicular to the film surface. The curve, obtained from the film with 4% of nanoparticles, is displaced for clarity.

(a), 2% (b) and 4% (c) volume fraction of nanoparticles. The pure copolymer film does not show a good lamellar alignment. The Bragg peaks around $Q_z = 0.016$ and $0.03 \text{ \AA}^{-1}$ become more pronounced and shift to smaller values with increasing concentration of the nanoparticles (see figure 2.15). This indicates that the lamellar arrangement parallel to the sample surface develops and approaches a more perfect lamellar arrangement for higher concentration of the nanoparticles. The bilayer thickness L , which determines the position of the Bragg peak, also increases with nanoparticles concentration [1].

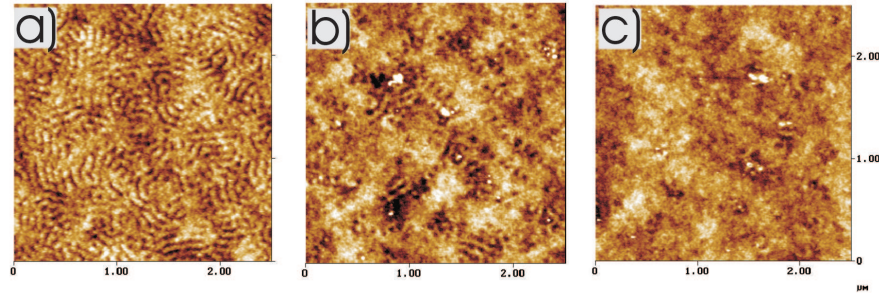


Figure 2.16:

AFM images from the annealed samples with the volume concentration of nanoparticles 0% (a), 2% (b) and 4% (c). The color scale range is from 0 to 5 nm.

Additional measurements with atomic force microscopy (AFM) showed that for a pure copolymer film the surface of the sample has lamellae of PS and PMMA with perpendicular arrangement (fig 2.16a). This is a new phenomena because up to now the perpendicular orientation was only obtained on specially prepared surfaces and confined films [2] or for very thin films (in the present study the thickness of the films was about $4L$). After the incorporation of only 2% of nanoparticles the system switches to a lamellar structure parallel to the surface (fig 2.16b). The analysis of the neutron data show that the pure copolymer film has a part with the lamellae parallel to the substrate and a top part with the lamellar perpendicular to the free surface. In contrast to our previous experiment [1] the off-specular Bragg-sheet scattering is nearly absent for the pure copolymer film and develops with the increasing of concentration of the nanoparticles. This is connected to two effects. The first is that the Bragg peaks become apparent (see figure 2.14), showing the

evolution of the lamellar structure. The second is that the roughness is correlated between different interfaces across the film.

In conclusion, the pure copolymer P(S-b-MMA_{d8}) film showed an unusual structure with two phases of the lamellae' orientation, perpendicular and parallel to the surface. Incorporation of nanoparticles induces a parallel alignment of the polymer matrix. Further increasing of the nanoparticles concentration leads to a more perfect lamellar structure, which shows that the limit for a highest concentration of nanoparticles important for nanotechnology is not yet reached.

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Structures in thin diblock copolymer films

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Block copolymers in the bulk form various, mesoscopically ordered structures, for instance lamellae with thicknesses between 100-1000 Å. Block copolymer films can thus be used for patterning surfaces on a submicrometer length scale. In order to understand the surface structures observed as well as their stability and their response to outer stimuli, it is important to gain knowledge both on the surface structure and the inner film structure. The combination of direct visualization of the surface texture by atomic force microscopy (AFM) with scattering methods elucidating the inner film structure has proven to give a wealth of information. By means of grazing-incidence small-angle X-ray scattering (GISAXS), structures normal to the substrate as well as lateral structures can be detected simultaneously (Fig. 2.17). In addition, time-resolved GISAXS measurements can be used to study the structural changes of the films upon outer stimuli in-situ.

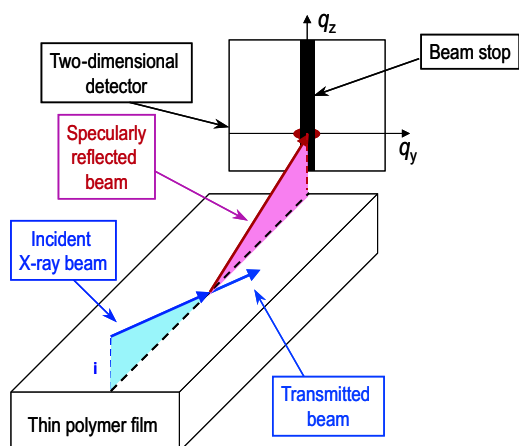


Figure 2.17:

Set-up used for GISAXS experiments. The X-ray beam hits the sample at an angle α_i slightly larger than the critical angle of external reflection. The transmitted beam serves as the primary beam for small-angle scattering from the polymer film, which is detected by a CCD camera. The beam stop protects the camera from the intense reflected beam.

At the University of Leipzig, we have studied thin films of a series of polystyrene-polybutadiene diblock copolymers, and have found a previously unknown molar-mass dependence of the lamellar orientation [1,2]. The surface textures from low molar mass samples (13.9-22.6 kg/mol) reveal terraces, indicating the parallel lamellar orientation (Fig. 2.18a), whereas high molar mass samples (148-183 kg/mol) show a lamellar texture, pointing to the perpendicular orientation (Fig. 2.18b) [1,2]. The corresponding two-dimensional GISAXS maps show intensity maxima in the plane of incidence (Fig. 2.18c) for low molar mass samples and Bragg rods for high molar mass samples (Fig. 2.18d). We conclude that the lamellar orientation observed at the surface is prevalent in the film as well. The positions of the intensity maxima observed with parallel lamellae were modeled using the distorted-wave Born approximation [3]. The molar-mass dependence of the lamellar orientation can be understood in terms of a model not only taking into account the difference of surface tensions of the two blocks, but also entropic effects like chain stretching and chain end

enrichment near a wall [4]. In time-resolved in-situ GISAXS experiments during treatment of a high molar mass film with toluene vapor, we found that the lamellar orientation changes within minutes but the perpendicular orientation is regained after the solvent is removed [5].

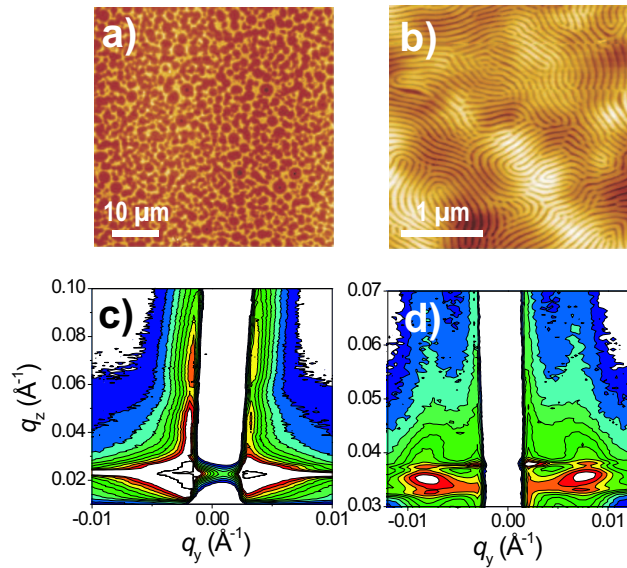


Figure 2.18:

Atomic force microscopy images (a,b) and corresponding two-dimensional GISAXS maps (c,d) from two thin polystyrene-polybutadiene diblock copolymer films. (a,c) Block copolymer molar mass $\bar{M}_n = 22600$ g/mol, lamellar thickness $D_{\text{lam}} = 197$ Å, film thickness $D_{\text{film}} = 422$ Å, (c) incident angle $\alpha_i = 0.16^\circ$, (b,d) $\bar{M}_n = 183000$ g/mol, $D_{\text{lam}} = 839$ Å, $D_{\text{film}} = 2320$ Å, (d) $\alpha_i = 0.21^\circ$.

In the future, we wish to continue the in-situ time-resolved measurements during vapor treatment of polystyrene-polybutadiene films having different lamellar orientations. Also other morphologies shall be studied, for instance the reaction of cylinders to vapor treatment.

In addition, we wish to study thin films of diblock copolymers having one crystallizing block. The interplay between mesophase formation of the two blocks and crystallization of one of the blocks together with the interaction with the substrate leads to a wealth of surface structures on various length scales [6,7]. For instance, parallel as well as perpendicular lamellae with high persistence lengths have been observed, depending on the preparation conditions and on film thickness. We wish to study the orientation of the mesoscopic structures (lamellae, cylinders) using GISAXS as well as the orientation of the crystalline chains with respect to the lamellar interfaces and the film surface using grazing-incidence wide-angle scattering. In this way, we hope to gain information on the influence of the enthalpic and entropic interactions at the film interfaces. Eventually, we hope to be able to control the surface structures by appropriate pre-structuring of the substrate.

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Aggregation behavior of amphiphilic block copolymers in aqueous solution

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Amphiphilic block copolymers in aqueous solution exhibit a very rich phase behavior: Depending on temperature, concentration, chemical composition and architecture of the copolymers and the solvent used, they form unimers, micelles, gels of micelles as well as lamellar phases [1-3]. We have chosen to study a new, very versatile system, namely polyoxazoline-based block copolymers (Fig. 2.19). The hydrophobicity of the monomers can be tuned by varying the length of the alkyl chain. Diblock copolymers (A-B), triblock copolymers with equal, hydrophobic end blocks (A-B-A) as well as triblock copolymers with different end blocks A-B-C (hydrophobic-hydrophilic-fluorophilic) have been synthesized [4,5]. Also the synthesis of polyoxazoline-based lipopolymers has been performed [5]. This polymer system has the additional advantage that fluorescence labels can be chemically attached at different locations in the polymer.

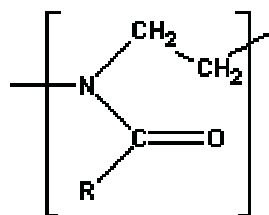


Figure 2.19:

Structure of the polyoxazoline monomer. R stands for an alkyl chain.

We are studying the aggregation behavior as well as the diffusion mechanisms in the various structures formed by this polymer system in aqueous solution as well as the diffusional mechanisms in the different structures formed by means of scattering and single-molecule techniques.

At the University of Leipzig, we have used fluorescence correlation spectroscopy (FCS) to study the self-diffusion of fluorescence-labeled poly(methyloxazolin)-poly(nonyloxazolin) diblock copolymers in aqueous solution. With this method, the diffusion of fluorescence-labeled particles through a detection volume of $\sim 1 \mu\text{m}^3$ is monitored, and the self-diffusion coefficient is determined [6]. The measurements are carried out on the basis of very few molecules in the detection volume, and only $\sim 10 - 100 \mu\text{l}$ of sample are necessary for one measurement. The fluorescence-labeled polymers were used as tracers in aqueous solutions of otherwise identical, non-labeled polymers. In this way, a large concentration range could be accessed without oversaturating the FCS detector, and we could determine the diffusion coefficients of the unimers and the micelles and identify the critical micelle concentration (Fig. 2.20).

In addition, we have carried out temperature-resolved dynamic light scattering (DLS) experiments and found, that after dissolution at room temperature, a metastable state is formed, consisting of very large aggregates. Only after heating the solutions, the micelles assume their equilibrium size of $\sim 12 \text{ nm}$. By comparing the hydrodynamic radii obtained using DLS with those from FCS on annealed samples, we could show that the hydrodynamic radii of the micelles can reliably be determined using FCS. In the future, we wish to extend our dynamic studies to triblock copolymers as well as to lipopolymers.

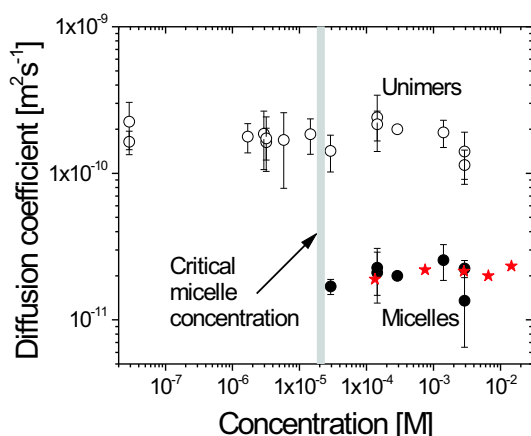


Figure 2.20: Diffusion coefficients from aqueous solutions of a low molar mass poly(methyloxazoline)-poly(nonyloxazoline) diblock copolymer in dependence on concentration with the fluorescence label TRITC attached at the end of the hydrophilic block. The solutions were annealed prior to measurement. Black symbols: results from FCS, red symbols: results from DLS.

In addition, we wish to study the aggregation behavior of A-B-C triblock copolymers in aqueous solution using small-angle X-ray scattering. The phase behavior is expected to depend strongly on the chemical nature and the incompatibility of the three blocks. In water, these polymers have been shown to aggregate into two kinds of micellar domains (e.g. hydrophobic and fluorophilic) to build a multicompartiment system [4]. We wish to determine the structures of these systems in dependence on block lengths and concentration in detail.

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3 Struktur und Dynamik von Kristallen und Schmelzen

Melts in a Pd and Ni base can in good approximation be regarded as hard-sphere like systems. As compared to simple liquids, these melts are characterized by a dense packing. As a consequence their microscopic dynamics are not described by concepts developed for simple liquids. Instead, atomic transport in Pd and Ni base melts is in excellent accordance with concepts developed in the context of glass formation [1]. Pd-Ni-Cu-P melts in quasi eutectic compositions [2] exhibit a relatively low liquidus temperature at 865 K – as compared to pure liquid Nickel at 1727 K. On approaching the liquidus structural relaxation becomes well separated from fast processes. This allows for the study of the atomic transport mechanism in hard-sphere like, metallic liquids.

We investigate microscopic dynamics in liquid Pd-Ni-Cu-P melts with inelastic neutron scattering [3]. The intermediate scattering function displays a fast relaxation process that precedes structural relaxation. Structural relaxation exhibits stretching and obeys a time-temperature superposition that extends over a temperature range of nearly 1000 K. The mode-coupling theory of the liquid to glass transition gives a consistent description of the dynamics which governs the mass transport in liquid Pd-Ni-Cu-P alloys. MCT scaling laws extrapolate to a critical temperature T_c at about 20 % below the liquidus temperature.

Mass Transport around Mode Coupling T_c

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Diffusivities derived from the mean relaxation times compare well with Co [4,5] and Ni diffusivities from recent tracer diffusion measurements and diffusivities calculated from viscosity via the Stokes-Einstein relation (Fig. 3.1). In contrast to simple metallic liquids, the atomic transport in dense, liquid Pd-Ni-Cu-P is characterized by a drastic slowing down of dynamics on cooling and a q^{-2} dependence of the mean relaxation times at intermediate q as a result of a highly collective transport mechanism. At temperatures as high as $2.5 \times T_c$ diffusion in liquid Pd-Ni-Cu-P alloys is as fast as in simple liquids at the melting point. However, the difference in the underlying atomic transport mechanism indicates that the diffusion mechanism in liquids is not controlled by the value of the diffusivity but rather by that of the packing fraction [3].

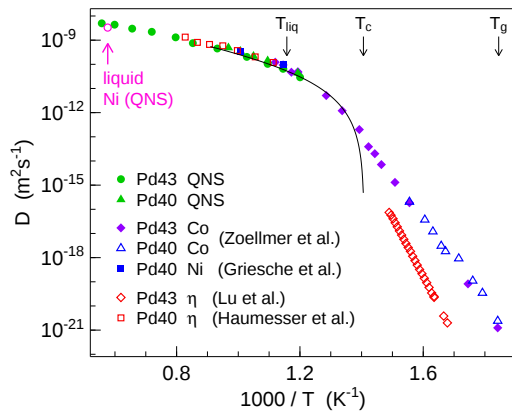


Abbildung 3.1:

Self diffusion coefficient D of Ni in liquid Pd₄₃Ni₁₀Cu₂₇P₂₀ and Pd₄₀Ni₁₀Cu₃₀P₂₀ derived from the mean relaxation times (QNS). The line represents the MCT τ scaling law using $T_c = 710$ and $\gamma = 2.7$ as obtained from the analysis of the fast, localized β relaxation. For comparison ⁵⁷Co and ⁶²Ni tracer diffusion and diffusivities calculated from viscosity η via the Stokes-Einstein relation are shown.

Figure 3.1 shows that the time scales for viscous flow and Co tracer diffusion decouple in the vicinity of T_c and differ already by more than 3 orders of magnitude at 600 K. Also around T_c Co tracer diffusivities merge into an Arrhenius-type temperature dependence that extends down to the glass transition. The temperature dependence of the transport coefficients strongly supports the MCT prediction of a change in the atomic transport mechanism from viscous flow to glasslike activated hopping at T_c .

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Microscopic Dynamics in Pd- and Ni- based Melts

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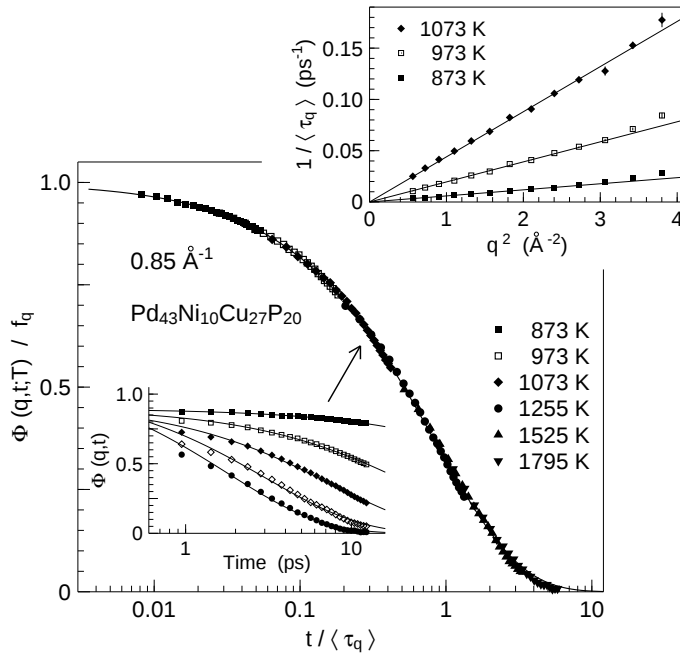


Abbildung 3.2:

Rescaling of the density correlation function in α relaxation regime (for $t > 1$ ps) using result from fits with a stretched exponential function: time-temperature superposition of structural relaxation holds., Inset: Normalized density correlation function $\Phi(q, t)$ of liquid $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$. The lines are fitted with stretched exponential function., Up: mean relaxation time τ_q of self motion in liquid $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$. $1/\tau_q$ shows a q^2 dependence as expected for long range atomic transport for $q \rightarrow 0$. The slope corresponds to the self diffusion coefficient D .

We investigated microscopic dynamics in PdNiCuP melts with inelastic neutron scattering. The intermediate scattering function displays a fast relaxation process that precedes structural relaxation. The structural relaxation exhibits stretching and obeys time-temperature superposition (Fig. 3.2).

Liquid Ni, NiP, PdNiP and PdNiCuP melts exhibit a similar packing fraction although liquidus and under cooling capabilities are quite different. A comparison of the inelastic neutron scattering data

shows that neither the absolute value of the Ni diffusivity nor the normalized correlation function of Ni dynamics are affected significantly by the change in the alloys composition (Fig. 3.3).

In contrast to simple liquids, atomic transport in dense, glass forming liquids are characterized by a drastic slowing down of dynamics on cooling and a q^2 dependence of the mean relaxation time at intermediate q as a result of a highly collective atomic transport mechanism. At temperatures as high as $2.5 \times T_c$ diffusion in these melts are as fast as in simple liquids at the melting points. However, the difference in the underlying atomic transport mechanism indicate that the diffusion mechanism in liquids is not controlled by the value of diffusivity but rather than that of the packing fraction [3].

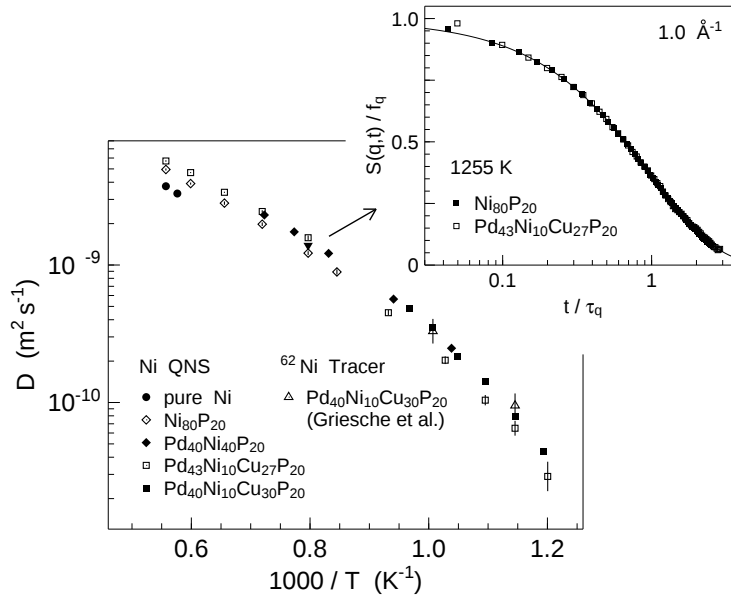


Abbildung 3.3:

Mass transport in Pd-Ni based melts: Self diffusion coefficient D of Ni in liquid $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$, $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$, $\text{Ni}_{80}\text{P}_{20}$ and pure Ni derived from the mean relaxation times (QNS). Shows similar Ni diffusivities and for comparison diffusivities by ^{62}Ni tracer diffusion is shown.

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Structure and Ni Diffusion in Al-Ni Melts

S. Mavila Chathoth, A. Meyer and W. Petry

Structure, thermodynamic and atomic transport (viscosity and diffusion) properties of Al-Ni alloys play an important role in the processing of many super alloys, and are therefore significant practical interest. Al-Ni alloys are strongly ordered in its solid state and appreciable chemical short range order(CSRO) known to exist in its liquid phase[1]. Al-Ni alloys therefore interesting form more basic point of view as a model system for studying CSRO and its consequence for physical properties in liquid metals.

In the present study we investigated Al-Ni melts using a cold neutron time of flight spectrometer IN6, at ILL, Grenoble, France with a measuring wavelength of 5.12 Å. We focused our attention to study structure (CSRO) and Ni diffusion in Al-Ni melts with different Ni concentration.

Al-Ni alloys was prepared from a mixture of pure elements by arc melting. Differential scanning calorimetry with heating rate 40K/m used to measure the liquidus temperature as a check for the right composition. For neutron time of flight experiment a thin walled Al₂O₃ container has been used giving a hollow cylinder sample geometry of 22mm diameter. For the chosen geometry and neutron wavelength the sample scatter less than 5%. Therefore, multiple scattering which would alter the data especially towards low q only has a negligible effect.

The incident wavelength $\lambda = 5.1$ Å give an accessible wavenumber range $q = 0.22$ to 2.1 Å⁻¹ at zero energy transfer. Regarding the scattering cross section of the individual elements, with the first structure maximum at $q_0 \cong 3.0$ Å⁻¹ our spectra are dominated by incoherent scattering from nickel since the incoherent scattering cross section of Al is negligible. The alloys were measured at room temperature to obtain instrumental energy resolution function. In the liquid, data were collected at 1000 K, 1175 K, 1350 K and 1525 K with a duration of 2 hours each. At each temperature empty cell run also was performed.

In order to obtain scattering law $S(q, \omega)$ raw data was normalized to vanadium standard, corrected for self absorption correction and container scattering interpolated to constant q , symmetrized with respect to energy with detailed balance factor.

We investigated pure Ni, Al₉₀Ni₁₀, Al₈₀Ni₂₀, Al₇₇Ni₂₃, Al₇₀Ni₃₀ and Al₂₅Ni₇₅ alloy melts. The figure.1 shows the static structure factor of these melt at 1525K, obtained by integrating $S(q, \omega)$ over the elastic range. It shows a prepeak in Al₈₀Ni₂₀, Al₇₇Ni₂₃ and Al₇₀Ni₃₀ melts indicating the presence of chemical short range order(CSRO) in these melts. Maret *et al* observed the CSRO in Al₈₀Ni₂₀ liquid by isotope substitution and neutron diffraction[1]. We observed that the CSRO exist in Al₇₀Ni₃₀, Al₇₇Ni₂₃ and Al₈₀Ni₂₀ melt and it does not exist in Al₉₀Ni₁₀ and Al₂₅Ni₇₅ melts.

In the hydrodynamic limit for $q \rightarrow 0$ one expects that the mean relaxation time $\langle \tau_q \rangle$ are indirectly proportional to the momentum transfer q square. The deviation from the q^2 dependence at higher q values is the fact that the low lying phonon that mediate the atomic transport[2]. The

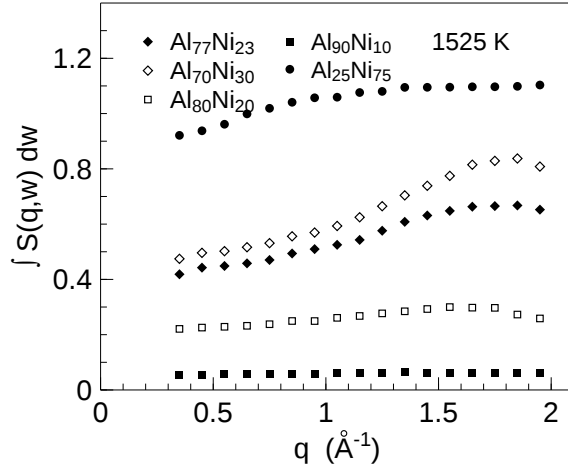


Figure 3.4:

The static structure of Al-Ni melts as a function of Ni concentration at 1525K. The pre-peak is more pronounced in Al₇₀Ni₃₀ and Al₇₇Ni₂₃ as compared to Al₈₀Ni₂₀. It does not exist in Al₉₀Ni₁₀ and Al₂₅Ni₇₅ liquids

$1/q^2$ dependence of the mean relaxation time demonstrate that structural relaxation leads to long range atomic transport with diffusivity $D = (\langle \tau_q \rangle q^2)^{-1}$

The figure.2 shows the Ni diffusivities in the melts. The Ni diffusivities in these melts shows a concentration dependence of the Ni. As the Ni concentration increases the diffusivities start decreasing. But the Ni diffusion in Al₇₅Ni₂₅ melts show the similar Ni mobilities as in pure Ni.

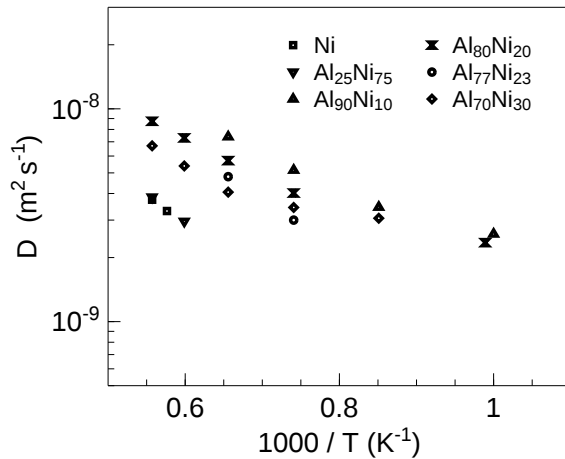


Figure 3.5:

The Ni self diffusion coefficient in Al-Ni melts with different Ni concentration. The Ni diffusivities shows that an decreasing Ni mobilities as increasing Ni concentration

To conclude we studied the structure(CSRO) and Ni diffusion in Al-Ni Melts. It was found that CSRO is existing in Al₇₀Ni₃₀, Al₇₇Ni₂₃ and Al₈₀Ni₂₀ liquids and not found in Al₉₀Ni₁₀ and Al₇₅Ni₂₅ liquids. The Ni diffusivity data shows an increasing Ni mobility as the Ni concentration decreases and similiar Ni mobilities in pure Ni and Al₂₅Ni₇₅.

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Mikroskopische Dynamik und Struktur in Natrium-Aluminosilikat Schmelzen

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Untersuchungen von Natriumsilikatschmelzen mittels inelastischer Neutronenstreuung erklären in Kombination mit Molekulardynamiksimulationen (J. Horbach (Mainz), W. Kob (Montpellier)) den Zusammenhang zwischen makroskopischem Verhalten und mikroskopischer Dynamik und Struktur [1,2]. Als Ursache für die ebenfalls in der Schmelze von der Relaxation des Netzwerkes um mehrere Größenordnungen entkoppelte schnelle Na-Relaxation wurde die Ausbildung einer Struktur von Kanälen im dynamischen Sinne, welche in die bestehende SiO-Matrix eingebettet ist, identifiziert. Ein Hinweis auf eine Korrelation auf Längenskalen von 6-8 Å, welche im Rahmen von MD-Simulationen dem typischen Abstand zweier Kanäle zugeordnet werden konnte, zeigt sich in einem im elastischen Strukturfaktor $S(q, \omega = 0)$ anwachsenden Prepeak bei $q \simeq 0.9 \text{ Å}^{-1}$. Dieser Prepeak wurde experimentell nur in der Schmelze, jedoch nicht im Glas beobachtet. MD-Simulationen, die im Gegensatz zu Streuexperimenten Zugang zu partiellen Strukturfaktoren ermöglichen, zeigen, dass diese Korrelationen auf intermediären Längenskalen ebenfalls im Glas vorhanden sind, jedoch erst in der Schmelze in $S(q, \omega = 0)$ durch die Dichteänderung sichtbar werden.

Wir haben unsere Untersuchungen auf das ternäre System der Natrium-Aluminosilikate erweitert. Der hohe Prozentsatz in natürlicher Magma, sowie die enthaltenen einfachsten geologisch relevanten Magma, Albit, Jadeit und Nephelin, begründen das seit mehreren Jahrzehnten bestehende Interesse der Geowissenschaften an dieser Materialklasse. Neben makroskopischen Untersuchungen (z. B. Viskosität) [3] trugen vermehrt mikroskopische Methoden wie Raman-Streuung [4] und NMR [5] zur Modellbildung bei. In diesem Zusammenhang wurden intensiv die strukturellen Einbaumöglichkeiten für Si und Al untersucht (Annahme der Ausbildung von Triclustern). Die Ionendynamik wurde mittels Tracerdiffusionsmessungen untersucht [6].

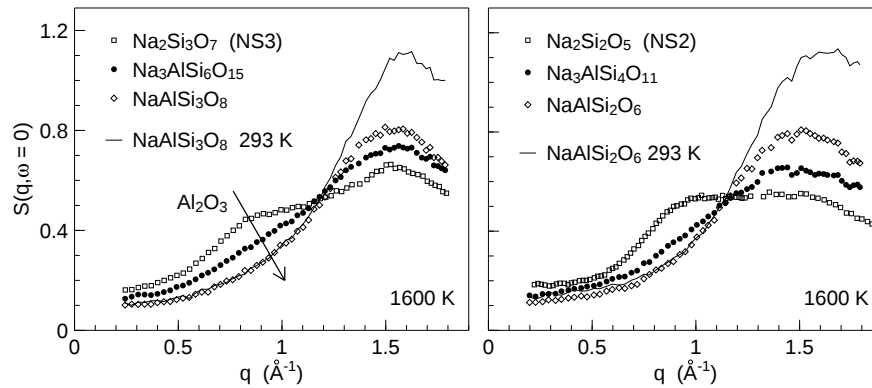


Abbildung 3.6:

Elastischer Strukturfaktor von NS3 Basis Aluminosilikaten (links) und NS2 Basis Aluminosilikaten (rechts) in der Schmelze bei 1600 K und im Fall der Na/Al = 1 Proben Albit und Jadeit zum Vergleich bei Raumtemperatur (durchgezogene Linie).

Ausgehend von unseren Experimenten an binären Natrium-Silikaten ($\text{Na}_2\text{Si}_2\text{O}_5$ (NS2), $\text{Na}_2\text{Si}_3\text{O}_7$ (NS3), $\text{Na}_2\text{Si}_4\text{O}_9$ (NS4)) untersuchen wir mittels inelastischer Neutronenstreuung den Einfluß der

Zugabe eines weiteren Netzwerkbildners Al_2O_3 auf die Struktur und Na-Dynamik in der Schmelze. Die Messungen wurden am Instrument IN6 (ILL) mit einer einfallenden Neutronenwellenlänge von $5.9 \text{ \AA}$ durchgeführt. Die elastische Auflösung betrug $50 \text{ } \mu\text{eV}$ (FWHM). Ein q -Bereich von $0.2 - 1.75 \text{ \AA}^{-1}$ (elastisch) war zugänglich. Die Rohdatenreduktion beinhaltete Normierung auf einen Vanadiumstandard, Selbstabsorptions- und Leerbecherkorrektur, sowie eine Interpolation auf konstante q . Zur Auswertung der Dynamik wurde das Streugesetz $S(q, \omega)$ in die Dichtekorrelation $S(q, t)$ mittels Fouriertransformation und Entfaltung der Auflösung umgewandelt.

Im elastischen Strukturfaktor zeigt sich ein Abnehmen des Prepeaks mit zunehmender Al_2O_3 Konzentration bei 1600 K (vgl. Fig. 1). Der Anstieg des Prepeaks mit der Temperatur ist weniger stark ausgeprägt als in den Na-Silikaten. In Albit ($\text{NaAlSi}_3\text{O}_8$) und Jadeit ($\text{NaAlSi}_2\text{O}_6$) ist weder im Glas noch in der Schmelze ein Prepeak zu beobachten. Bei kleinen q -Werten dominiert in den Natrium-Aluminosilikaten ebenfalls die inkohärente Streuung an Na, welche im Strukturfaktor zu einem flachen Untergrund führt. Durch die Dominanz der inkohärenten Streuung erhalten wir Zugang zur Na-Selbstkorrelationsfunktion. Wir beobachten für alle untersuchten Konzentrationen eine verlangsamte Dynamik des Na bei 1600 K . Im Vergleich zu NS3 sind in der $\text{Na/Al} = 3$ Zwischenkonzentration $\text{Na}_3\text{AlSi}_6\text{O}_{15}$ (NS3A) die Na-Relaxationszeiten einen Faktor 2.5 und in Albit etwa einen Faktor 10 größer. In den Aluminosilikaten auf $\text{Na}_2\text{Si}_2\text{O}_5$ Basis ist die Na-Dynamik bei 1600 K ebenfalls verlangsamt. Im Fall der $\text{Na/Al} = 1$ Probe Jadeit verlangsamt sich im Vergleich zu dem in Albit beobachteten Verhalten die Na-Dynamik weniger stark.

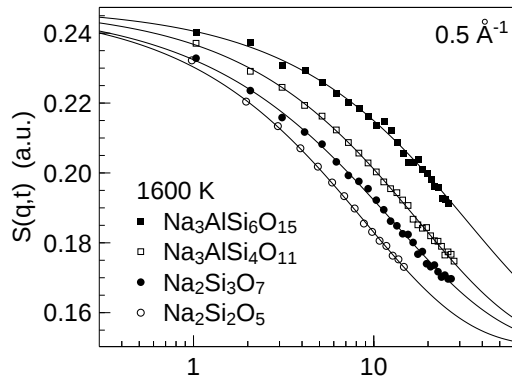


Abbildung 3.7:
Dichtekorrelation von NS2, NS3, NS2A und NS3A in der Schmelze bei 1600 K und $0.5 \text{ \AA}^{-1}$. Durchgezogene Linien repräsentieren Anpassungen mit einer Summe aus einer Konstanten (b) und einer gestreckten Exponentialfunktion ($a \cdot \exp\{-(t/\tau)^\beta\}$). Aufgrund der gewählten y-Grenzen (b , $a + b$) sind die Relaxationszeiten direkt vergleichbar.

Aus der Abnahme des Prepeaks in Natrium-Aluminosilikaten schließen wir, dass die Zugabe von Al_2O_3 eine Störung der Na-Kanalstruktur bewirkt. Dies zeigt sich in einer nichtlinearen Verlangsamung der Alkaliionendiffusion mit der Zusammensetzung und der Temperatur. Um Informationen über eine Kompositionsabhängigkeit der strukturellen Änderungen und der Dynamik zu erhalten, sind Untersuchungen bei niedrigerem SiO_2 -Gehalt geplant. Zusätzlich sollen die gemessenen Neutronenstreudaten mit im Rahmen der Kollaboration mit Mainz und Montpellier an Aluminosilikaten durchgeführten MD-Simulationen verglichen werden.

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Martensitic transition in $\text{Ni}_{50}\text{Al}_x\text{Mn}_{50-x}$ shape memory alloys

T. Mehaddene, J. Neuhaus, W. Petry

Shape memory alloys have found many applications in the medical and fastener industries. However, many potential high-temperature applications require a higher transition temperature than commercially available NiTi alloys. Currently, there are only a few experimental shape memory alloys known to exhibit martensitic transition temperatures well above room temperature, among them the ternary alloy NiAlMn. A better understanding of the driving force of the martensitic transition is required for further extensive applied research in this system. For this purpose we are going to investigate the lattice dynamics of NiAlMn alloys. Preliminary measurements of the martensitic transition temperatures have been performed using differential scanning calorimetry.

Ternary alloys $\text{Ni}_{50}\text{Al}_x\text{Mn}_{50-x}$ ($16 \leq x \leq 20$) were prepared from an appropriate mixture of pure Nickel (3N7), Aluminium (3N7) and Manganese (4N) by arc-melting. Several re-melts were carried out to insure a homogenous composition. For the calorimetric measurements, small pieces of about $1 \times 3 \times 3 \text{ mm}^3$ have been cut from the alloy ingots by spark erosion. Then, all samples were solution annealed for three days at 1273 K under Argon atmosphere and subsequently water quenched. The calorimetric measurements were performed by differential scanning calorimetry (DSC) with a liquid nitrogen cooling accessory when necessary. The measurements were carried out at a heating rate of 20 K min^{-1} . Typical heat-flow curves obtained for $x=16, 17, 18$ and 19 are shown in Figure 3.8

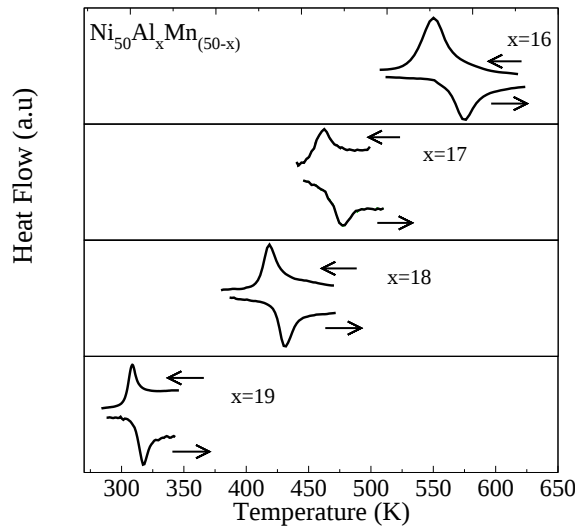


Figure 3.8: Differential scanning calorimetry measurements of the martensitic transition in NiAlMn ternary alloy for several Al concentrations recorded during heating up and cooling down at a constant rate of 20 K min^{-1} .

The martensitic start temperatures (M_S) obtained from our measurements are summarised together with the results of Inoue *et al.* [1] in Figure 3.9. The measurements show that all over the composition range investigated, our samples undergo a unique stage transformation whereas Inoue *et al.* have measured a two steps transformation for Aluminium compositions equal to 16, 16.5 and 17. A Microprobe Analysis measurement performed on our samples showed a systematic deviation from the nominal composition because of the evaporation of Al and/or Mn during the repeated melts.

The next step of the study consists in the phonon measurements which play an important role in the martensitic transitions. However, even for $\text{Ni}_{50}\text{Al}_{19.5}\text{Mn}_{31.5}$ ($M_S=277 \text{ K}$), the transition

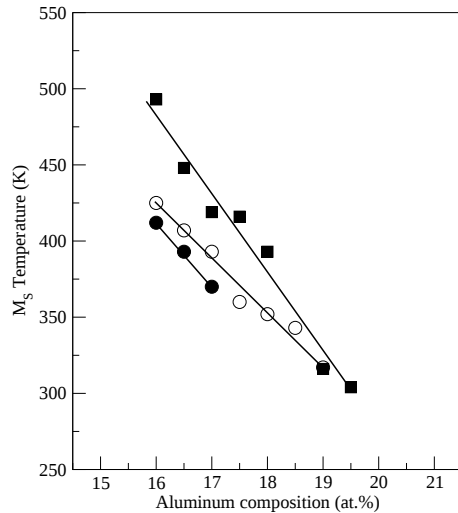


Figure 3.9:
Martensitic start temperature (M_s) of $\text{Ni}_{50}\text{Al}_x\text{Mn}_{50-x}$ alloys as a function of nominal Aluminium composition. Filled squares are the result of the present work, open and filled circles are the results of Inoue *et al.* [1]. The lines are guide for eyes.

temperature is too high to grow the single crystal using conventional techniques. An in-situ single crystal growth on neutron scattering experiment is required. We intend to perform the growth using the floating zone technique on a combined furnace for crystal growth and neutron scattering [2].

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Structural Properties of Silicates

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In recent years the structural and dynamical properties of silica (SiO_2) and silicate melts have attracted the interest of many experimental groups due to their importance in geology (e.g., magmatic flow in the earth crust) as well as technology (e.g., glassy optical fibers). Especially the addition of water has important consequences on the visco-elastic properties of these melts. Spectroscopic measurements suggest that the mechanism of dissolution of water in silica(ite) melts varies strongly with the composition of the bulk. In particular aluminosilicate compositions seem to have different dissolution mechanisms than Al-free silicates. In addition to dissolved water, molecular water may be present. The ratio of dissolved and molecular water depends on temperature and governs the viscosity of the melts above the glass transition temperature T_g . For reviews on the subject see [1,2]. Despite a tremendous amount of work that has already been done, it is currently not clear how water is exactly accommodated in the silicate melts.

Here we apply neutron scattering techniques to the subject. It is well known that neutrons due to the different scattering lengths of hydrogen and its isotope deuterium are one of the most suitable tools to investigate water containing systems. In addition, both, structure (e.g. the static structure factor $S(q)$) and dynamical properties like the vibrational density of states are accessible with this

experimental probe. In this report the structure factors of dry and hydrous SiO_2 , dry and hydrous NS3 and dry and hydrous albite ($\text{NaAlSi}_3\text{O}_8$) are presented. The measurements have been carried out at the D20 diffractometer at the Institute Laue Langevin, Grenoble/France. The obtained raw data have been corrected for detector efficiency and empty can contribution and were normalized to the number of scatterers in the beam.

Fig. 3.10 shows the structure factor $S(q)$ of the dry silicates.

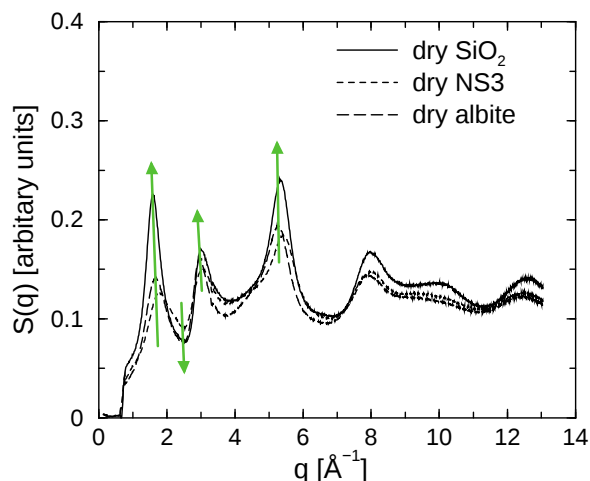


Figure 3.10:

Structure factor of dry amorphous SiO_2 , dry NS3, and dry albite. Peak heights seem to follow the rule (from low to high) NS3, albite, SiO_2 . The arrows indicate the order (from low to high) in the tetrahedral network that we associate to the peak heights.

The main peaks at $1.7 \text{ \AA}^{-1}$, $3.0 \text{ \AA}^{-1}$ and $5.2 \text{ \AA}^{-1}$ are due to typical distances in the tetrahedral network of the silicate. Their position seems to vary only slightly when the network modifiers are added. In contrast, their heights are well affected by the modifier addition. In particular, the heights seem to follow the rule (from low to high) NS3, albite, SiO_2 . We associate this behavior to the extent the perfect tetrahedral network is destroyed by the addition of the modifiers. According to this, the SiO_2 network has naturally the highest order, followed by albite and NS3.

It occurs somehow strange to find a higher order in the sodium aluminosilicate than in the sodium silicate. This behavior can be understood taking into account the structural properties of the two compounds. It was found that sodium silicates show a pre peak effect in the structure factor at roughly $1.0 \text{ \AA}^{-1}$ [3,4]. This pre peak was associated by molecular dynamics studies to channels that maintain sodium diffusion in the silicate [4,5]. These sodium rich channels disrupt the network. The disruption results obviously in smoother network related peaks at $1.7 \text{ \AA}^{-1}$, $3.0 \text{ \AA}^{-1}$ and $5.2 \text{ \AA}^{-1}$ in the structure factor and on the other hand in the channel related pre peak at roughly $1.0 \text{ \AA}^{-1}$. It was also found that the channel system is re destroyed by the addition of aluminum [6]. This destruction may explain the more intense peaks in the albite $S(q)$.

In fig. 3.11 we compare the structure factor for dry SiO_2 to the one of deuterated and hydrated silica.

As it was already the case for the dry silicates compared to each other, the main structural characteristics hold also upon water addition. The three structure factor peaks at $1.7 \text{ \AA}^{-1}$, $3.0 \text{ \AA}^{-1}$ and $5.2 \text{ \AA}^{-1}$ are still present. Again, we can associate the relative heights of these peaks to the destruction of the tetrahedral network. As it was found by recent computer simulations [7] water is dissolved to the silica network in the form of SiOH groups which is therefore partly disrupted. Comparing e.g. the heights h_H and h_{dry} in fig. 3.11 this disruption finds its confirmation in the structure factor.

Further structural analysis will be possible employing recently developed numerical methods like the Reverse Monte Carlo (RMC) method [8].

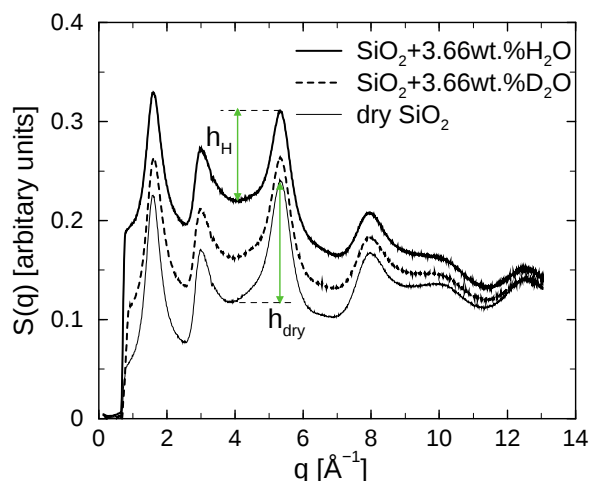


Figure 3.11:

Structure factors of dry, deuterated and hydrated SiO_2 . The heights h_H and h_{dry} demonstrate the differences in the “amplitude” of the structure factors that is related to the order of the network.

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Structural Properties Of Water Bearing Silicates - The Simulational Approach

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This project is an attempt to perform a quantum-chemical verification of the existing experimental data on (hydrous) silicates which are presented elsewhere in this report. In a first step we simulate pure (this means Al and Na free) SiO_2 systems with variable content of water. So far a system of silica containing 3.84wt% H_2O has been equilibrated in its liquid state at temperatures of 3000K and 3500K employing the ab-initio molecular dynamics code CPMD [1].

At the mentioned total water concentration of 3.84wt% we find the water in the liquid state completely dissolved in the form of SiOH groups. Due to the water speciation to SiOH groups, the silica tetrahedral network is broken. Water molecules are only found as transition states and play a role for the hydrogen transport in the liquid. Generally, we find three such intermediate states. These are 1. SiO dangling bonds 2. water molecules and 3. bridging hydroxyl groups.

Figure 3.12 presents the contribution of each of the mentioned groups to the number of composed OH units per time interval. The formation of new OH bonds gives us an idea of the hydrogen diffusion in the liquid.

The complete results of this simulation of the liquid were previously submitted for publication [2]. Currently we quench the liquid to ambient temperatures. These quenches will allow to obtain

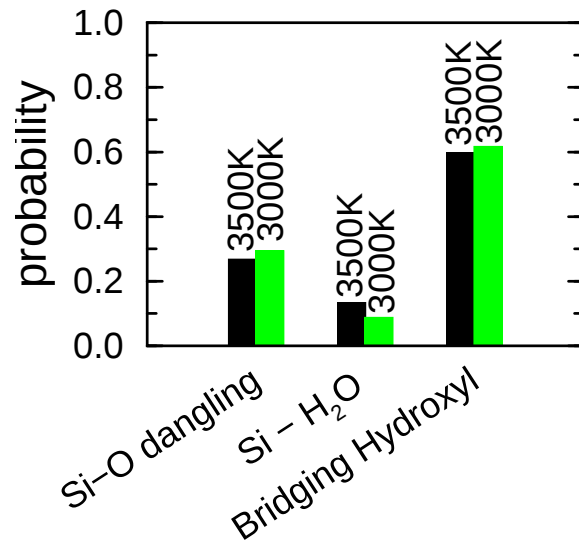


Figure 3.12:

Relative contributions of the transition states SiO dangling bonds, water molecules, and bridging hydroxyl groups to the formation of new OH groups. The formation of new OH bonds gives insight into the hydrogen diffusion mechanism.

glasses. Statistical quantities like the vibrational density of states and the neutron scattering structure factor can be extracted from the simulations in the glassy state. A detailed comparison to the recently obtained experimental data (see contribution by A. Müller et al.) is under way.

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- [2] M. Pöhlmann, M. Benoit, W. Kob. Submitted to Phys. Rev. B.

4 Moleküldynamik

Relaxation in flüssigem Benzol: inelastische Neutronenstreuung

S. Wiebel

Depolarisierte Lichtstreuungen an flüssigem und unterkühltem Benzol haben demonstriert, dass diese denkbar einfache molekulare Flüssigkeit auch mit Modellen beschrieben werden kann, die ursprünglich für glasbildende Systeme entwickelt wurden [1]. Messungen des optischen Kerr-Effekts bestätigten dieses Ergebnis und demonstrierten eindrücklich, dass hier dieselbe Observable wie bei den Lichtstreuungen aufgenommen wird.

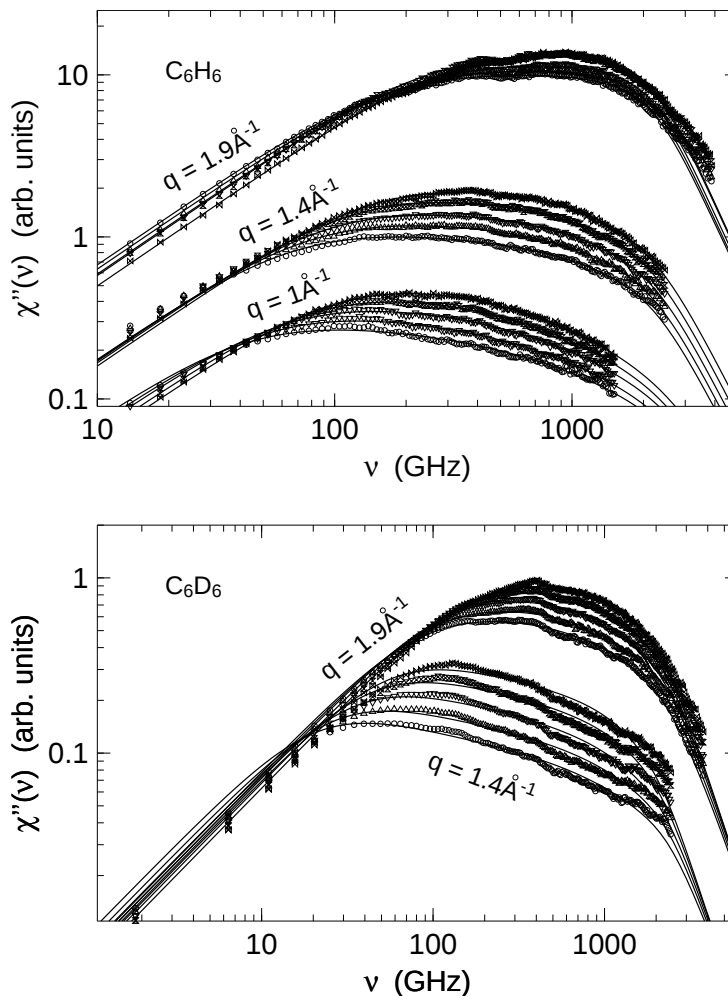


Abbildung 4.1:
Neutronenstreudaten von Benzol im Temperaturbereich zwischen 280 und 350 K bei ausgewählten Wellenvektoren. Oben sind die dynamischen Suszeptibilitäten aus inkohärenter Streuung an C_6H_6 gezeigt, unten aus kohärenter Streuung an C_6D_6 . Die durchgezogenen Linien zeigen die Anpassung durch das schematische F_{12} Modell der Modenkopplungstheorie.

Um jedoch die universelle Anwendbarkeit des F_{12} -Modells der Modenkopplungstheorie auf Benzol im Detail zu überprüfen, ist es notwendig, auf weitere Observablen zurückzugreifen. Dafür bieten sich Neutronenstreuexperimente an, die gleichzeitige Messungen bei unterschiedlichen Streuwinkeln und damit Wellenvektoren q ermöglichen, um die Dynamik der Flüssigkeit auf verschiedenen Längenskalen zu testen. Gleichzeitig werden durch gezieltes Deuterieren der Probe kohärente und inkohärente Streuung getrennt zugänglich. Wir haben deshalb Streuexperimente

an gewöhnlichem Benzol C_6H_6 und an deuteriertem Benzol C_6D_6 für eine ganze Serie von verschiedenen Wellenvektoren q zwischen 0.3 und 2.0 Å an dem Flugzeitinstrument IN6 am Institut Laue-Langevin in Grenoble durchgeführt.

Abbildung 4.1 zeigt die in Suszeptibilitäten umgerechneten Flugzeitspektren bei ausgewählten Wellenvektoren für beide Molekülsorten. Die Daten wurden mit dem bereits in den letztjährigen Jahresberichten beschriebenen F_{12} -Modell der Modenkopplungstheorie [2] angepasst, das auf den Bewegungsgleichungen

$$0 = \Omega^{-2}\ddot{\Phi}(t) + \gamma\dot{\Phi}(t) + \Phi(t) + \int_0^t dt' m(t-t')\dot{\Phi}(t') \quad (4.1)$$

$$0 = \Omega_s^{-2}\ddot{\Phi}_s(t) + \gamma_s\dot{\Phi}_s(t) + \Phi_s(t) + \int_0^t dt' m_s(t-t')\dot{\Phi}_s(t') \quad (4.2)$$

und den Gedächtniskernen

$$m(t) = v_1\Phi(t) + v_2[\Phi(t)]^2 \quad (4.3)$$

$$m_s(t) = v_s\Phi(t)\Phi_s(t), \quad (4.4)$$

beruht.

Wir beschreiben dabei die intrinsische Dynamik des Systems durch die Korrelationsfunktion $\Phi(t)$, und verwenden für die Anpassung der Messdaten Korrelatoren, die jeweils einem $\Phi_s(t)$ entsprechen und die Ankopplung an die entsprechende beobachtete Observable beschreiben. Damit bleiben die Parameter Ω , γ , v_1 und v_2 für alle Wellenvektoren gleich und müssen zudem noch mit den aus den optischen Methoden bestimmten Werten übereinstimmen, während die Werte von Ω_s , γ_s und v_s von Wellenvektor und Messmethode abhängen dürfen.

Alle Parameter zeigen eine regelmäßige Temperaturabhängigkeit und nur geringe Abweichungen von dem verlangten monotonen Verlauf. Nach den Vorhersagen der Modenkopplungstheorie sollten die Kopplungen mit steigender Temperatur schwächer werden, wir finden das im Absinken der Parameter v_1 , v_2 und v_s bestätigt. Die dem Korrelator $\Phi(t)$ zugeordnete Frequenz steigt mit zunehmender Temperatur an. Das gleiche beobachten wir für die Frequenzen der angekoppelten Korrelatoren $\Phi_s(t)$ für die optischen und die inkohärenten Neutronenmessungen. Gleichzeitig fällt die Dämpfung γ in etwa der gleichen Größenordnung ab. γ_s wurde für jede der entsprechenden Observablen auf einem annähernd konstanten Wert gehalten. Lediglich in der kohärenten Neutronenstreuung beobachten wir zum Teil gegenläufige Tendenzen, insbesondere im Bereich des Strukturfaktormaximums.

In der inkohärenten Neutronenstreuung wird der Zusammenhang zwischen Ω_s und q bei größeren Wellenvektoren in guter Näherung linear, und genau das erwarten wir aus der mikroskopischen Theorie. Die zugehörigen Dämpfungen γ_s fallen gleichmäßig mit wachsendem Wellenvektor q ab. Der Kopplungsparameter v_s sinkt hier ebenfalls mit größer werdendem Wellenvektor. Im Bild der Korrelationsfunktionen entspricht das dem Absinken der Plateauwerte f_q^s mit steigendem q , was qualitativ mit den MCT-Asymptoten in glasbildenden Flüssigkeiten [3] zusammenpasst. In diesem Zusammenhang wäre eine Proportionalität $v_s \propto (1/q)$ zu erwarten, die Funktion $1/q$ ist zum Veranschaulichen mit in Abb. 4.2 eingetragen.

In der kohärenten Neutronenstreuung spiegelt sich in allen Parametern das Strukturfaktormaximum wieder, wie es in Abb. 4.2 am Beispiel von V_s gezeigt ist. In diesem Bereich ändert sich die Plateauhöhe des Korrelators sehr stark, was sich vor allem auf den Kopplungsparameter v_s

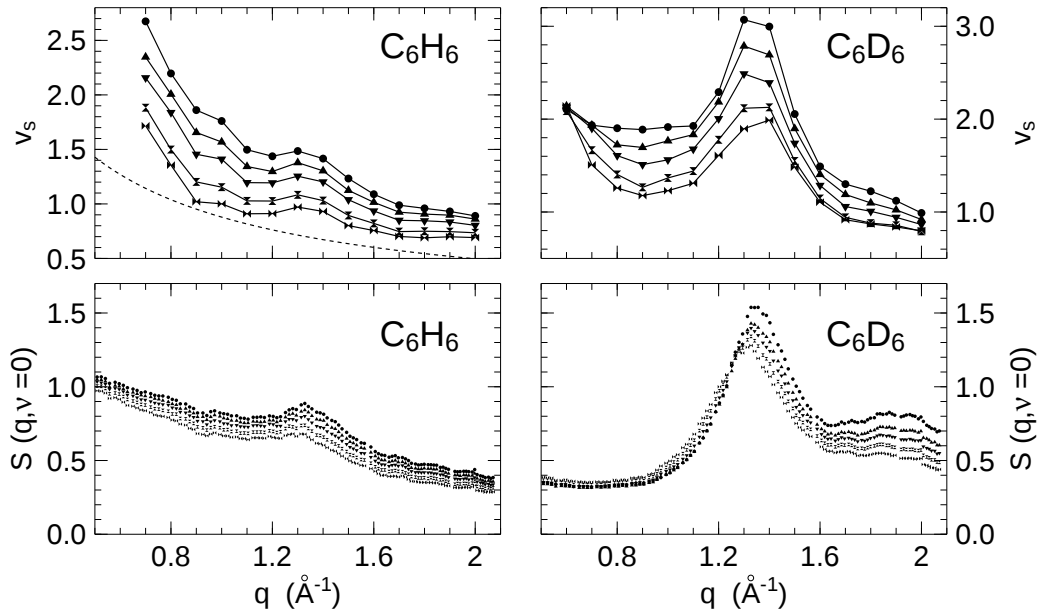


Abbildung 4.2:

Elastischer Strukturfaktor von Benzol (oben), im Vergleich mit dem vom Wellenvektor abhängigen Fitparameter v_s .

auswirkt. Ein Vergleich mit dem elastischen Strukturfaktor zeigt, dass v_s tatsächlich den gleichen q -abhängigen Verlauf nimmt wie $S(q, \nu = 0)$. Diese entspricht den Ergebnissen, die Rufflé et. al. in dem Glasbildner $\text{Na}_{0.5}\text{Li}_{0.5}\text{PO}_3$ gefunden haben [4] und bestätigt auch unsere Beobachtung bei den α -Relaxationszeiten. Die Variation in v_s bei den Messungen an protoniertem Benzol ist ebenfalls auf Anteile von kohärenter Streuung zurückzuführen.

Insgesamt bestätigt die simultane Anpassung der mit unterschiedlichen Methoden aufgenommenen Daten — depolarisierter Lichtstreuung, optischem Kerr-Effekt, kohärenter und inkohärenter Neutronenstreuung — die Aussagekraft dieses Modells für die Dynamik von Benzol. Für alle Techniken lassen sich die Messdaten über mehrere Dekaden durch ein einziges Modell beschreiben.

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Slow glass dynamics in confined geometry investigated by nuclear resonant scattering

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Studying the relaxational dynamics of liquids and glass formers in restricted geometries is currently attracting much interest [1], both under the aspect of the interaction of fluid systems with inner surfaces, e.g. in a catalyst, and from the viewpoint of glass physics, where the existence of a characteristic length scale remains an unsolved question up to date. The latter effect may however be masked by the former one, i.e. layer structures in pores may mask true bulk behaviour.

The aim of the present project was to check the influence of confined geometry on the slow dynamics of a glass in confined geometries, using quasielastic nuclear forward scattering (QNFS), over a more extended time window as compared with a previous study [2]. Our aim was both to obtain a higher accuracy of quadrupole splittings, Lamb-Mössbauer factors, and relaxation times and to assess the influence of confinement on the Kohlrausch stretching parameter β , since molecular-dynamics simulations [3] and dielectric spectroscopy on glasses in confinement [4,5] have given evidence for a broadening of the distribution of relaxation times.

The experiment was carried out at the Nuclear Resonance Beamline ID18 at ESRF in single-bunch mode with a time window of 2816.56 ns between subsequent bunches, using a three-bounce high-resolution monochromator with 2 meV resolution on two samples of ferrocene/dibutyl phthalate (where the ferrocene was enriched to 95.3 % in ^{57}Fe) loaded into nanoporous silica matrices with 50 and 25 Å pore size. The temperature was varied in the range between 15 and 205 K using a closed-cycle cryostat.

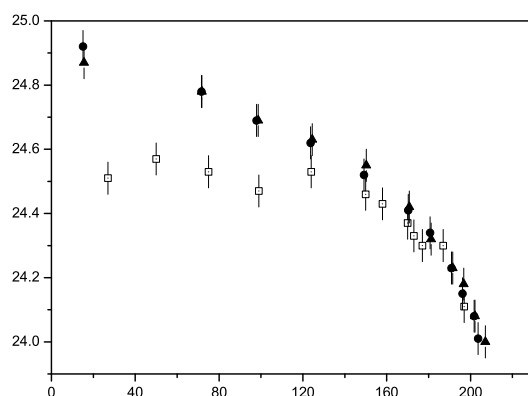


Figure 4.3:
Effective quadrupole splitting for bulk (open squares) and confined (50 Å pores: triangles, 25 Å pores: full circles) ferrocene/dibutyl phthalate

The data treatment was carried out in a similar way as described in [2], but instead of the delayed rocking curve, an extrapolation formula for the Lamb-Mössbauer factor (LMF) was used to obtain the relaxation time and the LMF separately from the slope of the time spectra. Comparison was made with data on bulk ferrocene/dibutyl phthalate as described in [6].

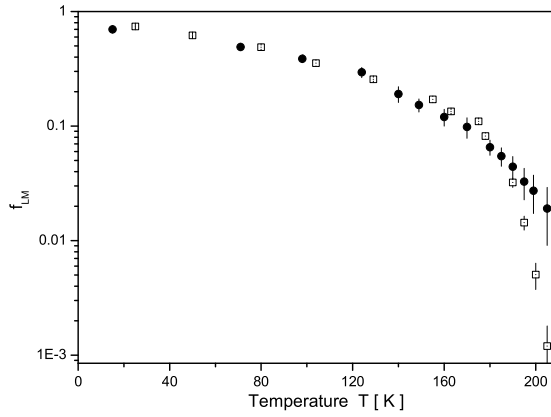


Figure 4.4:
Lamb-Mössbauer factor for bulk (open squares) and confined (full circles) ferrocene/dibutyl phthalate

Fig. 4.3 shows the effective quadrupole splitting of the ferrocene molecule for bulk and nanopores. For low temperatures, the T dependence of the quadrupole splitting clearly differs from the bulk. The reason for this phenomenon is still unclear. For temperatures above 160 K, the characteristic decrease of the effective quadrupole splitting, which is due to the onset of rotational relaxation, is the same for bulk and nanoporous samples, indicating that rotational dynamics is in first approximation independent of confinement.

Fig. 4.4 shows the Lamb-Mössbauer factor for bulk and nanopores. For low temperatures, all samples exhibit roughly the same LMF, whereas above the glass transition temperature for the bulk (180 K), it decreases less strongly for the confined samples (both of them having the same LMF within experimental accuracy) than for the bulk. Hence, it seems that the fast dynamics sets in somewhat later than in the bulk when T increases. This finding differs from our results in [2], where the LMF was observed not to change significantly in confinement within the (lower) experimental accuracy of that experiment.

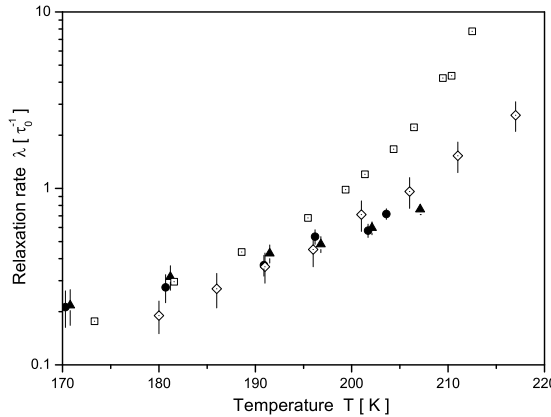


Figure 4.5:
Total relaxation rate for bulk and confined ferrocene/dibutyl phthalate (symbols as in Fig. 1) and rotational relaxation rate for the bulk (open diamonds)

Fig. 4.5 shows the relaxation rate (in units of the natural lifetime of the ^{57}Fe nucleus, $\tau_0 = 141$ ns) of the confined samples in comparison with the total (translational plus rotational) relaxation rate for the bulk, as determined by classical Mössbauer spectroscopy [7], and the pure rotation rate for the bulk as determined by SRPAC [8]. The total relaxation rate in pores seems to approach the

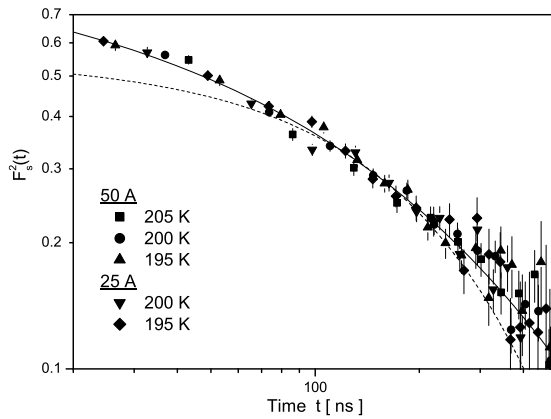


Figure 4.6:

Master curve for the self-correlation function for confined ferrocene/dibutyl phthalate, scaled to (50 Å, $T = 200$ K); solid curve: $\beta = 0.5$, dotted curve: $\beta = 1$ (Debye relaxation)

purely rotational one of the bulk. This might be a hint that whereas in the confined liquid the ease of molecular rotation remains largely unchanged, the translational motion is strongly hindered.

Fig. 4.6 finally shows a master plot of the square of the self-correlation function, together with the shape for a Kohlrausch parameter $\beta = 1$ (dotted curve) and $\beta = 0.5$ (solid curve). The latter value clearly gives a better description of the experimental data. Within the experimental accuracy we can state that β is not or only very weakly dependent on confinement. Theoretical predictions [3] and experimental observations [4,5] give evidence for a broadening of the distribution of relaxation times for an ensemble of Debye relaxators and hence a smaller β in confinement.

Compared with our findings from [2], where QNFS data were taken in a much shorter time window of only 176 ns, the accuracy of all data could be increased. The LMF now appears to be increased by confinement, whereas the Kohlrausch parameter β is almost unaffected.

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5 Festkörpertheorie

Influence of anharmonic interactions on the boson peak

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The present authors have developed recently a field-theoretical treatment of a disordered solid which allows for the inclusion of anharmonic interactions into the considerations [1,2]. The mean-field theory derived within this formalism boils down to the self-consistent Born approximation (SCBA) in the absence of the anharmonicity. The SCBA is equivalent to the coherent-potential approximation (CPA) for small degree of disorder. Within the SCBA experimentally measured boson peak data (i. e. the reduced DOS $g(\omega)/\omega^2$ with a characteristic maximum in the meV regime) can be explained quantitatively with only two adjustable parameters, namely, the mean sound velocity c_0 and its mean-square fluctuations (“degree of disorder“) $\gamma \propto \langle (\Delta c)^2 \rangle$. As mentioned in Refs. [1,2], in the presence of the anharmonic coupling the mean-field equations derived from the field-theoretical treatment are mathematically equivalent to the quantum-mechanical analogon of Götze’s [3] mode-coupling equations for the dynamic susceptibility of glass-forming viscous liquids.

Until now it was difficult to solve the quantum mode-coupling equations because the small-frequency asymptotics involves a cancellation of two very large numbers. We now made use of the fact that in this limit one can use the classical approximation. Furthermore, in the non-classical regime $\hbar\omega > k_B T$ the spectrum is dominated by the harmonic excitations, which are the same in the classical and in the quantum case. So we calculated the density of states in classical approximation.

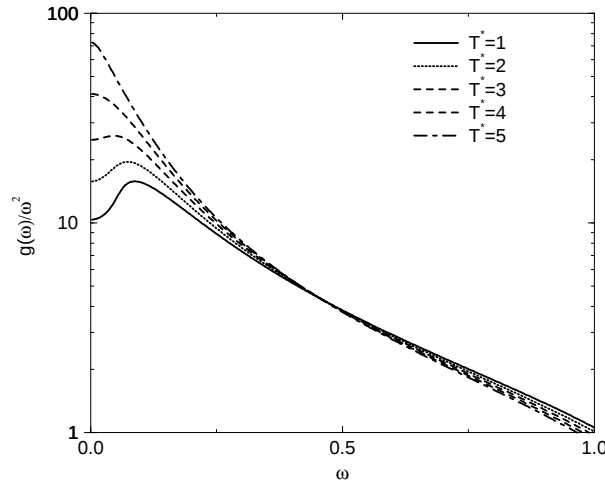


Figure 5.1: Reduced density of states $g(\omega)/\omega^2$ for four values of the anharmonic parameter T^* .

In fig. 5.1 we have plotted the reduced density of states $g(\omega)/\omega^2$ for four values of the “anharmonic parameter“ $T^* \propto T\gamma g^2$, where g is the Grüneisen constant $g = d \log c / d \log \rho$, c is the sound

velocity and ρ is the density. The temperature dependence displayed in Figure 5.1 is very similar to that observed in disordered solids above the limiting temperature below which the reduced density of states does not depend on temperature at all.

We are going to improve our calculations in order to incorporate the the influence of the quantum nature of the excitations.

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Break-Junction Tunneling Spectroscopy in the Hopping Regime

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In our long-term cooperation between the disordered-solid theory groups of the University of Magdeburg and the TU Munich and the experimental low-temperature Group of the FU Berlin we have developed [1,2] a new spectroscopic method to investigate the density of localized states of disordered semiconductors. This method makes use of the tunneling characteristics between the two parts of a sample which has been broken into two parts in a controllable way. Usually planar tunnel junctions are used to probe the density of states (DOS) of a metal or of a semiconductor. A superconducting counter-electrode with a known quasi-particle DOS serves then as reference.

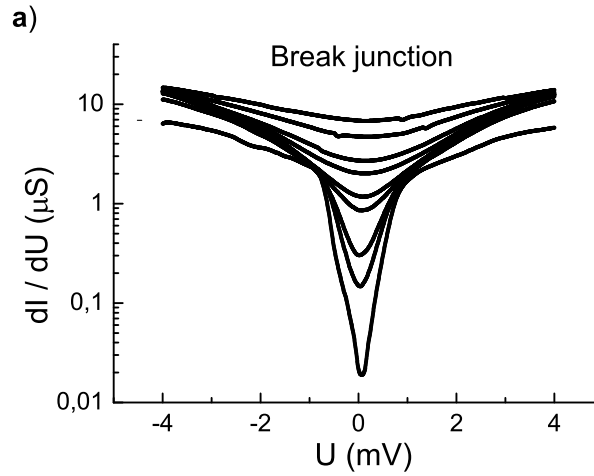


Figure 5.2:
differential conductivity dI/dU of doped Ge:As in the hopping regime (i. e. lightly doped and at low temperature) using the break-junction technique

Mechanical-controllable break(MCB) junctions offer an improved alternative spectroscopic method because those junctions can be prepared in situ at ultra-high vacuum conditions to yield clean interfaces. For clean electrodes the scattering from defects in the barrier region should become less important than the reflection and transmission characteristics of the proper vacuum potential barrier, allowing one to systematically study the characteristics of the junction.

In the hopping regime tunneling spectroscopy has proven useful in investigating the influence of the electron-electron interaction on the density of states of impurity bands. In this transport regime tunneling experiments have been performed with conventional metal-barrier-semiconductor contacts [1] and mechanically controllable break junctions [2]. In the latter investigation the traditional formula

$$I(U) \propto \int N(V)N(V - eU)f(V)[1 - f(V - eU)] dV$$

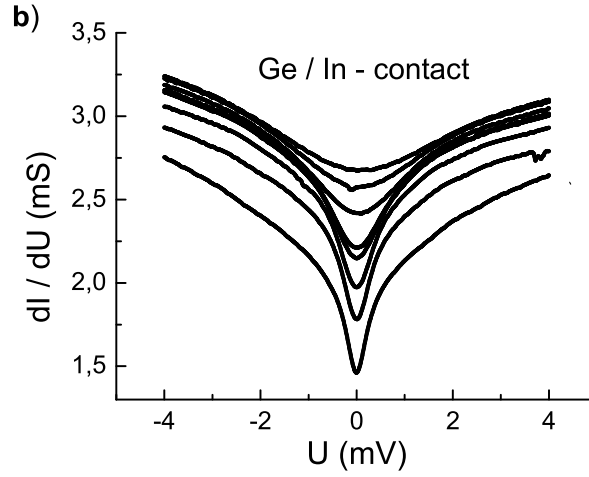


Figure 5.3:
differential conductivity dI/dU of doped Ge:As in the hopping regime using an indium contact

for the tunneling current has been applied, where $N(V)$ is the density of states and $f(V)$ the Fermi function. According to this formula the tunneling current is a convolution of the density of states of the contact materials. However, since the nature of the electronic states in such system is very different from that in metals or superconductors it is not obvious that the traditional expression for the calculation of the tunneling current can also be applied to tunneling spectra in the hopping regime.

therefore we derived an expression for the tunnel current between the two disordered-semiconductor samples using the general theory of electronic hopping transport [3]. In our derivation we took advantage of the fact that the tunnel transition probabilities per unit time are several (realistically 3) orders of magnitude smaller than the hopping transition probabilities. This establishes a separation of time scales which, in turn leads to separate equilibria in the two samples during the tunnel measurement. We obtain the following expression for the tunnel current:

$$I(U) = e\tilde{W} \int_0^{eU} dV' \int_0^{V'} dV N(V) N(V' - eU) \nu(V' - V).$$

Here $\tilde{W}$ is an averaged tunnel intensity and $\nu(E)$ is the spectral electron-phonon interaction function. In order to get a feeling for the influence of the latter quantity on the tunnel current we studied the example of a partially filled Coulomb gap

$$N(V) = N_0 + N_\gamma |V|^\gamma$$

and two functional forms for $\nu(E)$:

deformation-potential approximation:

$$\nu(E) = \nu_0 \frac{|E|}{(1 + (\frac{E}{2\hbar s\alpha})^2)^4}$$

quasi-elastic approximation:

$$\nu(E) = \nu_0 \theta(\omega - |E|).$$

In the former case one obtains a vanishing differential conductivity dI/dU for zero bias voltage U in spite of the finite DOS N_0 . In the latter case a finite DOS at the Fermi level leads to a finite differential conductivity at zero bias. Comparing to our measurements on As-doped Germanium we concluded that the quasi-elastic approximation is superior to the deformation-potential approximation. The quasi-elastic approximation takes into account that at low temperatures only a very small amount of energy can be exchanged with the phonon heat bath.

In order to obtain an experimental proof which shows that the break-junction differential conductivity is sensitive to the electronic density of states we have performed a conventional tunneling experiment on the same material using a conventional Indium Schottky contact. Clearly the dependence on voltage and temperature are very similar in the two data sets. The differences stem from the fact that in the break junction one deals essentially with the semiconductor DOS convoluted with itself, whereas in the conventional tunneling device one measures the semiconductor DOS convoluted with that of the metal contact.

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6 Biomoleküle unter Hochdruck

Pressure dependence of association- and dissociation processes of protein complexes

R. Gebhardt, W. Doster

Proteins are involved in various tasks in organisms. Our current research is focused on myoglobin and hemocyanin which serve as an oxygen transporter, the LHC-2-complex that collects light for the photosynthesis in plants and bacteria, casein-micelles, that store calcium and F-actin, which acts as an structural protein. To get some insights in the modes of action and function we study the structure and the thermodynamics of these proteins. Focusing on hemocyanin we illustrate how pressure affects oligomeric protein-complexes. Protein structures can be classified in different levels. The primary structure determines the sequence of amino acids and the length of the chain. Certain areas are able to fold in special secondary structure motives, which again can form the tertiary structure - the final 3D-structure. However, the association of several folded polypeptides (subunits) to a so called quaternary structure offers new possibilities to regulate the biological activity. For example F-actin acts as an structure building protein. By association of G-actin subunits F-actin grows up to a μm -scale to build the cytoplasmatic skeleton of cells. The increase in size by formation of a 9-meric ring is also important for the LHC-2 complex to efficiently collect light in photo-synthesis. As an important component in the milk, casein-micelles store Ca^{++} in the secretory cells using oligomerisation. The addition of Ca^{++} ions leads to aggregation of the micelles while the absence of Ca^{++} causes the micelle dissociate in isolated casein-molecules. In case of hemocyanin, oligomerisation is connected with the important property of cooperativity, which means that the interactions between the subunits can change the affinity of the subunits to the oxygen. This allows the molecule to react on very small changes of oxygen concentration. 6.1 gives a schematic overview over the 24meric hemocyanin-molecule and shows the effect of hydrostatic pressure on the degree of subunit-association.

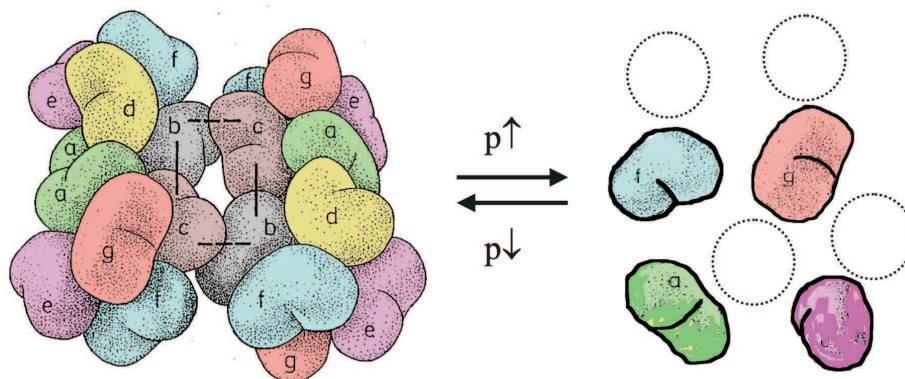


Figure 6.1: Pressure dissociation of the 24 meric hemocyanin.

The equilibrium of the oligomer with its subunits is shifted to the associated state under normal conditions due to entropic forces: The formation of contact areas between the subunits leads to enhanced flexibility. On the other hand, enthalpic contributions are often small and positive and work against association. We use hydrostatic pressure to dissociate protein-complexes and to modulate the interactions between their subunits. Following the principle of Le Chatelier, proteins

should dissociate due to the fact that the sum of the volumes of the subunits is smaller than the volume of the dissociated macromolecule. The difference can be explained by some intramolecular voids between the subunits, which become filled by water if the protein dissociates. Another important feature is the surface-effect, because water is packed more densely on the surface of the proteins than in bulk-water. Dissociation enlarges the surface of the protein and therefore the total volume. In a more microscopic view pressure destabilizes protein-protein-, protein-water- and water-water-bonds. The strongest effect is on protein-protein-interactions favouring dissociation. Using static and dynamic light scattering we measure the degree of oligomerisation and radius of macromolecules versus pressure. 6.2 (partA) shows a transition curve of a dissociation process

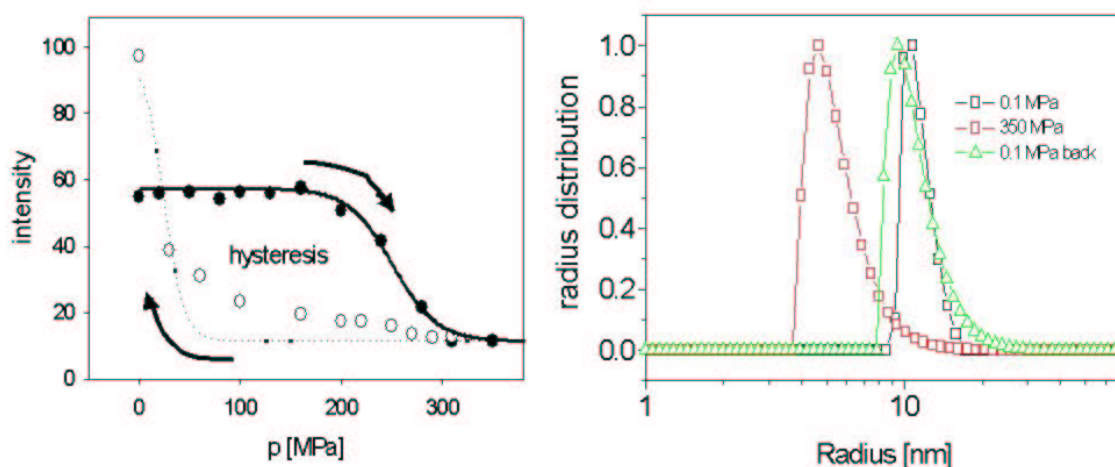


Figure 6.2:

A: Transition curve of the hemocyanin-dissociation from static light scattering ; B: Radius distribution obtained by dynamic light scattering

of hemocyanin - a 24meric oxygen transporter in the blood of a bird-eating-spider. The data can be fitted by a dimer-monomer-dissociation-model by using a nonlinear fit-procedure. The fitted parameters indicate a dissociation volume of 106 ml/mol and a dissociation constant by ambient pressure of $1.0 \cdot 10^{-11}$. This is consistent with values found in other similar proteins. After pressure release the subunits reassociation of the molecule displays a hysteresis. Fig 2. shows the number weighted radius distribution of the particles. The distribution has a maximum value of 11 nm corresponding to the hydrodynamic radius of the 24meric hemocyanin. Pressurisation shifts the radius-distribution to 3.5 nm, which corresponds now mainly to the hydrodynamic radii of the isolated subunits. By releasing pressure the distribution recovers to 11 nm with a broader shape and a tail to larger radii. This fraction corresponds to aggregates which are responsible for the increased static light intensity.

Pressure effects on casein micelles studied by FT-IR spectroscopy

N. Takeda, R. Gebhardt, W. Doster

Casein is a family of phospho-proteins synthesized in the mammary gland and the major component of milk, constituting about 80% of the total milk protein. In milk, caseins exist in colloidal particles known as the 'casein micelles' (CM) of 100-300 nm in diameter. They have 93.3% casein and 6.6% inorganic constituents. Casein in the micelles is composed of α S1-, α S2-, β -, and κ -casein in proportions of approximately 3:0.8:3:1 by weight. The conformation of each casein is open and flexible, and prefers random coil like unfolded globular proteins [1]. The main inorganic constituent is 'micellar' or 'colloidal' calcium phosphate (MCP) which is present in the form of amorphous nanometer-sized particles throughout the matrix of the CM [2, 3]. The whole structure of the CM is generally accepted as a roughly spherical, fairly swollen particle [4]. However, several different models for the internal structure have been proposed. In sub-micelle model, some important elements are as follows [4]. The CM is built of smaller spherical units of about 14 nm in diameter, called 'sub-micelles', primarily consisting of a mixture with a different composition of the four elemental casein molecules. The sub-micelles are linked together by MCP particles generating larger micellar structures. The deposition of MCP particles into the sub-micelles causes them to condense and to lose their negative charge. This process is also likely to induce the aggregation of sub-micelles. Another model, called 'open' or 'spaghetti' model, suggests that the whole casein micelle has more dense and less dense regions inside, but less of a well-defined internal structure like sub-micelles, which is assumed to be a three-dimensional network of four different kinds of casein molecules partly cross-linked by MCP particles [5]. In both models, the MCP particles may be bound to the serine phosphate residues, and play an important role in maintaining the whole structure of casein micelle. It is well known that application of high pressure to oligomeric proteins in aqueous solution promotes the dissociation to its monomer, frequently accompanying a release of some ligands [6]. Pressure treated casein micelles in milk or aqueous solution display structural changes [7, 8]. We have shown by in situ light scattering measurements, that micelles dissociate into fragments. This dissociation is not completely reversible. We have installed a diamond anvil cell, which is the special tool to generate high pressure, in FT-IR spectrometer, and can directly measure the infrared spectrum of proteins in aqueous solution under high pressure. The change in the amide I band (1600 1700 cm^{-1}) arising from the backbone peptide groups of casein, which is very sensitive to the secondary structure of proteins, is insignificant with increasing pressure up to 1000 MPa. This indicates that the backbone conformation of casein molecule remains unfolded. In the PO stretching band region (950 1150 cm^{-1}), two new bands appear clearly. One is attributed to the two protons dissociated from of phosphate ion (HPO_4^{2-}), another to the two protons dissociated form of the serine phosphate residue of casein ($\text{PO}_4^{2-}\text{-Ser}$). The appearance of a PO stretching band suggests that some kind of ligand is released from the serine phosphate residues with increasing pressure. Because the casein treated by EDTA, which is used to deplete calcium compounds bound to casein [9], has the same PO stretching band arising from $\text{PO}_4^{2-}\text{-Ser}$ with more absorbance than native one at ambient pressure, the released ligands may be calcium ions and or MCP particles. Further experiments are needed to reveal, which ligand is predominately released. The whole structure of casein micelle should be destabilized by the electrostatic repulsion due to the increase of negative charge in casein molecules with increasing pressure. We will discuss the pressure-induced dissociation of whole casein micelles, including the release behavior of ligands when compressed.

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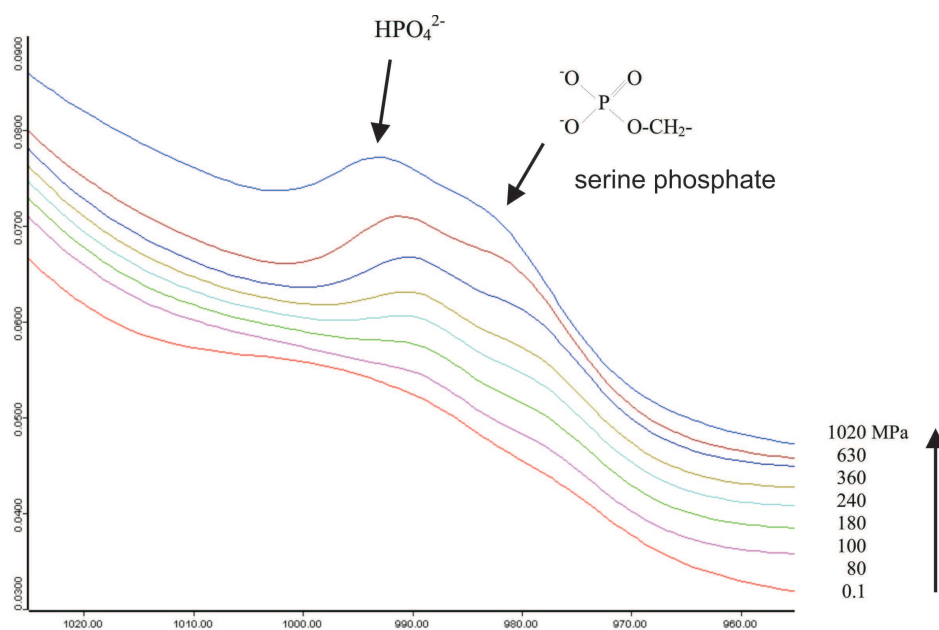


Figure 6.3:
Infrared spectra in the PO stretching band region of casein micelle dissolved in D₂O (pD 7.0) upon pressure increase at room temperature.

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- [3] C. Holt, D. W. L. Hukins, Int. Dairy J. **1**, 151-165 (1991)
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- [5] C. Holt, D. S. Horne, Netherlands Milk and Dairy Journal **50** 85-111 (1996)
- [6] J. L. Silva, G. Weber, Annu. Rev. Phys. Chem. **44** 89-113 (1993)
- [7] T. Huppertz, A. L. Kelly, P. F. Fox, Int. Dairy J. **12**, 561-572 (2002)
- [8] R. Regnault, T. E. Dumay, J. C. Cheftel, Int. Dairy J., in press
- [9] T. Morçöl, Q. He, and S. J. D. Bell, Biotechnol. Prog. **17**, 577-582 (2001)

7 Veranstaltungen

Vorlesungen und Praktika

Sommersemester 2003

PD Dr. Wolfgang Doster, *Proseminar Biophysikalische Methoden*

PD Dr. Andreas Meyer, *Festkörperphysik mit Neutronen*

PD Dr. Peter Müller-Buschbaum, *Angewandte Physik: Polymerphysik 2*

Prof. Dr. Ralf Röhlsberger, *Experimentalphysik für Vermessungsingenieure und Geologen 2*

PD Dr. Walter Schirmacher, *Mathematische Ergänzungen zur Experimentalphysik 2*

Wintersemester 2003/2004

PD Dr. Wolfgang Doster, *Thermodynamik weicher Materie*

Prof. Dr. Andreas Meyer, *Experimentalphysik 1 für LB - Mechanik und Wärme*

PD Dr. Peter Müller-Buschbaum, *Angewandte Polymerphysik 1*

Prof. Dr. Winfried Petry, *Physik mit Neutronen 1*

PD Dr. Walter Schirmacher, *Mathematische Ergänzungen zur Experimentalphysik 1*

PD Dr. Walter Schirmacher, *Computational Physics I.0030*

Betreute Praktikumsversuche

Statische und dynamische Lichtstreuung
Biophysikalisches Praktikum

Theoretische und praktische Einführung in AFM
Fortgeschrittenenpraktikum

Thermische Analyse
Fortgeschrittenenpraktikum

Fortbildungsveranstaltung für Gymnasiallehrer

EDGAR-LÜSCHER-PHYSIKSEMINAR ZWIESEL 2003

Thema: Geologie, Kunstgeschichte und Archäologie mit physikalischen Methoden

Datum: Freitag, 4. April bis Sonntag, 6. April 2003

Tagungsort: Gymnasium Zwiesel

Veranstalter: Der Ministerialbeauftragte für die Gymnasien in Niederbayern, G. Rauprich

Wissenschaftliche Leitung: Prof. Dr. F. Wagner, Dr. U. Wagner und Priv. Doz. Dr. W.

Schirmacher, Technische Universität München

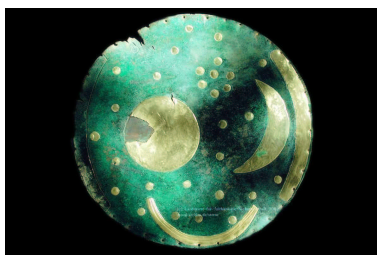
Organisation am Ort: OStD H. Kratzer, OStR G. Haller

Freitag, 4. 4. 2003

- 15.30 – 16.00 PD Dr. W. Schirmacher, TU München
Begrüßung, Organisatorisches
- 16.00 – 17.15 Prof. Dr. F. Wagner, TU München:
Einführung
- 17.45 – 19.00 Prof. Dr. D.B. Dingwell, Universität München
Vulkanologie

Samstag, 5. 4. 2003

- 9.00 – 10.30 Prof. Dr. F. Wagner, TU München:
Datierung mit kernphysikalischen Methoden
- 11.00 – 12.30 Dr. G. Lehrberger, TU München
Archäologie mit naturwissenschaftlichen Methoden
- 13.30 – 16.30 Dr. G. Lehrberger, C. Schink, TU München:
Archäologische Exkursion
- 17.00 – 18.30 Prof. Dr. G. Grasshoff, Univ. Bern:
Die Himmelsscheibe von Nebra



Sonntag, 6. 4. 2003

- 9.00 – 10.30 Dr. Ina Reiche, CNRS Paris:
Untersuchung von Gemälden mit Synchrotronstrahlung
- 11.00 – 12.30 Dr. U. Wagner, TU München
Keramikanalysen - Südamerika

EDGAR-LÜSCHER-LECTURES DILLINGEN 2003

Thema: Kondensierte Materie

Datum: Dienstag, 30. September bis Donnerstag, 2. Oktober 2003

Tagungsort und Veranstalter: Bay. Lehrerfortbildungsakademie Dillingen (Donau)

Wissenschaftliche Leitung: Priv. Doz. Dr. W. Schirmacher, Technische Universität München

Organisation am Ort: OStD Dr. R. Fichtner

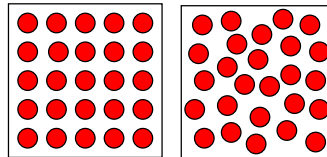
Montag, 30. September:

15:00-16:15 Dr. Walter Schirmacher, TU München

Einführung

18:30-19:45 Dr. Walter Schirmacher, TU München

Ungeordnete Festkörper



kristallin

amorph

Dienstag, 1. Oktober:

9:00-11:00 Priv.-Doz. Dr. Peter Feulner, TU München

Oberflächenphysik

15:00-16:15 Prof. Dr. Winfried Petry, TU München

Untersuchung von weicher Materie mit Neutronen

18:30-19:45 Priv.-Doz. Dr. Erwin Schuberth, TU München

Festkörper und Flüssigkeiten bei sehr tiefen Temperaturen

Mittwoch, 2. Oktober:

9:00-11:00 Prof. Dr. Martin Stutzmann, TU München

Moderne Halbleiterphysik

Tagungen

Klausurtagung der wissenschaftlichen Mitarbeiter und Studenten von E13, E21 und dem FRM-II

Burg Rothenfels

Workshop on Neutron Scattering – Advanced Materials

Programm:

	Montag 21.7.03	Dienstag 22.7.03	Mittwoch 23.7.03	Donnerstag 24.7.03
8:45-10:45		Magnetism 1 P. Böni R. Georgii P. Link S. Valloppilly	Applied Science C. Hugenschmidt T. Unruh J. Kornmeier B. Petersen K. Lorenz M. Schlapp	Soft Matter P. Müller-Buschbaum T. Titz P. Panagiotou S. Loi M. Bleuel A. Ostermann
11:15-13:00		Structure R. Kampmann R. Gilles M. Hölzel M. Meven K. Hradil	Methods U. van Bürck J. Brunner F. Grünauer N. Arend	Magnetism 3 S. Campbell M. Hofmann A. Mirmelstein C. Schanzer
14:30-16:15	Lattice Dynamics W. Petry J. Neuhaus T. Keller W. Schirmacher	Nuclear Physics K. Schreckenbach O. Zimmer A. Türler	Ausflug	
16:45-18:30	Viscous Melts A. Meyer S. M. Chathoth M. Pöhlmann A. R. Müller	Magnetism 2 R., Röhlberger E. Steichele J. Mayor E. Clementyev		

1st MagneTUM Workshop

Nanoscale Magnetism as seen by X-rays and Neutrons

organized by Ralf Röhlsberger

13.3.2003, Seminarraum E13, Physikdepartment, TU München

Duration of the talks: $(30 - x)$ min + x min Discussion with $5 \text{ min} < x < 10 \text{ min}$

9:30	Welcome and Introduction into Nuclear Resonant X-ray Scattering	R. Röhlsberger
Session 1	Magnetic Nanoparticles	Leitung: P. Böni
10:00	Investigation of Magnetism in Low-Dimensional Systems Using Polarized Soft X-rays	Joachim Bansmann
10:30	Magnetic Properties of Large Iron Clusters on Ultrathin Co Films on W(110)	Armin Kleibert
11:00	Magnetic Nanoparticles in Polymer Matrices	Peter Müller - Buschbaum
11:30	Refreshments	
Session 2	Spin Structures I	Leitung: J. Bansmann
12:00	Spin Structure in Pulsed-Laser-Deposited (PLD) Fe on Cu(001) by Nuclear Forward Scattering	Yafeng Lu
12:30	Observation of the Magnetic Spiral Structure in Fe/SmCo Exchange Spring Bilayers by Mössbauer Spectroscopy	Werner Keune
13:00	Lunch	
Session 3	Magnetic Layer Systems and Nanostructures	Leitung: H. Meyerheim
14:30	Probing Magnetic Nanostructures by Specular and Off-Specular Reflectometry with Polarized Neutrons	Christian Schanzer
15:00	Interface Magnetism of Neutron Polarizer Multilayers	Shah Valloppilly
15:30	Magnetism under High Pressure and Perspectives for the Study of Magnetic Layers	Kirsten Rupprecht
16:00	Coffeebreak	
Session 4	Spin Structures II	Leitung: W. Keune
16:30	Nanomagnetism - Exchange Springs, Superparamagnetism and Nanostructured Materials	Beni Braun
17:00	Mössbauer Investigation of the Spin Structure in Exchange-Biased Fe/MnF ₂ Bilayers	Balaram Sahoo
17:30	X-ray Waveguides for the Investigation of Exchange-Coupled Magnetic Films	Kai Schlage
18:00	Discussion and Closing Remarks	
19:00	Dinner	

8 Allgemeine Zusammenstellungen

Diplomarbeiten, Dissertationen, Habilitationen, Auszeichnungen

Diplomarbeiten

Andreas Götzendorfer

Ultradünne Polymerfilme zwischen homogenen und nanostrukturierten Oberflächen

April 2003

Axel Müller

Struktur und Dynamik wasserhaltiger Silikatgläser untersucht mit Neutronenstreuung

Dezember 2003

Tobias Titz

Gradientenproben: Heterogene Polymerfilme

Oktober 2003

Anita Widmann

Inelastische Neutronenstreuung an Alkaligermanatschmelzen

Februar 2003

Dissertationen

Sabine Wiebel

Untersuchungen zur Dynamik niedermolekularer Flüssigkeiten, von der Glasphase bis zum Siedepunkt

Juli 2003

Habilitationen

Andreas Meyer

Akademischer Vortrag: Explosiver Vulkanismus

Januar 2003

Auszeichnungen

Sabine Wiebel

Promotionspreis des Bundes der Freunde der Technischen Universität München e.V.

Dezember 2003

Drittmittelförderung

Deutsche Forschungsgemeinschaft

Im Rahmen des Schwerpunktprogrammes: “Phasenumwandlungen in mehrkomponentigen Schmelzen”

Untersuchung des Einflusses der atomaren Dynamik auf Materietransport, Segregation und Erstarrung mehrkomponentiger Schmelzen

Förderkennzeichen: Me 1958/2-1, Folgeprojekt: Me 1958/2-2

Im Rahmen des Normalverfahrens:

Dynamik von einfachen und zähen Flüssigkeiten untersucht mit dynamischer Lichtstreuung und inelastischer Neutronenstreuung

Förderkennzeichen: Me 1958/3-1

Im Rahmen des Schwerpunktprogrammes: “Bildung, Transport und Differenzierung von Silikatschmelzen”

Untersuchung des Zusammenhangs von intermediärer Struktur, struktureller Relaxation und atomarem Transport

Förderkennzeichen: Me 1958/6-1

Im Rahmen des Normalverfahrens:

Dynamics of supramolecular aggregates of amphiphilic polymers studied by fluorescence correlation spectroscopy

Förderkennzeichen: Pa 771/2-1

Im Rahmen der Forschergruppe “Einfluss von Hochdruck auf molekulare und zelluläre Systeme in Lebensmitteln“:

Denaturierungsphasendiagramme von Proteinen

Förderkennzeichen: For358/2-1

Im Rahmen des Normalverfahrens:

Wärmeleitfähigkeit von Gläsern

Förderkennzeichen: Schi308/6-1

Im Rahmen des SFB 533 “Lichtinduzierte Dynamik von Biopolymeren“:

Zeitaufgelöste Kalorimetrie an lichtinduzierten Prozessen in Proteinen

Förderkennzeichen: SFB533 - 3001748

Bundesministerium für Bildung und Forschung

Weiterentwicklung der Infrastruktur der ESRF-Messplätze für Kernresonanzstreuung

Förderkennzeichen 05KS1WOC/2

Kollektive Dynamik von Proteinen und Proteinkomplexen

Förderkennzeichen 03DOE2M/1

Die Morphologie einer neuen Klasse von Verbundmaterialien: Dünne Copolymerfilme mit eingebauten magnetischen Nanopartikeln
Förderkennzeichen 03DUOTU1/4

Wechselwirkung von Polymermatrizen mit magnetischen Nanostrukturen und Studium der magnetischen Eigenschaften
Förderkennzeichen 03DU03MU

Multiskalige Polymermischungsfilme
Förderkennzeichen 03MBE3M1

Abhängigkeit des Haftvermögens dünner Polymerfilme von der Oberflächenmorphologie
Förderkennzeichen 03CO333

Bau eines thermischen Dreiachsenspektrometers am FRM-II
Förderkennzeichen 03EC5SRM/1

Sonstige Drittmittel

Forschungsstipendium vom Bund der Freunde der Technischen Universität München:
Einfluss von Wasser auf die atomare Dynamik und Struktur von Silikatschmelzen und -Gläsern
Förderkennzeichen: 02 / 23 19

NATO Collaborative Linkage Grant:
Structure formation in thin block copolymer films
Förderkennzeichen: PST.CLG.978046

Veröffentlichungen

- V. L. Aksenov, V. Lauter-Pasyuk, H. Lauter Y. V. Nikitenko, A. V. Petrenko
Polarized neutrons at pulsed sources in Dubna
Physica B **335**, 147 (2003).
- T. Asthalter, M. Bauer, U. van Bürck, I. Sergueev, H. Franz, A.I. Chumakov,
Confined phonons in glasses – A study by nuclear inelastic absorption and Raman scattering
Eur. Phys. J. E, im Druck.
- T. Asthalter, I. Sergueev, H. Franz, W. Petry, K. Messel, R. Verbeni,
Glass dynamics and scaling behaviour under pressure using quasielastic nuclear forward scattering
Hyperfine Int. (C) **5**, 29 (2003).
- T. Asthalter, H. Franz, U. van Bürck, K. Messel, E. Schreier, R. Dinnebier
Structure and dynamics of octamethyl-ethinyl-ferrocene: an organometallic rotator phase
J. Phys. Chem. Solids **64**, 677 (2003).
- T. Asthalter, M. Bauer, U. van Bürck, I. Sergueev, H. Franz, A.I. Chumakov,
Phonons in confinement and the Boson Peak using nuclear inelastic absorption
Hyperfine Int. **144/145**, 77 (2002).
- M. Bellisent-Funel, W. Doster, R. Gähler, I. Köper, S. Longeville, W. Petry
Performance of neutron resonance spin echo in biology
Neutron News **14**, 3, 35 (2003).
- U. van Bürck
Nuclear Resonant Scattering of Synchrotron Radiation
Mössbauer Effect Reference and Data Journal **26**, 80 (2003).
- W. Doster, M. Diehl, R. Gebhardt, R.E. Lechner and J. Pieper,
TOF-elastic resolution spectroscopy: time domain analysis of weakly scattering biological samples
Chem. Phys. **292**, 487 (2003).
- W. Doster, R. Gebhardt,
High-pressure unfolding of myoglobine studied by dynamic neutron scattering experiments
Chem. Phys. **292**, 383 (2003).
- W. Doster, R. Gebhardt and A. Soper
Pressure-induced unfolding of myoglobin: neutron diffraction and dynamic scattering experiments
Advances in High Pressure Bioscience and Biotechnology II., R. Winter, Ed., Springer Verlag 2003, p. 29
- R. Gebhardt, W. Doster, J. Friedrich, W. Petry and A. Schulte
Pressure-induced critical association of myoglobin
Advances in High Pressure Bioscience and Biotechnology II., R. Winter, Ed., Springer Verlag 2003, p. 33

F. Kargl, A. Meyer

Sodium Dynamics and Intermediate Range Structure in Sodium-Aluminosilicate Melts
Chem. Geol. (eingereicht).

H. J. Lauter, V. Lauter-Pasyuk, B. Toperverg, L. Romashev, M. Milyaev, T. Krinitsyna,
E. Kravtsov, V. Ustinov, A. Petrenko, V. Aksenov

Domains and interface roughness in Fe/Cr multilayers: Influence on the GMR effect
Journ. Magn. Magn. Mat **258-259**, 338 (2003).

V. Lauter-Pasyuk, H. J. Lauter, B. Toperverg, L. Romashev, M. Milyaev, A. Petrenko, V. Aksenov, V. Ustinov

Ordering in magnetic multilayers by off-specular neutron scattering
Journ. Magn. Magn. Mat. **258-259**, 382 (2003).

H. J. Lauter, V. Lauter-Pasyuk, B. P. Toperverg, U. Rücker, M. Milyaev, L. Romashev,
T. Krinitsyna, V. Ustinov

Layer magnetization evolution in a Fe/Cr multilayer with uniaxial anisotropy
Physica B **335**, 59 (2003).

V. Lauter-Pasyuk, H. J. Lauter, G. P. Gordeev, P. Müller-Buschbaum, B. P. Toperverg,
M. Jernnikov, W. Petry

Nanoparticles in diblock copolymer films investigated by off-specular neutron scattering
Langmuir **19**, 7783 (2003).

S. Longeville, W. Doster, M. Diehl, R. Gähler, W. Petry

Neutron Resonance Spin Echo: Oxygen Transport in Crowded Protein Solutions
Lecture Notes in Physics **601** 325-335 (2003).

S. Longeville, W. Doster and G. Kali

Myoglobin in crowded solutions, structure and diffusion
Chem. Phys. **292**, 413 (2003).

C. Lorenz-Haas, P. Müller-Buschbaum, T. Ittner, J. Kraus, B. Mahltig, S. Cunis, G. Von
Krosigk, R. Gehrke, C. Creton, M. Stamm

*Crack propagation and defect formation of polymer interfaces investigated by ultra small
angle X-ray scattering*
PCCP **5**, 1235 (2003).

C. Lorenz-Haas, P. Müller-Buschbaum, O. Wunnicke, C. Cassignal, M. Burghammer,
C. Riekel, M. Stamm

*Scanning micro focus small angle scattering as a new technique to investigate defects at
polymer-polymer interfaces spatially resolved*
Langmuir **19**, 3056 (2003).

A. Meyer, R. M. Dimeo, P. M. Gehring, D. A. Neuman

The Backscattering Spectrometer at the NIST Center for Neutron Research
Rev. Sci. Instr. **74**, 2759 (2003).

A. Meyer

Wenn Vulkane schäumen: Zur Rolle von Wasser in Silikatschmelzen
TUM-Mitteilungen, 1-03/04 (2003).

- A. Meyer, W. Petry, M. Koza, M.-P. Macht
Fast Diffusion in ZrTiNiCuBe Melts
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Dynamics of Liquids and Disordered Solids
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Univ.-Prof. Dr. Ralf Röhlsberger, Leitung des Lehrstuhls im akademischen Jahr 2002/2003

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