Annual Report 2006

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title picture:

2d GISAXS scattering pattern of sol-gel templated nanostructures formed in a titanium dioxide based polymer nanocomposite film. The horizontal splitting corresponding to lateral structures and vertical interference fringes on the scattering pattern can be clearly recognized. From the latter can be deduced that the film completely nestles on the underlying substrate and the interface is correlated. Thus the measured interference pattern from the diffuse scattering experiment contains the correlation length corresponding to the film thickness.

The presented schematic diagram [1] shows interfaces of two fully correlated layers. For clarity, the roughness dimension is greatly enlarged with respect to the thickness of the layers. The dashed lines mark the averaged distance between the interfaces of the layers.

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Preface

The year 2006 was characterized by an ongoing growth of the E13 research groups and by distinct changes in the staff. In summer Prof. Andreas Meyer accepted the offer to become director of the DLR in Köln and full professor at the University Bochum. He left E13, but his group remains until the finishing of the PhD thesis of the group members. Our secretary Elke Fehsenfeld moved from E13 to E22 in summer as well. PD Walter Schirmacher was appointed as apl professor and Berhard Schmid joined his group as a diploma student. The bio-polymer group of PD Wolfgang Doster was enlarged by the diploma student Sebastian Stüber and Dr. Marie-Sousai Appavou. In the group of Prof. Christine Papadakis Dr. Ruzha Ivanova returned and Zhenyu Di joined for PhD. In my group the diploma student Matthias Ruderer, the PhD students Gunar Kaune and Weinan Wang and the postdocs Dr. Jean-Francois Moulin and Dr. Ezzeldin Metwalli joined. As a consequence, the activities related to polymer films, surfaces and nano-structures are broadened.

This broadening was accomplished with the new instruments available: A surface sensitive UV-Vis spectrometer and an imaging ellipsometer. Both instruments will be responsibly operated by members of my polymer interfaces group. On the instrument side, the leaving of Dr. Emmanuel Longueteau caused the light scattering laboratory to be unattended. With respect to the instrumental possibilities at the research reactor FRM-II, our TOF-TOF instrument came to a successful routine operation. Moreover, first test and first beamtimes were successfully performed at the MIRA and the REFSANS instrument. In addition, group members participated in many neutron scattering beamtimes at instruments at ILL, NIST, LLB and ISIS as well as synchrotron radiation beamtimes at instruments at ESRF and HASYLAB.

Regarding teaching activities of E13 we cover a large part of the export lectures: mechanical engineering (Müller-Buschbaum), teaching at colleges BT / ET / MT / EI (Papadakis) and teaching at colleges AW / EH / PF (Doster). The Edgar Lüscher lecture series was continued (Schirmacher) and its 30th anniversary was celebrated in Zwiesel at the end of March 2006. In addition, we offer a variety of special lectures devoted to the topics of interest of the chair E13.

This annual report comprises a selection of the different research topics and projects carried out in the individual groups of E13. It highlights the engaged and successful research activities and collaborations with other groups and large scale facilities. I wish all E13 members a fruitful continuation and a successful year 2007.

Peter Müller-Buschbaum

February 2007

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1 Polymer thin film and surface structures

Large scale structures in thin polymer blend films: A grazing incidence ultra small angle X-ray scattering study

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Blending different polymers and thereby obtaining new and tailored material properties is one of the bases of the success of polymer applications [1]. One prominent example is the tailoring of mechanical properties by mixing soft and hard polymer components, or combining a polymer with a glass transition temperature one well above room temperature with one well below. Coating solid surfaces with such polymer blends and conserving the properties of the bulk blend material in the blend film is an extremely attractive way to obtain functional coatings [2]. Large scale phase separation structures are typically formed due to the immiscibility of the blended polymers [3], ensuring a variety of applications, e.g. in optics or sensors [4]. The morphology is altered and tailored by changing the ratio of the components in the blend [5]. The characteristic structural size is modified through the amount of material deposited on the solid support and by the preparation technique applied. As recently demonstrated, the use of flow allows the creation of super-structures and thus enlarges the accessible regime of structures compared to simple phase separation The resulting surface structures are easily probed in real space with optical and scanning probe techniques. The large scale structures as well as the flow induced super-structures are pictured optically. Scanning probe techniques provide a topography information with a mechanical contrast. However, a non-destructive access to the interior of the blend films is impossible with both experimental methods. Within this report we describe recent experimental improvements which overcome restrictions of GISAXS related with the quite small upper limit of the detectable structural size. The presented experimental developments of GISAXS rely on focussing the X-ray beam. Focussing of the beam onto the sample position results in a high real space resolution at the position of the sample and allows for the probing of local structures instead of homogeneous samples. In contrast, focussing the X-ray beam on the detector yields a high reciprocal space resolution, which is necessary to probe large scale structures. To ensure a well controlled surface chemistry, native oxide covered Si(100) surfaces (CrysTec Kristalltechnologie, Berlin) were cleaned prior to solution deposition in an acid bath. The used model system consists of blend films of polystyrene (PS) and poly-n-buthylacrylate (PnBA) with molecular weights 207 kg/mol and 260 kg/mol, respectively. With a ratio of 3:7 and 1:1 wt%, PS and PnBA were solved in toluene with concentrations of 0.98 to 5.0 mg/ml. Varying the solution concentration as well as the amount of solution deposited on the solid support enabled the installation of different polymer film thicknesses. The smooth drying process in a special designed sample chamber at ambient conditions resulted in dry polymer blend films. Due to the immiscibility of PS and PnBA (polymer-polymer interaction parameter of PS and PnBA is 0.162 at 20° C) these blend films show marked surface structures. The high-resolution grazing incidence small angle X-ray scattering or grazing incidence ultra small angle X-ray scattering (GIUSAXS) experiments were performed at the BW4 beamline (HASYLAB, Hamburg) using a wavelength of 0.138 nm. An evacuated pathway of the X-ray beam was used to reduce background. The non-specular as well as the specular intensity was recorded with a two-dimensional detector (MARCCD), which consists of a 2048×2048 pixels array, as a function of the exit angle and the out-of plane angle. At the selected incident angle of 0.41° both features, the specular peak and Yoneda peak, were well separated on the detector area along the vertical direction. This allowed to use a small beamstop which only shadowed the specular peak (second beamstop was used to block the direct beam) without shadowing the central part of the Yoneda peak as well. The beam divergence in and out of the reflection plane was set by two narrow entrance cross-slits together with focussing the X-ray beam on the detector to match the detector resolution in terms of pixel size (79 μ m). A very large sample-detector distance of 13.0 m was chosen so that a resolution of approximately 2.75×10^{-4} nm⁻¹ was achieved. The maximum accessible lateral length scale (21 μ m) of this ultra-high resolution set-up [6] was confirmed by the means of Monte-Carlo ray tracing simulation of the beamline BW4.



Figure 1.1:

a) High-resolution GIUSAXS data (dots) displayed with a simple model (solid line) introducing two characteristic lateral lengths, denoted A and B. b) Optical micrograph picturing the marked phase separation structure installed after solution casting of the PS:PnBA=1:1 - toluene solution with concentration of 5 mg/ml on Si.

in thin blend films with mesoscopic phase separation structures. In addition, in the thin film regime the interplay with dewetting has to be taken into account. Solution casted films have larger thicknesses then spin-coated films. According to scaling laws, the increase in film thickness results in a coarsening of the structures installed by phase separation. Figure 1.1b shows a typical optical micrograph picturing the structures in case of a blend ratio 1:1. Large, glassy PS domains are embedded in a matrix of PnBA. By making use of Fourier transformation, the analysis of optical micrographs at several different sample position and with different magnifications leads to a typical lateral length of 13 μ m, which describes the structures at the film surface. With typical GISAXS experiments the detection of structures comparable to this size is impossible. However, with GIUSAXS this large scale structure is resolved [6]. Figure 1.1a shows a horizontal cut from the 2d intensity measured at BW4 using the set-up described above. Well outside of the theoretical resolution limit obtained from ray tracing, two intensity features are visible. The peak in the intensity, labelled with A, corresponds to the lateral length of 13 μ m as probed with optical microscopy. Thus it resembles a surface feature of the blend film. Moreover, a shoulder in the intensity marked with B is visible as well. The corresponding lateral length is 2.2 μ m and cannot be assigned to a surface feature. Therefore, with GIUSAXS an additional internal structure, located within the blend film, is detected, which was not accessible with optics. At larger q_y -values the data and the model fit deviate. This can originate from the presence of smaller structures, which are not taken into account in the model. Alternatively, the polydispersity of the object shape is overestimated. However, the good agreement at small q_y -values demonstrates the capability to resolve several micrometer sized structures in the GISAXS geometry.

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Nanoscale patterning of colloids in confined geometry using solution casting

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Nanostructuring noble metal surfaces is of great importance for many scientific and technological applications. Especially the possibility to assemble nanometer-sized monodisperse colloids in large two-dimensional (2D) domains is of utmost interest in material science [1]. This is due to the fact that such domains of noble metal nanoparticles on solid substrates show specific optical properties [1-3]. Their optical properties depend strongly on the morphology and structure of the nanoparticle layer. Thus, they are ideal materials for optical data storage [2], anti-counterfeiting [4], and biological applications [3].

One very convenient method to obtain thin nanoparticle layers made of colloids is solution casting [1]. The ordering of the nanoparticles is is determined by evaporation of the solvent, convection, diffusion of the nanoparticles and capillary forces [5,6]. Typically, ring-shaped pattern occur. In our case we used a model system of colloidal gold (Au) nanoparticles deposited on a cleaned Silicon (Si) wafer. The colloidal solution had a concentration of 5×10^{13} particles per ml, the nominal diameter of the spherical Au particles was of 5.4 nm. As substrate for the nanoparticle layer we used silicon wafers with a Si (111) orientation. The wafers were cleaned in an acid bath to ensure a well defined oxide layer. The acid bath consist of a solution containing 110 ml deionized water, 160 ml sulfuric acid and 70 ml hydrogen peroxide at 80°C. The wafers were stored in the bath for 15 min, afterwards rinsed several times with deionized water and dried carefully with nitrogen. A 25 μ l-drop of colloidal solution was deposited using a microliter motorized syringe system at T= 21° C. The evaporation rate of the droplet was 0.42 μ l/min, after one hour the solvent was evaporated.

One very powerful method to investigate the structure and morphology of thin films and interfaces is grazing incidence small-angle x-ray scattering (GISAXS). As dried droplets typically show a very heterogeneous ring-like structure, scanning experiments are most useful to obtain the local structure and morphology of such ring-like pattern. To do so, we combined the nanofocused beam provided by the microfocus beamline ID13 of the European Synchrotron Radiation facility (ESRF) with a GISAXS setup, obtaining a new method, namely nanoGISAXS. The nanofocused beam was produced using Fresnel lenses, the beam size was 300 nm both horizontally and vertically. The



Figure 1.2:

a) Optical micrograph of the droplet after solvent evaporation. beam denotes the incident x-ray beam, SD the scanning direction. The rim of the droplet is situated at y=0 μ m. b) Four typical nanobeam grazing incidence small-angle x-ray scattering (nanoGISAXS) pattern. SB denotes the specular beam stop. For the first two, the position is indicated in the optical micrograph a). At the rim of the droplet at y=0 μ m, the nanoGISAXS pattern is dominated by the form factor of the Au nanoparticles, while for larger distances to the rim a nanostructure in the wetted area (WA) emerges. F denotes contribution from the form factor of the colloidal spheres. c) Enlargement of the nanoGISAXS pattern at y= 654 μ m distance to the rim. The arrows denote the nanostructure in the range of approximately 100 nm. d) For comparison the nanoGISAXS signal of the pure cleaned Si wafer is shown. No nanostructure is visible.

wavelength used was = 0.9755 Å, the sample-to-detector distance LSD= 0.802 m. A 20 μ m guard aperture 20 mm in front of the sample was used to remove parasitic scattering. The incident angle was $\alpha_i = 0.6^{\circ}$. Both direct and specular reflected beam were shielded by two point-like separated beam stops to avoid saturation of the detector. The nanoGISAXS pattern were recorded using a 2D MARCCD 165 detector.

Figure 1.2a shows a micrograph of the drop area, including the beam direction and the scanning direction. The rim of the dried droplet is situated at $y=0 \ \mu m$. After evaporation of the solvent the remaining drop pattern was scanned through the beam with a step size of 2 μm (*nanoGISAXS*-*stitching*) starting at the three-phase boundary at the rim of the drolpet. At every scan point a nanoGISAXS pattern was taken with 20 s acquisition time. Figure 1.2b shows four typical scattering patterns and their corresponding scan positions. The first two are indicated in figure 1.2a. Starting at the rim, we first recognize a clear scattering signal from a frozen-in colloidal solution. The nanoGISAXS pattern is governed by the form factor of the closely packed colloidal spheres. Moving outwards (> 0), the signal completely changes. As the colloidal solution partially wets the cleaned Si surface (area marked *WA* in figure 1.2a, a thin 2D colloidal layer is installed. Figure 1.2c shows an enlargement of one such typical image. Distinct nanostructures marked by arrows are visible. The corresponding length scale is in the order of 100 nm. For comparison, we show in fig. 1d the nanoGISAXS signal from a cleaned Si surface - no nanostructures are visible.

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Influence of polymer substrate patterning on noble metal layers

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Nanostructuring of thin noble metal films is of utmost importance for many technological and biophysical areas, e.g. anti-counterfeiting and DNA scanning [1]. Usually a multilayer geometry is chosen consisting of noble metal layer-polymer-substrate. The optical properties of such multilayer systems depend crucially on the structure and morphology of the noble metal layer [2]. They are determined by key parameters like deposition method [3, 4] or metal-polymer interaction affecting the self-assembly of the metal atoms [5, 6]. To study the interaction of the noble metal layer with the underlying polymer film, combinatorial studies are very useful. They are widely applied in materials science and engineering [7]. Single- or multidimensional gradients are especially adapted for this kind of experiments, as they allow for distinguishing the different morphologies prepared under exactly the same environmental conditions on one single substrate. As we have shown in [3, 4], they allow for studying e.g. the influence of deposition rate or method with all other parameters being kept constant.

Polymer blends offer a tremendous variety of morphologies [8]. Hence, as the polymer-metal interaction strongly depends on the polymer used, our investigation aims to the possibility of imprinting the local micro-phase separated structure of a thin polymer onto the noble metal film, thus offering an additional route to nanostructuring the noble metal layer. In addition with a gradient noble metal layer, this allows for determining the influence of the deposition rate on roughness replication. The sample preparation was as follows. A polymer blend of deuterated polystyrene (dPS) and polyisoprene (PI) with a ratio of 5.5:4.5 was spincoated on top of an acidly cleaned silicon (Si)-wafer. In the next step, a gold (Au) layer of nominally 8 nm thickness was evaporated on top of the blend. Using standard methods [3, 4], a one-dimensional (1D) gradient in mass thickness of the Au layer was attained during evaporation.

The experiment was conducted at the beamline BW4 of HASYLAB. Here we used the new microfocus setup [9] allowing for a beam size of $32 \times 17 \ \mu m^2$. The wavelength used was 0.138 nm, the sample-to-detector distance LSD= 1.266 m and the fixed incident angle $\alpha_i = 0.778^\circ$. As detector we used the standard two-dimensional (2D) detector [9]. Both direct and specular reflected beam were shielded with two separate point-like beamstops to ensure full information content between specular and Yoneda peak [9]. The 1D gradient was oriented perpendicular to the beam



Figure 1.3:

a) Modeling of the microbeam grazing incidence small-angle x-ray scattering (μ GISAXS) pattern at the beginning of the gradient (y=0 μ m) and of the polymer film (y=480 μ m). The horizontal lines denote the position of the specular beamstop and of the Yoneda peaks for Au (YAu) and the blend (YP). b) Most prominent in plane length x_L,P and diameter D_L,P of the nanostructure dominating in the different regions (Au nanoparticles in regions A and I, polymer island in region P) as derived from the modeling as function of the scan position. c) Schematic view of the nanocomposite in regions A,I and of the microphase-separated blend structure in P. D_P: Diameter of the polymer islands in the matrix, x_P: distance of the droplets. The triangle sketches pictorially the decreasing gold coverage with increasing y.

and scanned with a step size of y=30 μ m. At each position a μ GISAXS pattern was taken. In figure 1.3a, two typical μ GISAXS pattern at y=0 μ m (beginning of the gradient) and at y=480 μ m (end of the gradient, pure blend film) are displayed. At every scan point, the data were fitted to extract the local structure and morphology, using the software IsGISAXS [10]. In figure 1.3a, additionally, to the right of the data, the corresponding 2D simulations based on fits to the data are shown. The modeling shows excellent agreement with the data. From the modeling, a bimodal distribution of nanoparticles classes is derived, namely large ($R_L = 80 \text{ nm}$) and small ($R_S = 2 \text{ nm}$) ones. The polymer film shows a most-prominent in-plane length scale $x_{L} = 110$ nm due to the presence of polymer islands. In figure 1.3a, the length scales corresponding to the large particles is shown. In the case of the Au covered part, this corresponds to the diameter of the large Au nanoparticles and their distance, in the purely polymer covered part to the diameter of the phaseseparated polymer islands and their distance. In figure 1.3b, we present a schematic view of the gradient. From figure 1.3a, we derived three regions. In region A, the large gold nanoparticles have length scales considerably larger than those of the polymer islands. In P, no Au particles are present. The intermediate region I shows matching diameters and distances for the polymer island and the large Au nanoparticles. Hence, in region I, the Au layer shows strong indication to reproduce the underlying substrate island morphology.

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Fast swelling kinetics of thin polymer films

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In typical applications polymer coatings are subjected to a surrounding atmosphere. The permeability of the polymer-atmosphere interface with respect to small molecules yields an incorporation of molecules from this atmosphere inside the thin polymer film. As a consequence, the polymer film swells with increasing amount of molecules added. In case of extreme applications the surrounding atmospheres might be aggressive. Most crucial with respect to the stability of the polymer coating are solvent molecules, which in a reversed concentration scenario simply act as solvents for the particular polymer. Depending on the vapour pressure of the solvent atmosphere and the wetability of the interfaces (substrate-film and film-atmosphere) different morphological scenarios arise as demonstrated in self-consistent field calculations. While these equilibrium structures are well predictable [1] and probed in several experiments, the underlying kinetic evolution driven by the transport of the solvent molecules across the film-atmosphere interface is neither predicted theoretically nor experimentally fully probed. The early stages of this kinetic evolution are best characterized in terms of a fast swelling of the initially dry polymer film.

In the model system of polystyrene and a block copolymer with a polystyrene block the fast swelling in toluene atmosphere is probed with neutron scattering. The changes in the density profile are monitored with neutron reflectivity with a very high time resolution of 30 seconds at D17 in TOF mode [2, 3]. The use of neutron scattering allows for the determination of film thickness, roughness and polymer volume fraction in-situ to the swelling kinetic.

At D17 the largest available sample-detector distance of 3.4 m was operated. The diffracted intensity were recorded on a two-dimensional (2d) detector without the movement of any motors. The absence of motor movements is crucial for achieving a high time resolution as well as for avoiding mechanically induced vibrations which destabilize the swollen polymer films (by activation of long wavelength surface waves).

The as prepared, dry polymer films were mounted in an own-made vapour chamber. Before starting the swelling experiment, each individual film was measured with a high resolution D17 set-up, yielding the total film thickness, surface roughness and scattering length density. The vapour chamber was thermostated to 30° C. The injection of 4 ml protonated toluene marked the start



Figure 1.4:

a) Example of neutron reflectivity data recorded during the fast swelling of the polystyrene (PSd) film [2]: With increasing time t (reflectivity of the initial film plotted in black) the film thickness increases and the scattering length density decreases due to the incorporation of protonated toluene. For comparison the reflectivity of the finally swollen film is plotted in light blue. b) Change in the total film thickness d as a function of the storage time t resulting from a fit to the reflectivity data.

(time t= 0 s) of the kinetic. By installing a relaxed resolution of the D17 (increased projected sector opening of the chopper system and slit opening optimised to a complete illumination of the 70*70 mm2 surface area) an extremely high time resolution of only 30 s between to successive measurements was reached. The probed q_z range between 0.08 and 0.58 nm⁻¹ was optimised to cover the critical edges of protonated (toluene) and deuterated (polymer) substances, thereby allowing for the detection of 3 full fringes of the reflectivity curve of the dry film and nearly four order of magnitude in reflectivity (see figure 1.4a). Due to the incorporation of protonated toluene the film thickness increases and the position of the total reflection edge shifts towards smaller q_z values (see figure 1.4a).

The swelling experiments were repeated to optimise the time resolution necessary to probe the initial stages and the fast swelling as well as to ensure reproducibility of the reported results. After the ending of the fast swelling (1 hour), the counting time was increased to 600 s to follow the successive slow swelling with improved statistics. After 385 min the kinetic investigation was stopped, because with respect to the fast as well as slow swelling kinetics equilibrium was reached. The vapour chamber was rapidly opened and thus the swollen polymer film quenched to ambient conditions. On significantly larger storage times a second process, the destruction of the highly swollen polymer/toluene film by dewetting would occur [4]. However, after 385 min the quenched polymer film remained homogenous, as neutron reflectivity and optical microscopy have proven. With respect to film thickness and scattering length density the treated films are indistinguishable from the as prepared, dry ones.

Figure 1.4b pictures the changes in the total film thickness during the fast swelling. Whereas during the initial stages (solvent uptake) the thickness basically remains unchanged, with respect to the swelling induced increase of the film thickness the data are in agreement with a simple Flory approximation (solid line in figure 1.4b) accounting for the entropic contribution and an excluded-volume interaction contribution [5]. Due to the chosen small film thickness of 4 R_g , no indication of formation of a gelation layer, present in bulks samples, is observed. In the final state, the film has doubled its initial thickness, reaching a value of 101.4 \pm 0.4 nm.

A more detailed investigation of the time evolution of the swelling induced roughness is accessible from the off-specular reflectivity recorded simultaneously with the specular reflectivity [2]. It allows for the detection of four different regimes. Only due to the very high time resolution of the experiment the first regime, identified with solvent uptake becomes accessible. Homopolymer and diblock copolymer exhibit both the four characteristic regimes. Differences occur in the late stages of the swelling process. In these final stages the diblock copolymer creates a marked surface structure due to micro phase separation, whereas the homopolymer establishes surface roughness due to capillary waves [3]. Moreover, the diblock copolymer deviates from the simple swelling of coiled chains characterised by a parabolic density profile which expands in space as $t^{1/3}$, as well described by a Flory-like continuum equation for the monomer density.

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Lateral structures in pressure sensitive adhesive films

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Pressure sensitive adhesives (PSA) are characterized by the releasability of the bond connecting two materials [1]. Most of the systems used for application are multi-component blends [2]. Each of the components has its own function, e.g. increasing the adhesion and increasing the cohesion of the PSA [3]. Thus the easiest scientific model system including the adhesion and cohesion responsible component is a binary blend of two homopolymers. In case of blend films containing a tacky polymer and a filler polymer such as a binary blend of poly(n-butylacrylat) (PnBA) and polystyrene (PS) the PSA surface shows a marked surface topography. As a result the force maximum in tack test decreases which cannot be understood just by the reduced size of the tacky surface area [4]. Nevertheless the surface topography and hence the size of the tacky surface area have been investigated with optical techniques so far and thus the investigation by microscopy is restricted towards small length scales by the optical resolution limit. In order to overcome this limit we applied grazing incidence small angle neutron scattering (GISANS).

Our model system consisted of a fully deuterated PS (M_w =207 kg/mol, M_w/M_n =1.02) blended with PnBA (M_w =260 kg/mol, M_w/M_n =3.78). Samples with different blend compositions were examined. In contrast to other frequently investigated blend systems, in our system one component has a glass transition temperature below and one above room temperature. Thus one component (PnBA) is tacky and one (PS) is rigid, fulfilling the requirements of a PSA system.

Figure 1.5a shows a typical 2 dimensional GISANS pattern probed at D22 (sample PSd:PnBA= 50:50). An incident angle well above the critical angle of all components PSd, PnBA and Si was selected and thus the signals are well separated along the exit angle direction on the detector. A beamstop was applied to shield the direct beam and enable a recording of the transmitted signal



Figure 1.5:

a) Example of 2 dimensional GISANS scattering pattern probed at an incident angle above the critical angle of the components. The sample horizon (white vertical line) separates the transmitted signal (negative exit angles α_f) from the GISANS signal (positive exit angles α_f). b) Model calculation of the diffusely scattered GISANS intensity exhibiting the characteristic features. [5]

(negative exit angles α_f) together with the reflected GISANS signal (positive exit angles α_f). The GISANS signal is dominated by the strong splitting of the Yoneda peak, indicating well ordered surface structures. In the 2 dimensional model calculation based on the program IsGISAXS [6] these typical features of the intensity distribution are well reproduced. Because only the diffuse part of the scattering was modelled, the specular peak as well as the transmitted intensity are missing in figure 1.5b.

For a detailed analysis, selected cuts from the 2 dimensional intensity map were taken. Figure 1.6a comprises the cuts at the critical angle of PSd, emphasising on the structure formed by PSd, for 5 different blend compositions. The solid lines are fits using a model based on a structure and form factor contribution with a Gaussian-type of size distribution including the resolution of the D22 set-up. As a result of the fits, two typical lateral length were obtained as shown in figure 1.6b.

Whereas the larger length is attributed to the distance between the polymer structures on top of the substrate (structure factor contribution), the shorter one is due to the size and shape of the structures (form factor contribution). No evidence for the presence of a lateral phase separation structure within the probed length scale regime was observed. As a consequence, the extension of the probed lateral lengths down to the size of the molecules does not explain the observed mechanical behaviour in terms of a reduced surface area. This pictures the high complexity of PSA systems even in the case of a simple blend out of one tacky and one glassy component.

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Figure 1.6:

a) Selected cuts from the 2 dimensional intensity map cut at the critical angle of deuterated PS. From the bottom to the top the PSd:PnBA ratio is 50:50, 60:40, 70:30, 80:20 and 90:10. The solid lines are fits to the data as explained in the text and the dashed line marks the resolution limit of the D22 set-up. The curves are shifted along the y-axis for clarity. b) Lateral lengths resulting from the fit to the GISANS cuts plotted as a function of the PSd contend of the blend films. [5]

Effect of the molar mass of diblock copolymers on the lamellar orientation in thin films: Theory and experiment

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In thin films of symmetric poly(styrene-*b*-butadiene) diblock copolymers on silicon substrates with a native SiO_x layer, the lamellar orientation depends mainly on block copolymer molar mass. Whereas low molar mass samples form lamellae having the interfaces parallel to the film surface, the lamellae are perpendicular to the film surface in high molar mass samples. We have investigated this behavior as a function of molar mass and film thickness using atomic force microscopy (Figure 1.7, left card) and grazing-incidence small-angle X-ray scattering (Figure 1.7, middle card) [1].

However, theoretical approaches to thin, supported block copolymer films having one free surface are scarce. One reason may be that the thickness of the films with parallel lamellar orientation is not a fixed parameter. It is determined by the condition of thermodynamic equilibrium: If the amount of polymer in the film does not conform to the optimum (equilibrium) periodicity of the lamellae, the film is macroscopically separated in two phases differing in film thickness but each having the equilibrium lamellar thickness. We have previously formulated theoretical predictions for the lamellar orientation in free surface films in the strong segregation approximation [2]. However, this approach holds only for high molar masses and is thus not appropriate for all samples studied in Ref. 1.



Figure 1.7:

Atomic force microscopy (left card) and grazing-incidence small-angle scattering (middle card) data were instrumental to establish the lamellar orientation as a function of the interaction parameter χN and the ratio of film thickness over lamellar thickness D_{red} . The relevant free-energy contributions are discussed that determine the boundary between the observed orientational phases (right card).

In order to describe the behavior of samples with intermediate and lower molar masses, we have introduced corrections to the total free energy [3]. The lamellar interfaces have not been treated as infinitely sharp any longer, but their finite width in the intermediate segregation regime has been taken into account. Moreover, the degree of stretching of the two blocks behaves differently in the intermediate and in the strong segregation regime. In this way, we could show that the perpendicular orientation of the lamellae formed by the high molar mass samples is stabilized, which reproduces the experimental results (Figure 1.7).

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Surface and buried layers in thin films of poly(styrene-b-butadiene)

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Diblock copolymers form spontaneously oriented structures in thin film geometry, which may be useful for a number of applications, such as the creation of nanoporous films. Accurate knowledge of the thin film structure is of key importance. We have previously found that the lamellar orientation in thin diblock copolymer films of symmetric poly(styrene-*b*-butadiene) diblock copolymers mainly depends on the block copolymer molar mass [1]. In supported films of a poly(*d*-styrene-*b*-butadiene) (*d*PS-PB) diblock copolymer (molar mass 150 kg/mol), we have previously detected using grazing-incidence small-angle X-ray scattering (GISAXS) that the lamellae are perpendicular to the substrate [2], in agreement with our results on non-deuterated PS-PB [1]. However, one may anticipate a thin overlayer of PB (which has a lower surface tension than *d*PS) or a buried layer of *d*PS or PB near the substrate surface (Figure 1.8). The existence of such layers is important for the accurate calculation of the free energy of the films, which allows the prediction of their orientation [3]. Since the neutron contrast between *d*PS and PB is significantly higher than the X-ray contrast between PS and PB, we attempted neutron reflectometry in order to detect possible buried layers or overlayers.



Figure 1.8:

A few of the possible structures of the film consisting of perpendicular lamellae with an overlayer and/or a buried layer. Dark grey: dPS, light grey: PB. Medium grey symbolizes the average of dPS-PB which is relevant in the reflectometry experiment. The hatched areas represent the Si substrate.

Films from *d*PS-PB (molar mass 150 kg/mol) were spin-coated from toluene solution (26 mg/ml) onto a Si wafer with a native oxide layer. The sample size was $3 \times 8 \text{ cm}^2$. Neutron reflectivity curves were measured at the time-of-flight reflectometer REFSANS. Three incident angles between 1.50 and 3.75° were used. In this way, step widths Δq_z as low as $7 \times 10^{-4} \text{ Å}^{-1}$ were obtained. The measuring times amounted to 13 - 45 h per curve.

The curves obtained are shown in Figure 1.9a. A dynamic range of 10^{-6} could be achieved, and a large number (16) of Kiessig fringes related to the thickness of the polymer film could be resolved. A comparison of the resolution of the Kiessig fringes obtained in the three measurements shows that the higher the incident angle, the better they are resolved (Figure 1.9b). An analysis of the positions of the minima of the fringes (Figure 1.9c) indicates that the film thickness amounts to approx. 1300 Å. The resolution of the instrument is thus sufficient to resolve such large film thicknesses. The overall decay of the curve follows approximately a Fresnel law, i.e. the film surface is smooth.

Thin buried or surface layers are expected to give rise to variations of the reflectivity with large periodicities in q_z . From the inset in Figure 1.9b, a slight deviation from a horizontal line may be anticipated. In order to identify such layers, i.e. deviations from the Fresnel law, the measurements should be extended to higher q_z -values, possibly with relaxed resolution in q_z .



Figure 1.9:

(a) Reflectivity curve from a thin film of *d*PS-PB. The different symbols indicate different incident angles. The smooth line represents Porod behavior. (b) Reflectivity curve from (a), normalized by the Fresnel law. The inset shows the entire q_z -range. (c) Positions of the minima read off from the curve in (b).

We conclude that a thin, supported film of dPS-PB diblock copolymers gives rise to an excellent signal in neutron reflectivity at REFSANS. A large number of Kiessig fringes are resolved, and film thicknesses of more than 1000 Å can be resolved. The precision of the intensity is high enough to detect thin buried or surface layers. Future experiments will focus on identifying the optimum conditions for detection of such layers.

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Transient states during vapor treatment of thin diblock copolymer films: A structure and stability study

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The mesoscopic structures formed by self-assembly of diblock copolymers in thin film geometry are interesting for a variety of applications, such as high-density arrays for use in data storage or optical elements. However, the fast kinetics during spin coating typically leads to domain structures with domain walls and defects. Vapor treatment has been shown to be a route to anneal defects and increase the long-range order [1].



Figure 1.10:

2D GISAXS images of a high molar mass P(S-*b*-B) diblock copolymer film with thermal annealing in the dry state (a) and during the vapor treatment (b). In (b) the ellipse used for determination of the axis ratio of the ring of scattering is shown. Axis ratio of the ellipse (c) and variation of the position of the Bragg rods as a function of time (d).

We have studied the structural changes in thin films of poly(styrene-*b*-butadiene) (PS-PB) diblock copolymers and their kinetics during vapor treatment. In this system, the initial lamellar orientation (parallel or perpendicular to the substrate) can be controlled by the block copolymer molar mass [2]. We have investigated both initial orientations as well as the influence of the solvent selectivity and the film thickness. In-situ grazing-incidence small-angle X-ray scattering (GISAXS) is ideally suited for this task because of its good time resolution (seconds), compatibility with sample environments, and its non-invasive character [3]. Experiments have been carried out at D-line at CHESS.

A thermally annealed film which initially has the perpendicular lamellar orientation, shows quite complex behavior when stored in (non-selective) toluene vapor. During the first minutes, reorientation of a part of the initially perpendicular lamellae takes place (Fig. 1.10a), as evidenced from the axis ratio of the ellipse of scattering (Fig. 1.10b). Only after approx. 10 min, i.e. when the re-orientation is finished, swelling of the perpendicular lamellae sets in. After approx. 20 min, equilibrium is reached.

In a thin film which was not thermally annealed prior to vapor treatment, no clear lamellar orientation is present initially (Fig. 1.11a). Storing this film in a selective solvent(cyclohexane)



Figure 1.11:

2D GISAXS images of a low molar mass P(S-b-B) diblock copolymer film after spin-coating (no thermal annealing step) (a), during vapor treatment with cyclohexane (b-d) and after drying (e).

leads to a splitting of the ring into Bragg sheets at finite q_z and distinct out-of-plane scattering after approx. 10 min (Fig. 1.11b,c), i.e. domains consisting of parallel or perpendicular lamellae have formed. However, after approx. 30 min of treatment, the out-of-plane scattering is more pronounced (Fig. 1.11d), i.e. the perpendicular orientation prevails. This structure persists upon drying (Fig. 1.11e). We conclude that also in this film, transient states are encountered after 10-15 min of vapor treatment with improved structures for both lamellar orientations.

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Effect of solvent vapor treatment on the structure of thin diblock copolymer films

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Block copolymer thin films form spontanously mesoscopically ordered long-range structures which may have a number of applications, e.g. as templates for the preparation of nanoobjects [1]. However, self-organization is associated with domain formation and defects which hamper the use of block copolymer thin films. Vapor treatment constitutes a route to the formation of well-defined, long-range order structures [2]. By means of grazing-incidence small-angle X-ray scattering (GISAXS), normal and lateral inner film structures can be characterized simultaneously [3].

We present here results from thin films of poly((4-octylstyrene)-*b*-(butyl methacrylate)) (OB) and poly((4-octylstyrene)-*b*-(methyl methacrylate)) (OM) before and after vapor treatment with different solvents. In the bulk, OB is lamellar, whereas OM forms connected struts [4]. The films were treated with different solvent vapors which vary in their quality and selectivity.

The surface structures of similar samples have been presented in Ref. 4. For GISAXS measurements, the films were prepared by spin-coating. GISAXS experiments were performed at BW4 at HASYLAB/DESY [5] and at D-line at CHESS.



Figure 1.12:

GISAXS images from thin films of OB treated in different ways. The horizontal and vertical arrows indicate the Bragg sheets from structures along the film normal and the Bragg rods from lateral structures, resp. The other peaks are due to the specularly reflected beam (upper peaks) as well as the Yoneda peak (lower peaks).

Figure 1.12 shows GISAXS images of thin films of OB before treatment and after treatment with acetone and cyclohexane, respectively. Before treatment, Bragg sheets along the film normal (q_z) are present and can be associated with a lamellar structure having a repeat distance of approx. 400 Å. Treatment with cyclohexane (a poor solvent for O, but a good solvent for B) leads to the additional appearance of Bragg rods indicating the presence of perpendicular lamellae of the same repeat distance. This is in agreement with the surface texture which shows meandering lamellae [4]. Treatment with acetone (a non-solvent for O and a good solvent for B) preserves the normal structure. The surface texture reveals large islands [4], thus the parallel lamellar orientation is confirmed by GISAXS.

In-situ time-resolved GISAXS allowed us to follow the development of the lamellar structure in a thin film of OB during the treatment with cyclohexane. Bragg rods develop during the first 10-15 min. The film swells by a factor of two, as evidenced by the decrease of the period of the Kiessig fringes in X-ray reflectivity. When the vapor pressure is decreased again, the Bragg rods persist. The film thickness decreases again to approximately the initial value. Treatment with cyclohexane vapor thus constitutes a method to induce lateral order in the film.

The GISAXS maps of the OM sample do not reveal a pronounced structure before vapor treatment (not shown). Treatment with 1,4-dioxane (a poor solvent for O and a good solvent for M) or acetone (a non-solvent for O and a good solvent for M), however, result in a lateral structure (Figure



Figure 1.13: GISAXS images from thin films of OM treated in different ways. The incident angle was 0.35° . Same notation as above.

1.13). This confirms the observations on the surface texture, which showed dots [4]. Tetrahydrofurane, a good solvent for both blocks, on the other hand, does not result in the development of a surface texture [4]. GISAXS reveals that vapor treatment with THF leads to a structure only along the film normal.

We conclude that treatment with solvent vapor has a significant effect on the resulting film structure. The solvent quality and selectivity have a strong influence on the structure obtained by vapor treatment. Solvents which are poor for one block and good for the other block lead mainly to lateral structures. GISAXS is an ideal method to elucidate the inner film structures formed in thin block copolymer films upon vapor treatment.

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Thin films of diblock copolymers having one crystalline block

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In thin films of diblock copolymers with one crystallisable block [1,2], the structures formed depend on the competition between three transitions: the order-to-disorder transition of the diblock copolymer, the crystallization of the crystallisable block, and the vitrification of the amorphous block [3]. The space requirements of the two blocks at the lamellar interface play an important role. They depend on the degree of folding of the crystalline block, the orientation (tilt) of the crystallites with respect to the lamellar interface and the degree of stretching of the amorphous block. The resulting surface textures are often complex, and methods giving insight into the inner film structure on a large range of length scales are desirable in order to obtain complete information on the various parameters contributing to structure formation.

We have studied the interplay between crystallization and mesophase formation in lamellaeforming poly(styrene-*b*-ethylene oxide) (P(S-*b*-EO)) diblock copolymers with the blocks having molar masses of 3,000 g/mol. Samples were prepared by spin-coating from toluene solution onto Si wafers. In order to investigate the influence of crystallization kinetics, crystallization was performed at different temperatures, T_x . Grazing-incidence small-angle X-ray scattering (GISAXS) allows us to determine the lamellar orientation and the lamellar thickness. Grazing-incidence X-ray diffraction (GIXD) gives detailed information on the crystalline order. These results can explain the surface textures measured by atomic-force microscopy (AFM).



Figure 1.14:

AFM topographical images from thin films of lamellar P(S-*b*-EO) crystallized at $T_x = 25^{\circ}$ C (a), 40° C (b) and 50° C (c).

The surface textures depend strongly on T_x (Figure 1.14): At $T_x = 25^{\circ}$ C (Figure 1.14a), crystallization results in a weakly textured morphology, whereas at higher temperature, larger and stronger textures are observed. For instance, $T_x = 50^{\circ}$ C results in large terraces with a height of 20 ± 0.5 nm. The 2D GISAXS maps give insight into the lamellar orientation and thickness (Figure 1.15a). The peak near $q_z = 0.054$ Å⁻¹ (black arrow) is located at the position expected for parallel lamellae of thickness 16.5 nm [4]. The lamellae are thus parallel to the film surface with their thicknesses increasing with T_x .

The reciprocal space map and the in-plane scans from GIXD show a number of reflections due to the crystalline order of the PEO block (Figure 1.15b). A preliminary analysis has been carried

out using the PEO unit cell known from the bulk [5,6]. It has been found that, at $T_x = 25^{\circ}$ C, the *c*-axis and thus the crystal stems are inclined with respect to the film normal. In contrast, the crystal stems orient perfectly parallel to the film normal at $T_x = 50^{\circ}$ C. The size of the crystallites increases with T_x , as evidenced by the increase in the relative intensity of the (120) reflections (Figure 1.15c).



Figure 1.15:

(a) GISAXS image from a thin P(S-*b*-EO) film crystallized at $T_x = 25^{\circ}$ C, measured at BW 4 (HASYLAB/DESY). (b) Reflections observed in the GIXD experiment as a function of the lateral and the normal component of the scattering vector, q_{xy} and q_z , from a film crystallized at $T_x = 25^{\circ}$ C. The measurement was carried out at BW 2 (HASYLAB/DESY). (c) GIXD in-plane intensity profiles for different crystallization temperatures. The indexing has been made for a crystal orientation with the chain stems parallel to the surface normal.

We conclude that the lamellae preferentially orient parallel to the film surface. The lamellar thickness increases with crystallization temperature. The average orientation of the PEO chain stems depends on the crystallization temperature as well: With increasing temperature, their orientation deviates more and more from being perpendicular to the lamellar interfaces. Also the crystalline sizes increase with T_x which is consistent with the increase of lateral structures in surface texture. We attribute these changes to the vast difference in the growth rate of the crystallites. We are currently investigating the effect of secondary crystallization on the structures.

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Substrate surface induced morphology transition in triblock copolymer films

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In contrast to A-B diblock copolymers, the mean-field phase diagram of A-B-A triblock copolymers is highly asymmetric as a result of the higher entropic penalty in deforming the central B blocks so as to accommodate the two outer blocks into the A domains. The phase diagram is dominated by the lamellar phase, with smaller regions of hexagonally packed cylindrical and cubic phases (i.e., the classical phases). [1]

The investigated system consists of the A-B-A triblock copolymer polyparamethylstyreneblock-polystyrene-block-polyparamethylstyrene with a fully deuterated central polystyrene block (PpMS-b-PSd-b-PpMS). Due to the high molecular weight of M_w 280 000 g/mol (with a narrow molecular weight distribution M_w/M_n = 1.10) the strong segregation regime is addressed. Both components are nearly symmetrically distributed with f = NPSd/N = 0.51. Films are spin-coated out of a toluene solution on top of silicon substrates with different surface chemistry [2]. The different investigated surface chemistries cover hydrophilic, hydrophobic, polydimethylsiloxane (PDMS) grains covered and PS-brush surfaces.



Figure 1.16:

a) Example of 2 dimensional GISANS scattering pattern probed at an incident angle above the critical angle of the components. The direct located at $\alpha_f = \alpha_i$ is blocked with a beamstop, the horizon at $\alpha_f = 0$ separates the transmitted and the reflected intensity. b) GISANS cuts probing the bulk structure of the triblock copolymer film (from the bottom to the top: hydrophilic, PDMS grains covered, hydrophobic and PS-brush surface).

In the performed experiment the impact of the underlying Si substrate chemistry on the structure of the triblock copolymer film was probed in terms of morphology and characteristic length. For this purpose the GISANS experiments were performed through the Si substrate to address the buried Si-triblock interface only. Surface sensitivity was be achieved by a variation of the incident angle similar to previous experiments [3].

A typical scattering pattern is shown in figure 1.16a. Due to the low absorption of neutrons in addition the reflected signal a transmitted signal was detected as well. The transmitted signal

(SANS of the bulk film measured at a very shallow angle) shows an elliptically shaped intensity maximum. The elliptical shape results from refraction effects due to the presence of the film surface. In a common SANS experiment a ring shaped intensity maximum occurs due to the powder-like orientation of the lamellae. In addition the reflected signal is visible on the 2d detector. From the GISANS cuts the bulk lamellar spacing was obtained (L= 48 nm), which is not altered due to the surface chemistry (see figure 1.16b).



Figure 1.17:

a) GISANS cuts with fit to the data (lines) probing the near substrate surface structure of the triblock copolymer film (from the bottom to the top: hydrophilic, PDMS grains covered, hydrophobic and PS-brush surface). b) Resulting relative change of the lamellar spacing (with same colour coding as in a).

At the substrate surface the situation changes. As shown in figure 1.17 all GISANS cuts probing the near substrate surface structure of the PpMS-b-PSd-b-PpMS film exhibit a peak which proves the presence of a perpendicularly oriented lamella structure. However, the peak intensity and thus the degree of perfection of this orientation as well as the peak position and thus the lamellar spacing depend strongly on the surface energy. At a hydrophilic surface and at a surface covered with PDMS grains the lamellar structure is well oriented, whereas at the hydrophobic and PSbrush surface it is strongly perturbed. The higher degree in orientational order comes along with an unchanged lamellar spacing. In contrast on the PS-brush surface an increase by 8% (from 48 to 52 nm) is observed and on the hydrophobic surface a slight increase was observed as well.

Although in diblock copolymer films, the presence of external surfaces was reported to alter the morphology [4, 5] in this investigation no deviation from a lamellar structure was observed. In combination with the results of the previous work focussing at the free polymer film surface (no alteration of morphology as well) [3] we can therefore conclude that the higher entropic penalty in deforming the central PSd blocks so as to accommodate the two outer blocks into the PpMS domains prevents morphological transitions.

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Solvent content in thin spin-coated polymer films

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The detection of remaining solvent in thin polymer films is of importance due to its effect on chain mobility and film homogeneity. Moreover, it gives an estimate on possible aging effects caused by the reduction of the solvent content, which typically yield an increased brittleness.

In the present investigation, we focus on a well controlled model system, which consists of protonated polystyrene (PS) with different molecular weights M_w of 7, 27, 207, 514, 908, 1530 kg/mol, spin-coated out of protonated or deuterated toluene (solvent) onto silicon (Si) wafer substrates. Directly after spin-coating the thin PS films were investigated with neutron reflectivity (NR) at the MIRA instrument at a wavelength of 16 Å. A narrow q_z range (0 Å⁻¹ to 0.02 Å⁻¹) around the critical edge was probed with high resolution. Due to the high sensitivity of the position of the critical edge on the ratio of protonated PS and deuterated toluene (toluene-d8), the exact position of the critical edge enables to determine the solvent content. In addition to the deuterated solvent samples, samples with thin PS films spin-coated out of protonated toluene were also prepared for a direct comparison of the different sample types [1]. In order to rule out all kinds of measurement errors precautions on the sample part, e.g. preparation and repetitions with different but identical samples, are very important. With respect to the instrument, a very accurate alignment of the experimental set-up is crucial for those measurements.

The recent experiment focuses *on two different key parameters* which influence the solvent content: the molecular weight of PS and the film thickness investigated in the range of 10 to 100 nm. Thus, two respective sample series were prepared. Focussing on the molecular weight as key parameter, thin PS films with a fixed thickness of 50 nm are investigated: The expected shift of the critical edge position, which is observed in neutron reflectivity simulations on this model system, is verified by the MIRA measurements. Figure 1.18a shows one particular example for a molecular weight of 7 kg/mol. In direct comparison the reflectivity of the sample prepared out of deuterated and protonated solvent is plotted. The intensity is shown on linear scale to emphasize on the region of total external reflection.

The obtained reflectivity data of thin PS films with different molecular weights and a fixed film thickness are shown in figure 1.18b. The data show a shift of the critical edge with increasing molecular weight, although the measured critical edges of much higher M_w shift not completely but rather indicate a slightly changed slope of the critical edge. For the investigation of the film thickness as the second key parameter, PS with a molecular weight of $M_w = 207$ kg/mol is dissolved in toluene-d8. The thickness of the thin PS film is depending on the viscosity of the solution and thus the concentration of PS in the solution. Therewith the concentration is chosen in such a way to achieve a desired film thickness [2]. The thickness series comprises thin PS films of a thickness of 10, 30, 50, and 100 nm. Figure 1.19a shows the obtained reflectivity data for films with thickness of 10, 30 and 100 nm at fixed molecular weight. The data of the critical edge indicate an influence on the film thickness, but prevent a definite conclusion about the behaviour in dependence of the film thickness without fitting the data.



Figure 1.18:

(a) Neutron reflectivity data obtained from spin-coated thin polystyrene (PS) films with a molecular weight $M_w = 7$ kg/mol and fixed film thickness. Depending on the use of protonated and deuterated (d8) toluene, the position of the critical edge shifts significantly. (b) Neutron reflectivity data of a selection of thin PS films prepared of different molecular weights M_w of 7, 27, 907 and 1530 kg/mol and fixed film thickness. With increasing molecular weight the position of the critical edge shifts towards higher q_z values.

The simulation and data analysis of the neutron reflectivity measurements is performed with Parratt32, a simulation tool for neutron and x-ray reflectivity. The model layer stack in ambient air consists of bulk Si with a single layer on top, representing the PS film. In order to match the simulated curve with the measured curve of the PS/toluene-d8 film only the scattering length density of the PS film is adjusted, whereas the magnitude of the adjustment represents a measure for the ratio of protonated PS and deuterated toluene. Since the relation SLD_{tol} < SLD_{PS} < SLD_{tol-d8} applies for the sample materials and since the film will be a mixture of PS and toluene-d8, the SLD for deuterated toluene is a reasonable maximum for the adjustment. To rule out the indetermination of the PS film thickness, x-ray reflectivity (XRR) measurements are performed, since the NR measurements in the narrow q_z range provide no estimation of the PS film thickness. In figure 1.19b the NR simulations for a PS film are shown, whereas the measurements should lie within the regions defined by the extreme values of the SLD.

In summary, *the experiment was very successful*. A direct comparison indicates a clear distinction between thin films prepared of PS dissolved in protonated or deuterated toluene. This directly transforms into the amount of solvent remaining in the polymer film. Depending on the molecular weight of PS the shift of the critical edge is pronounced to a greater or lesser extent, but clearly visible. In total, the actual sample preparation conditions are of importance and affect the amount of solvent inside the PS films. As a consequence, well defined experimental conditions of the PS film are essential to work out the solvent content. Due to the close vicinity of the MIRA instrument and the polymer preparation laboratories, this is perfectly fulfilled.

Following MIRA experiments will be expanded to a technically more relevant sample system consisting of nanocomposite films, prepared by the combination of an amphilic diblock-copolymer, which acts as the templating agent, and an inorganic sol-gel chemistry. This particular nanocomposite films are employed in new photovoltaic devices. The investigation of such a system is of importance, since starting from the naturally remaining solvent content in the film after preparation and the subsequent decrease during aging alters the structural properties of the nanocomposite film and thus results in loss of performance.



Figure 1.19:

(a) Neutron reflectivity measurements from spin-coated thin films with PS molecular weight M_w =207 kg/mol and film thicknesses of 10, 30 and 100 nm. An influence of the film thickness is indicated by the reflectivity data. (b) Simulated neutron reflectivity data for a single PS film on top of bulk Si. Simulated for a film SLD of protonated PS and deuterated toluene. Since the measured data is a mixture of both, the measured reflectivity lies within the simulated borders.

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Preparation and characterization of nanocomposite films with switch effect

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In recent years, colloidal microgel particles attracted more and more scientific and technical interest due to their fast response to external stimuli [1-3]. Based on the control of their swelling/deswelling behaviour, the production and characterization of a kind of inorganic-organic hybrid thin films is of major importance for various applications in the fields of electrics and optics. In this respect, in a first step, detailed information on the properties of the microgels after adsorption to solid substrates is required. Within this investigation polystyrene-co-poly(N-isopropylacrylamide)(P(S-co-NIPAM)), a thermo-responsive copolymer, is focussed. PNIPAM macro- and microgels show a temperature induced de-swelling in water at 32° C [4] and this temperature is not effected by the PS comonomer [5].

P(S-co-NIPAM) micelles composed of a PS core and a cross-linked PNIPAM shell form in hydrophilic solution [5-6]. Out of this solution thin P(S-co-NIPAM) films will be prepared by spincoating on the pre-cleaned, oxide covered silicon (100) substrates as well as glass slides. As the chemical and physical behaviour of the thin films is strongly influenced by their morphology, atomic force microscopy (AFM) is routinely used to monitor the surfaces of polymer films giving rise to a real-space visualization of the surface topography. A meaningful statistical analysis of film thickness and roughness is advantageously performed with conventional X-ray reflectivity measurement. Then, the combination of atomic AFM and grazing incidence small angle X-ray scattering (GISAXS) measurements will allow the investigation of lateral structure and in-plane composition of the thin film.

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Microbeam GISAXS investigation of sol-gel templated nanocomposite films

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We focus on the creation of nanostructured TiO_2 thin films, which are of great interest for many applications, due to their electrical performance. The performance is strongly dependent on the morphology of the nanocomposite films, therefore it is very important to prepare the desired morphology with high reproducibility and homogeneously spread out over areas of cm². For the preparation of the TiO₂ nanocomposite films we combine the amphilic diblock-copolymer PSb-PEO, which acts as the templating agent, with an inorganic sol-gel chemistry [1]. First, the diblock copolymer is dissolved in 1.4-dioxane, which is a good solvent for both, the hydrophobic as well as the hydrophilic block of PS-b-PEO. Afterwards, hydrochloric acid (HCl) and titanium tetraisopropoxide (TTIP) are added into the polymer solution as the source for the sol-gel process. Because HCl and TTIP are poor solvents for the hydrophobic block, a so-called good-poor-solvent pair induced phase separation leads to the formation of nanostructures by film preparation via spincoating. The different morphologies can be controlled by the solvent concentration. In order to obtain crystalline TiO₂ films as the final step calcination is conducted at higher temperature in air.

For the investigation of the morphologies of the sol-gel templated nanocomposite films microbeam grazing incidence small angle x-ray scattering (μ GISAXS) is performed at the beamline BW4 [2,3]. For the experiments a morderate micro-focussed beamsize is used, which also enables to investigate local gradients of the thin film morphology. The measurements are conducted on samples with Si-wafer substrate material and spin-coated TiO₂ nanocomposite films with variations in the morphology. The film thickness is about 60 nm.

In figure 1.20(a) horizontal cuts at the critical angle of TiO_2 are shown, whereas each cut corresponds to an individual sample and specific morphology.

The measurements of the samples after the subsequent calcination are shown in figure 1.20(b). By focussing on the cut at the bottom of the diagram a pronounced structure peak (see arrow) can be observed, which gives the clear evidence for further ordering of the TiO₂ nanoparticle film induced by the calcination process. For all other investigated morphologies this effect can be observed to a greater or lesser extent. Figure 1.20(c) shows the recorded 2D μ GISAXS pattern from where the cut is extracted and the evident splitting of the Yoneda peak can be found. The obtained μ GISAXS results are in good agreement with results from the AFM characterization.



Figure 1.20:

Horizontal cuts at the critical angle of TiO_2 displaying the logarithm of intensity versus horizontal momentum transfer q_y in log-scale for the two sample groups: before (a) and after (b) calcination. Each cut corresponds to an individual sample. The arrow marks a position of a well defined lateral structure. The dashed line indicates the resolution limit. All curves are shifted along the y-axis for clarity. A typical two-dimensional GISAXS scattering pattern is shown in (c) corresponding to the bottom curve (black) in diagram (b). The intensity is shown on a logarithmic scale (blue = low and purple/white = high intensity).

In addition to the investigation of structure forming on Si-wafer substrates, an experiment with a similar sample preparation procedure is performed on ITO-coated glass substrates. In contrast to the wafer and bare glass substrates, the ITO coating exhibits a surface with ordered nanoscale roughness, whereas its influence to the scattering patterns is investigated. Figure 1.21(a) shows a direct comparison of the horizontal cuts at the critical angle of TiO_2 . The difference between the measurement on the ITO-coated substrate with (III) and without (IV) a nanocomposite film is clearly observable, whereas the pronounced structure peak of cut (IV) originates from the nanoscale roughness. From the position of the plateau-like feature in cut (III) its identical origin, generated from the nanoscale roughness, can be concluded. The strong intensity increase induced by the nanocomposite film for $q_u < 10^{-2} \text{\AA}^{-1}$ leads to a relative decrease of the ITO signal. For the glass substrate only a minor indication of a structure can be found. In figure 1.21(b) the corresponding AFM image of the bare ITO surface is shown, indicating a high nanoscale roughness. In contrast, the roughness is reduced by the spin-coated nanocomposite film inducing a smoothing of the surface. A meandering or nanowire-like morphology of the film is recognizable. Due to this low-ordered nanocomposite structure an additional pronounced structure peak cannot be found in the GISAXS scattering pattern. However, further experiments will also cover the investigation of highly ordered nanocomposite films on top of surfaces with nanoscale roughness.

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Figure 1.21:

(a) Horizontal cuts at the critical angle of TiO_2 displaying the logarithm of intensity versus q_y for ITO-coated glass substrates: in comparison bare glass with (II) and without (I) the nanocomposite film, ITO-coated glass with (III) and without (IV) film. In (b) the corresponding AFM image of an ITO-coated sample without film is shown. In (c) the respective AFM image of ITO with a spin-coated film is shown.

Nanostructures of hybridmaterials for photovoltaics

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The usage of organic systems for photovoltaic applications instead of the classic materials like silicon or gallium arsenide has many advantages. First of all, the easier processing of polymers results in lower overall costs. While inorganic materials require high temperature and high vacuum processing conditions, polymers are liquid processable at room temperature. Polymers can be deposited with e.g. ink-jet printing on large areas. Because of the mechanical flexibility of polymers the solar cells are stable concerning bending and can be used in new applications. Furthermore the properties of the polymers are easily tuneable, i.e. the absorption spectrum can be tailored modifying the side chains of the monomers.

For an organic photovoltaic system conducting polymers are needed. Most known polymers are insulators whereas the so called conjugated polymers are conductive. These molecules have a backbone of sp_2 -hybridized carbon atoms with free electrons in the p_z -orbitals. The alternating bond length results in a band gap at the Fermi level. As a consequence the conjugated polymers have the behaviour of a semiconductor and can be used for optoelectronic applications. [1]

By absorbing a photon an electron is excited from the valence to the conduction band and forms an electron-hole pair. This neutral Frenkel-exciton diffuses through the material until it recombines or splits. Because of the high binding energy of the exciton a polymer interface is required to split the electron and the hole. Thus a combination of an electron conducting and a hole conducting polymer is used. To get an efficient splitting of the exciton structures in the order of 10 nm are needed because of the small diffusion length of the excitons in polymers [2]. Such structures are achieved by a blend of two polymers.

We investigate the binary polymer blend of MEH-PPV (Poly(1-methoxy-4-(2-ethylhexyloxy)-pphenylenevinylene)) and P3BT (poly(3-butylthiophene-2,5-diyl). Both homopolymers are soluble in chloroform. We dissolved both homopolymers with different ratios of the polymers. Thus we got solvents with the MEH-PPV ratio of 100% to 0% in steps of 10%. We prepared the thin films via spin-coating on glass slides. In the first series, the film thickness increases with increasing MEH-PPV ratio.

Optical absorption spectra are obtained by using a Perkin-Elmer Lambda 35 spectrometer (UV/Vis) in reflection and transmission geometry. We measure in the range of 350 to 700 nm with a scan velocity of 7.5 nm/min and a step size of 0.1 nm.

In Fig. 1.22a the normalized absorption spectra of MEH-PPV:P3BT thin films are shown whereas each curve corresponds to a different blend of MEH-PPV and P3BT. Because of more clarity there are only five spectra shown. Due to the change in thickness, the spectra are normalized concerning the maxima of the absorption curves. The absorption maxima are at 500 nm and 530 nm for pure MEH-PPV [2, 3] and P3BT, respectively. The spectrum of the pure P3BT film shows two shoulders at 550 nm and 600 nm. The blended films show absorption of both components. The maximum is shifted to lower wavelength with increasing rate of MEH-PPV. Furthermore, the shoulders vanish with increasing MEH-PPV ratio.

In Fig. 1.22b the integrated absorption spectra of the MEH-PPV:P3BT thin films against the rate of MEH-PPV is shown. The data shows an indication of a maximum at 70% MEH-PPV ratio. The increasing of the integrated absorption at the pure P3BT film is attributed to the normalization of the absorption data. To obviate this normalization effect, sample series with the same thickness have to be prepared and measured.



Figure 1.22:

(a) Selected UV/Vis absorption spectra of MEH-PPV:P3BT thin films with different blending ratios. Shown is the rate of MEH-PPV (0, 10, 20, 40, 70, 100%). The spectra are normalized concerning the maxima of the absorption curves. (b) Integrated absorption spectra of the MEH-PPV:P3BT thin films against the rate of MEH-PPV. The error bars were calculated from the deviation from measuring the same film six times.

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GIUSAXS study of conducting polymer thin films prepared under high electric fields

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New application perspectives can be envisioned for conducting polymer materials if their properties can be tuned by controlling their organization and/or morphology. In particular, creating anisotropic structures or inducing ordering over tunable length scales is of high interest. One possible way to induce such structures is to prepare the films under a strong external electric field that could promote some molecular orientation due to molecular polarisability [1]. These preferential orientations could in turn affect the phase behaviour of an incompatible blend system. In this experiment thin films of poly(1-methoxy)-4-(2-ethylhexyloxy)-p-phenylenevinylene (MEH-PPV) with polydimethylsiloxane (PDMS) blends spin coated under high electric field were investigated by Grazing Incidence Ultra Small Angle X-ray Scatterring (GIUSAXS). These measurements were performed at HASYLAB beamline BW4.

GIUSAXS was chosen as the investigation technique for our samples since we wanted to probe the lateral structure of ultrathin films both at the surface level but also at the level of the interface with the substrate (contrary wise to scanning probe techniques GIUSAXS gives access to buried structures) [2,3]. We first studied MEHPPV/PDMS spin coated thin films of increasing blending ratios in order to identify the scattering features of each region of the phase diagram. These films were then compared to those prepared under the same conditions except that a 10^6 V/m field was applied normal to the substrate during spin coating .



Figure 1.23:

 Q_y cuts for increasing MEH-PPV blend content (with and without external field). For 60% MEH-PPV (a) there is no clearly resolved lateral structure. For 80% MEH-PPV(b) A broad shoulder develops and is more clearly seen for the sample prepared under field. For 90% (c) The phase separation becomes clearer.

The lateral ordering of the thin film is evaluated via a cut of the 2D scattering patterns at a position corresponding to a given value of Q_z , the momentum transfer normal to the substrate. Figure 1-3 show such cuts performed at the critical angle of MEH-PPV.
As seen from figures 1.23 the application of a high field normal to the plane of the substrate induces a modification of the lateral ordering of the polymer blend. At 60% MEH-PPV concentration a broad, non resolved, shoulder can be seen to extend to larger q values for the sample spin coated under field. For the samples with a higher MEH-PPV content this effect becomes clearer and and a lateral ordering with a characteristic length in the range of $0.01nm^{-1}$ is observed. These result are a clear indication that the MEHPPV-PDMS system is a good candidate for such a morphological control technique.

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Correlated roughness in polymer film containing magnetic nanoparticles

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Nanocomposite materials based on polymeric matrix and inorganic fillers is a new topic of research in several different areas including standard fillers such as carbon black, clay and silica. The advantages of such materials like achieving desired mechanical, electrical and thermal properties have also been being reported since long. Rendering magnetic properties to the polymer by using magnetic nanoparticles in the diblock copolymer film is a rather new idea. We incorporate the magnetic nanoparticles into the template offered by a symmetric diblock copolymer through the self-assembly process. The nanoparticles distribute themselves inside the layers formed by diblock copolymer due to their selective affinity to one block. This leads to a spatially distributed ordered arrangement of the nanoparticles within the copolymer matrix [1, 2]. The surface topography of polymeric film influences the electrical, optical, mechanical and thermal properties [3]. For such kind of application it is very important to have a constant thickness all over the film. The roughness or topography of the film has then to be correlated to the roughness or topography of the substrate underneath. We have investigated the roughness correlation between the substrate and films of gradient thickness prepared by spin coating of such a new type of composite material by grazing incident small angle X-ray scattering (GISAXS) technique. The grazing incidence geometry enhances the surface sensitivity. GISAXS overcomes the limitations of conventional small angle x-ray scattering studies regarding extremely small sample volumes in the thin film geometry [4].

Magnetic (metal oxide) nanoparticles covered with polystyrene hairs from α -lithium polystyrene sulfonated (LPSS) were used as filler in the diblock copolymer Poly (styrene-b-isoprene) matrix. The solution of polymer in toluene containing 25%(wt.) nanoparticles was used for producing films with a gradient in thickness ranging from 10 nm to 700 nm on clean silicon wafer surface covered by a native oxide layer by spin coating. GISAXS measurements have been carried out without any further processing of the gradient film.

Microbeam GISAXS (μ GISAXS) measurements were carried out at the beamline BW4 at HA-SYLAB. The selected wavelength was 0.138 nm. The beam divergence in and out of the plane of



Figure 1.24:

Left: a composite image of scattering patterns at 20 positions of the film having gradient thickness on 2D detector. The thickness of film decreases from top left pattern to bottom right most pattern following the arrow. Right: detector cuts at $q_y = 0$, called detector scans, where, $\Phi = \alpha_i + \alpha_f$ with α_f as exit angle, showing roughness correlation over a wide range of film thickness. The curves are shifted along y-axis neglecting their change in intensity values for clear presentation. The film thickness decreases from bottom to top cut following the arrow.

reflection was set by two entrance cross-slits. The beam was focused to the size of (H \times B) 30 \times 60 μ m² by using an assembly of refractive beryllium lenses [5]. The sample was placed horizontally on a goniometer. A beam stop was used to block the direct beam in front of the detector. Besides, a second, point-like moveable beam stop was also used to decrease the specular peak intensities on detector. The whole gradient length was 1.4 mm and was measured in 20 steps (each step size is 70 μ m) starting from approximately 700 nm to 10 nm film thickness. The incident angle was $\alpha_i = 0.72^0$, well above the critical angles of polymers and nanoparticles. In this geometry the beam can penetrate the sample and the data gives access to the information of not only the surface structure but also the structural information inside the film. The scattered intensities were recorded by a two-dimensional (2D) detector positioned at D_{SD} =1.971 m behind the sample. The GISAXS patterns are shown in Fig. 1.24 (left). The vertical cut at $q_y = 0$, called detector cut, contains the information of the structure perpendicular to the surface. They are shown in Fig. 1.24 (right). Horizontal cuts at constant q_z allow extracting the information (geometry, size distribution and spatial correlation) of lateral structures. The short range modulation of intensity along the vertical direction starting near the Yoneda region at $q_y = 0$ was observed in the 2D detector images in Fig. 1.24(left). The modulation along vertical direction shows a local ordered structure perpendicular to the surface In Fig. 1.24(right), all detector cuts are plotted for comparison. At the specular position the intensity drops due to shielding by beam stop. The cuts show that there is a regular modulation between Yoneda and Specular peak (shielded) representing a local ordered structure. The order is present (see all 2d image and in all vertical cuts) in almost all areas of measurement i.e., from thick to thin areas of film. This kind of ordered phenomena has been reported [3] before as the roughness of film correlated to the substrate roughness. This means that the roughness of the substrate is reproduced on the film surface starting from large lateral lengths down to a critical cut-off length. As one can see in Fig. 1.24(right) that this roughness correlation decreases with decreasing film thickness. This kind of local observation was possible because of the micro-focused beam at the beam-line BW4 at HASYLAB. Further analysis of the data will yield quantitative values of roughness and of the cut-off length. Moreover, from horizontal cuts information on lateral structures will be obtained resembling the arrangement of the nanoparticles inside the polymer matrix.

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Asymmetric diblock-copolymer films with incorporated nanoparticles

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Among systems with a tendency to self-organization the advantage of using diblock-copolymers originates from their ability to form a rich variety of different morphologies. By changing the symmetry and molecular weight of the copolymer one can form polymer matrices with different morphologies [1], which can be used to re-print corresponding nano-particle structures. We use the polymeric matrix to bring nano-particles (NP) into a defined array. Induced order in the NP ensemble is achieved by coating them with one or the other species of the copolymer chain and hence providing an affinity of NP to selected lamellae of the self-assembling multilayer film. The interaction of the NP between themselves and with the host matrix is tuned by the NP density and size. Thus structural and physical properties of nanocomposite films are changing as a function of these parameters. In our previous study we produced nancomposite lamellar films with concentrations of PS-coated nanoparticles as high as 26% of the PS volume fraction. Even for high concentrations of nanoparticles the composite films have equilibrium lamellar morphology with local segregation of nanoparticles only within PS-lamellae [2].



Figure 1.25:

AFM images of asymmetric diblock copolymer films. Top panels show the surface structure of a film without nanoparticles ($v_f = 0\%$) before annealing (a) and its modification after annealing (a'). Panels b and b' correspond to the film with nanoparticles ($v_f = 10\%$) before and after annealing, correspondingly.

In the present study we investigate new composite films based on asymmetric diblock-copolymer. For the sample preparation we used poly(styrene-deuterated-block-buthylmethacrylate) (P(Sd7-b-BMA)) diblock-copolymer with the molecular mass of Mw=166.400 g/mol, Mw(PSd)=59.4 kg/mol and Mw(PnBMA)=107.0 kg/mol, Mw/Mn=1.17. Magnetite (Fe₃O₄) superparamagnetic

nanoparticles are coated with short PS chains. The mean size of coated nanoparticles as determined by light scattering is 10 nm [3]. P(Sd7-b-BMA) and coated nanoparticles were blended in a toluene solution. The volume fraction of nanoparticles was 0%, 5% and 10%. After the spincoating homogeneous films with magnetite particles were obtained. For each volume fraction we produced films with different total thickness ranging from 20 nm to 160 nm. The samples were annealed for 48 h at a temperature $T = 160^{\circ}$. The surface of the samples was characterized with atomic force microscope (AFM) before and after annealing (see figure 1.25). The aim of present study is to get complete information about the orientation of cylinders depending on the thickness D less than the effective total diameter of PBMA-PS-PS-PBMA) implies that the parallel alignment of cylinders may become unfavorable due to confinement by the reduced total thickness of the film, thus resulting in the vertical alignment of cylinders. The second important point is to get information about the orientation of cylinders with incorporation of nanoparticles, because the presence of nanoparticles changes the surface energy of the composite film and increases the size of the PS domain.



Figure 1.26:

Experimental intensity of neutrons scattered by asymmetric P(Sd7-b-BMA) lamellar films with $v_f = 0\%$ (a) and $v_f = 10\%$ (b) before annealing and the same films after annealing (a' and b'). 2-dimensional intensity maps are presented as a function of $p_i + p_f = q_z$ and $p_i - p_f$. Strong intensity along $p_i - p_f = 0$ corresponds to the specular reflection and is determined by the transverse structure of the multilayer.

Experiments on neutron reflectometry with off-specular scattering on composite films were performed on the IBR-2 reactor at Dubna on the time-of-flight reflectometer REMUR with wavelength band λ ranging from 0.8 Å to 14 Å at a fixed incident angle $\alpha_i = 8.5$ mrad. Experimental data for the two limiting cases of diblock copolymer films with D=160 nm with the volume fraction of the NP $v_f = 0\%$ and $v_f = 10\%$ before and after annealing are shown in figure 1.26. Two-dimensional intensity maps are presented in the coordinates $(p_i + p_f) = q_z$ and $(p_f - p_i)$ [3], where $p_{i,f} = \frac{2\pi}{\lambda} \sin \alpha_{i,f}$ are the surface-normal components of the incident and scattered wave vectors, and q_z is the wave vector transfer. The intensity scattered from both samples before annealing is shown in panels a) $(v_f = 0\%)$ and b) $(v_f = 10\%)$. Strong intensity along $p_i - p_f =$ 0 corresponds to the specular reflection and is determined by the transverse structure of the multilayer. The reflectivity lines from both samples contain only the Kiessig fringes which indicate the total thickness of the film. The off-specular intensity in a form of Yoneda scattering spreads out left and right from the specular intensity line indicating the presence of surface and substrate roughness. After annealing of the samples we repeated the measurements. Two - dimensional intensity maps from the annealed samples (figure 1.26 a' and b') are very different from the ones obtained from the as prepared samples and correspond to well ordered structures. The presence of strong Bragg peaks with corresponding off-specular sheets for the sample without nanoparticles (figure 1.26 a') confirms a rather perfect alignment of PS cylinders inside the PBMA matrix after annealing. The presence of the Bragg peaks for the sample with incorporated nanoparticles in figure 1.26 b' proves that the ordered structure persists and is not destroyed by a rather high concentration of the nanoparticles. However, the 2D pattern of intensity reflected and scattered from the sample with nanoparticles differs from the one of the pure copolymer film, that reflects changes in the structure due to the nanoparticles. A detailed quantitative data analysis follows.

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Polystyrene-b-polyisoprene diblock copolymer films with embedded maghemite nanoparticles investigated with GISAXS

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We investigate lamella-forming polystyrene-block-polyisoprene (denoted P(S-b-I)) diblock coploymer films with embedded γ -Fe₂O₃ nanoparticles. The used block copolymer is asymmetric and forms a microphase separation structure due to the incompatible block segments PS and PI. For the preparation of the thin films we apply two well-known techniques, spin coating and solution casting. From P(S-b-I)/ γ -Fe₂O₃ nanoparticles mixtures, dissolved in toluene, we are able to produce the desired thin polymer- γ -Fe₂O₃ composite films on precleaned silicon substrates. The γ -Fe₂O₃ nanoparticles are coated with polystyrene and therefore preferably settle in the polystyrene lamellae. Various concentrations of γ -Fe₂O₃-nanoparticles result in different physical properties of the polymer matrices.

Structural composition and topography of the nanoparticles within the thin layers are obtained by grazing incidence small angle X-ray scattering (GISAXS) [1]. GISAXS experiments are performed at beamline BW4 at HASYLAB. The synchrotron radiation is micro-focussed to a beamsize of $30 \times 60 \ \mu\text{m}^2$. An incident angle of 0.72° is used. The 2D-MarCCD detector is placed at a distance of 1.97 m to the sample to record the diffuse scattered X-rays. Two beam stops are used: A lead beam stop to shield the specular peak and a beam stop diode to protect the detector from the direct beam.

Figure 1.27 shows on the left a typical 2d-intensity distribution of diffuse scattered X-rays obtained during a GISAXS measurement. The lighter the colour, the higher is the intensity. The intensity decrease in the upper central region is caused by the shielding lead beam stop. The intensity distribution is recorded for eight different nanoparticle weight concentrations, ranging from





Left: Typical 2d-intensity distribution of diffuse scattered X-rays. The lighter the region, the higher the intensity. Right: Out-of-plane cuts of polyisoprene for different nanoparticles weight fractions. Increasing amount of nanoparticles results in decreased characteristic length.

0 % to 43 %. On the right side of Figure 1.27 the Yoneda-cuts of polyisoprene, implemented at the corresponding critical angle, are shown. At 0 % nanoparticle weight fraction no characteristic length is present (lower arrow). An increasing nanoparticle concentration results in forming smaller characteristic structures sizes, indicated by the lower arrow at lower qy-values (0.7 %) up to the upper arrow at higher qy-values for 43 % weight fraction. Another feature seen in the Figure 1.27, is a broadening of the structure peaks with increasing weight fraction.

The detector cuts within the scattering plan are displayed on the left in Figure 1.28 with logarithmic intensity versus exit angle α_f . At approximately α_f equal 0.7° the intensity drop is caused by the beam stop hiding the specular peak. The curve referring to 0 % weight concentration shows a very strong modulation starting at the Yoneda peak ($\alpha_f = 0.2^{\circ}$) and ending at a high angle of about 1.8° . This modulation originates from a strong roughness correlation [2, 3]. Correlated roughness means homogeneous adaption of the composite film on the silicon substrate and therefore exhibits the substrate surface on the composite film surface down to a characteristic size (cut-off length). For higher nanoparticle weight concentrations this correlated roughness is inhibited and vanishes for very high weight fractions (43 %). On the right side of Figure 1.28 X-ray reflectivity data are shown. With increasing concentration of nanoparticles the film thickness increases due to the addition of material. Moreover the films roughen upon the addition of nanoparticles. This roughning might be the key reason for the diminished correlated roughness due to added nanoparticles. From a detailed fit to the reflectivity curves the density profile perpendicular to the substrate surface is extracted. In combination with the GISAXS data, thus a complete structural picture of the composite films is gained, because the GISAXS yields information on the lateral correlations. As turned out, upon addition of nanoparticles the internal order is reduced with increasing nanopartricle concentration.

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Figure 1.28:

Left: Detector cuts of 2d-intensity distributions for different nanoparticle weight fractions. The logarithmic intensity is showed in dependence on the exit angle f. The correlated roughness (modulation) is diminishing with increasing amount of nanoparticles. Right: X-ray reflectivity measurement confirms inhibition of correlated roughness due to added particles.

GIUSAXS investigation of flow induced structure in conducting polymer thin films

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Conducting polymers are nowadays finding an expanding field of application, from electrostatic protection to devices and sensors. New perspectives can be envisioned for these materials if their properties can be tuned by controlling their organisation and/or morphology. In particular, creating anisotropic structures is of high interest. One possible way to induce such structures is to prepare the films under flow conditions [1,2]. Different effect (such as shearing, concentration fluctuations, Marangoni cell formation) can then play and induce orientation and/or ordered structures that would not be observed in samples prepared under static conditions or by conventional spin coating. The system chosen to study these effects is a blend of poly(butylthiophene) (PbuT) with polystyrene (PS). This systems includes a conducting polymer (PbuT) and was chosen as to provide a good scattering contrast. Grazing incidence x-ray scattering is the technique of choice to study structure formation in thin films since this geometry enhances the sensitivity to surface signal[3]. We first studied PbuT/PS spin coated thin films of increasing blending ratios in order to identify the scattering features of each region of the phase diagram. We then investigated a thin film presenting a gradient structure that was prepared by flowing a blend solution on a silicon substrate. The measurements were performed at beamline HASYLAB on the BW4 beamline using the ultra small angle setup in reflection mode (GIUSAXS) configuration[4].

As can be seen from Fig 1.29, the scattering patterns obtained for the spin coated samples showed a pronounced splitting of the Yoneda peaks.





(left): Q_y cuts at the critical angle of PbuT for blends of composition ranging from 10% to 100% PbuT from bottom to top

This demonstrates that lateral structure develops in the blends as a consequence of phase separation of the incompatible components. The characteristic dimension of the lateral structures was determined from the position of the peaks observed in cuts of the scattering patterns at a constant Q corresponding to the critical angle of PbuT. It was observed that the range of characteristic length observed varies between 0.009 and 0.05nm^{-1} .

Once established the patterns for the blend components, we performed a spatially resolved analysis of the surface of the gradient sample. The lateral resolution of this analysis was fixed by the width of the beam (300μ m), scattering patterns were recorded at equidistant locations separated by 500μ m along the gradient direction.



Figure 1.30:

(left): Detector cuts obtained along the gradient direction of a film prepared under flow (right): Q_y cuts at the critical angle of PbuT for the same positions (sampling points are separated by 500Å μ m along the gradient)

Fig 1.30 shows the cuts of these patterns along the Q_z (at $Q_y=0$) and Q_y (at the critical angle

of PbuT) direction respectively. The evolution of the Q_z cut shows that the composition of the blend varies along the direction of the gradient (variable intensity of the Yoneda peaks) and the Q_y cut indicates that structures of variable lateral dimensions were produced along the same direction. These results show that PbuT-PS blends are suited for producing structured film via flow preparation and that GISAXS is the appropriate tool to characterize these films.

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2 **Bio-polymer films**

Effect of calcium concentration on the structure of casein micelles in thin films

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Caseins, a family of phosphoproteins, form the largest protein component in most milks of industrial significance. Today, it is generally accepted that caseins assemble into casein micelles, the aggregates in which they are found in milk. Casein micelles are poly-disperse, roughly spherical aggregates with diameters ranging between 150 and 300 nm. In contrast to conventional surfactant systems, casein micelles are heterogeneous, composed of four different proteins, alpha(s1)and alpha(s2)-caseins, beta-casein, and kappa-casein [1]. Structure and stability of the casein micelles is still a matter of debate and different models are discussed in literature [2-5]. In the sub-micelle model, the caseins first aggregate via hydrophobic interaction into subunits of 15-20 molecules each, thereby creating a well defined sub-structure on a scale of 20 nm [6]. These units are linked by small calcium phosphate clusters, while other models deny the existence of casein sub-micelles and consider calcium phosphate clusters as seeds of micelle growth. Along this line, the dual binding model accounts for distinct hydrophilic and hydrophobic regions of the particular polypeptides. Analogous to diblock copolymers, the hydrophobic regions associate, stabilizing the core of the micelle and at the hydrophilic regions the colloidal calcium phosphate particles are attached.

A consensus of opinion exists that an outer hairy-layer of kappa-casein ensures the stability of the casein micelle through a steric stabilization mechanism and that calcium is essential for the micelle formation at all. The casein proteins divide themselves into two groups, the calcium-sensitive and the non-calcium sensitive, which prevent or inhibit also in mixtures the precipitation of the calcium-sensitive group by calcium. Kappa-casein is insensitive to calcium and alpha(s1)- and alpha(s2)-caseins and beta-casein are calcium sensitive. The main physiological task of the caseins is to dissolve calcium phosphate in neonates. Approximately 1 mM casein in milk binds 10 mM Ca₂PO₄ in aqueous solution, whose solubility is in the range of 10^{-3} mM.

Within the present investigation we focus on the effect of calcium concentration on the structure of casein micelles in thin films (prepared by spin-coating [7]). CaCl₂ was added, at room temperature, to casein micelles extracted from commercial-grade skim milk in a concentration range from 0 to 100 mM. As reference for the thin film investigation, bulk solutions were probed with static and dynamic light scattering experiments. To avoid problems related with dilution, native turbid solutions were analyzed at a concentration of 3%, using a backscattering technique, which records only light scattered from the surface of the sample. This procedure minimizes multiple scattering and yields approximate molecular parameters even of turbid solutions. The thin film investigation is based on grazing incidence small angle X-ray scattering (GISAXS) and complemented with optical microscopy and atomic force microscopy to picture the surface structure [7]. Due to the typical size of micelles on the order of 100 nm, these experiments addressing the mesoscopic structure require a high resolution. To probe nanostructured films GISAXS offers an opportunity to address large scale structures. In principle, with the present set-ups available at the BW4 USAXS beamline at HASYLAB/DESY in Hamburg lengths up to more than 10 micrometers are

accessible. This resembles a sufficient resolution to account for highly ordered structures resulting from casein micelles.

Extracted casein micelles of a desired concentration were dissolved in purified water. The pH of the solution was adjusted to 7.3. Casein films were prepared by spin-coating onto pre-cleaned glass slides. The cleaning was performed in base baths yielding a defined surface chemistry. The samples were freshly prepared in advance of the scattering experiment. Dry films were investigated. The GISAXS experiment was performed at a fixed wavelength of 0.138 nm and a sample-detector distance of 2.2 m a allow for a high resolution. To check for possible radiation damage, the total counting time was split into smaller slots and the resulting signals were compared. Within the presented concentration and pH range no signature of radiation damage was detected. The scattered intensity was recorded with a two dimensional detector. A the fixed angle of incidence 0.466° the major signals, namely the specular and the Yoneda peak are well separated and enable an easy detection of the GISAXS signal from the 2d intensity distribution via a horizontal cut. The horizontal slice contains only scattering contributions with an in-plane information. Because the flat glass surface gives no contribution with a marked intensity distribution to the diffuse scattering, the probed signal originated from the casein film. In case of c=100 g/l we assume bulk like films. A detailed analysis of the type of structural order is in progress.





a) Double logarithmic plot of the horizontal line cuts from the two-dimensional GISAXS signals (dots) measured at casein films prepared at different Ca concentrations together with model fits (solid lines) as explained in the text. From the bottom to the top the added amount of Ca increases from 0 to 100 mM in steps of 10 mM (except 70 and 90 mM). The curves are shifted along the y-axis for clarity. The resolution limit towards large length scales is shown by the dashed line. b) AFM image on a 5×5 and c) on a 10×10 micrometer scan range.

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Casein gradient films as prepared by solution casting techniques

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Caseins represent with about 80% the largest protein component in bovine milk. They are organized in casein micelles. During their synthesis, highly insoluble calcium phosphate (denoted CaP) is assembled in the casein micelle. This enables transport of the mineral to neonates and prevents calcinations of the mammary gland. The casein micelle of bovine milk consists of four different phosphor-proteins which can be divided into two groups: the calcium insensitive kappacasein and the calcium sensitive alphaS1-, alphaS2- and beta-caseins. While the self-association behaviour of the individual caseins in aqueous solution has been well investigated, the micellar substructure and the stability of casein micelles is still under debate. Casein submicelle models propose a well defined substructure on the scale of 20 nm, consisting of units which are rich of caseins and linked via small CaP clusters. Other models deny the existence of casein submicelles and consider CaP clusters as centres of micelle growth, instead .

Casein micelles are colloidal particles of spherical shape with diameters of about 100 nm [1]. The sizes are polydisperse and can be well approximated by a log-normal-distribution. Its generally accepted that the stability of casein micelles is ensured by an outer hairy layer of kappa-caseins [2]. The hydrophobic part of this block copolymer is graved inside the micelle while the non-adsorbing, hydrophilic block is sticking into solution and provides steric stabilisation as a polyelectrolyte brush. Thus, the outer kappa-casein layer plays a crucial part in the stability and arrangement of casein micelles.

Casein micelles are the raw material for the production of gelled and flocculated milk products, such as cheese, yogurt and ice-cream. Additionally, casein micelles find a broad application in casein films as adhesives or paint, prepared with solution casting or spray coating techniques. Due to their high initial tack, high wet strength and easy removal in the bottle washer, caseins containing adhesives are most suitable for labelling of bottles. Moreover, because of their ampholytic properties, caseins are able to bind pigments and can be coated as paint on multitude of smooth surfaces.

Our research focuses on size and arrangement of casein micelles in dependence of key-parameters such as calcium concentration, pH, hydrostatic pressure and temperature. So far, we performed experiments both in concentrated turbid casein solution using light scattering techniques (DLS) [3, 4] and in thin casein films, prepared with spin coating, using grazing incidence small-angle X-ray scattering (GISAXS) [5]. Apart from spin coating, casein films can be prepared by solution casting. It is of great interest to investigate both methods, because of different forces acting on different time scales. While spin coating acts as a rapid quench, during solution casting the solvent evaporates slowly [5]. Moreover, the solution casting technique enables the preparation of casein film gradients



Figure 2.2:

Schematic representation of the casein concentration gradient (3% - 20%) as prepared by solution casting technique. Optical micrographs showing different surface film morphology depending on casein concentration.

We want to investigate concentration- (0.1 to 100 g/l), pH- (5 to 9) and calcium concentration (0 to 100 mM) gradients, prepared by solution casting extracted casein micelles [6]. The gradients will be prepared by the method of droplet deposition. For example, to prepare a concentration - gradient casein film, solution droplets of increasing casein concentration will be placed stepwise on the top of precleaned glass slices and stored by room temperature under a slight nitrogen stream to allow solution casting. figure 2.2 depicts a sketch of the casein concentration gradient together with enlarged details, observed by optical microscopy, which we want to explore on the ID13-Beamline. The gradient replaces a big set of individual samples and allows for a detailed investigation of the influence of the individual key parameters.

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Effect of enzymatic cross-linking on casein micelles thin film structure

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Milk and milk components are mainly used for related food products. Nevertheless, some of the milk constituents such as casein have alternative non-food applications. In ancient Egypt casein-based glue was first used. Milk casein proteins are also used for other technical applications [1] including plastic manufacturing [2], fiber textile [3], methane gas production [4]. Casein proteins in bovine milk include four main types: α_{1s} -casein (38 %), α_{2s} -casein (10 %), β -casein (36 %) and κ -casein (13 %), that are involved in formation of hydrated casein micelles of sizes on the order of 150-300 nm [5]. Various models [6] are proposed for casein micelle structure including coat-core, sub-micelles, and the internal structure. The coat-core model describes the micelle as an aggregate of casein proteins with inner layer composition different from the outer layer. The sub-micelles model proposed the micelle as roughly spherically uniform sub-micelles which are linked together via a calcium phosphate ion cluster. The internal structure model specifies the mode of aggregation of different caseins.

Müller-Buschbaum et. al. [7] investigated thin casein films prepared using spin coating method. The GISAXS results [7] of these casein films indicated a decrease of micelle size at the glass surface compared with the micelles in solutions (probed by dynamic light scattering). The micelles are arranged on the surface in a compact structure due to the moderate force applied by spin coating. This information on the micelle size and their spatial distribution on the solid supports are important for application such as labeling of glass containers. Varying the micelle sizes using different concentrations of calcium chloride [8] have also been tested and showed a decrease in the number of small sub-micelles and a corresponding increase in the number of large size micelles. In the present study, we aim to manipulate the micelle size distribution using the enzymatic cross-linking technique prior to casein protein thin film preparations.

Pasteurized skim milk was used to prepare the casein micelles via micro-filtration and ultrafiltration processes [9] to completely remove the whey proteins without varying the calcium, salts and lactose contents. The casein micelles crosslinking process was performed by incubation of casein protein solution (2.8 %) in transglutaminase enzyme (3 U g^{-1}) for different time periods up to 180 minutes. The transglutamine enzyme incubation reaction was stopped by heating the samples after the specified times at 80°C for 2 min in order to inactivate the enzyme, followed by cooling in ice. One casein sample solution without crosslinking was used as a zero time sample. The casein micelles were applied by spin coating on precleaned glass microscopic slides.

The GIUSAXS experiments was performed at beamline BW4 of DORIS III storage ring at HA-SYLAB/DESY in high resolution set up to account for highly ordered structures up to 10 micrometers resulting from casein micelles. The selected beam wavelength was 0.138 nm and the sample-to-detector distance was 13.2 m. The sample was placed horizontally on a goniometer and the scattered intensities passed through an evacuated flight tube and detected using a 2D detector. Vertical cuts gives information on the structures perpendicular to the surface and the horizontal cuts contains infromations on the in-plane surface structures. Figure 1a shows the 2D GIUSAXS scattering patterns measured from the casein micelles thin films. The incident angle was chosen to avoid the overlap between the specular and diffuse scattering contributions along the vertical detector directions. The specular reflection was shielded using a beam stop to protect the detector form the extensive high intensity damage.

Figure 2.3b shows the horizontal scans from different film prepared from casein micelle solutions crosslinked using transglutaminase enzyme for different time. In Fig. 2.3b the incubation time increases from bottom to the top (0, 20, 40, 60, 80, 100, 120, 140, and 180 min.). At first sight, all out-of-plane cuts qualitatively look similar, however, a close look at the intensity of each cut near the resolution limit (very small q_v -values) indicates relatively higher fraction of large-scale

structures that reveals an increase in the assembly of larger casein micelles with increasing the enzymatic cross-linking time. Thus as expected, the cross-linking mainly creates larger sized structures, which however are well resolved by the high-resolution GIUSAXS set-up.

A quantitative analysis of these data will be performed by data-fitting programs such as IsGISAXS. Moreover, these samples will be further investigated using GISAXS to test the larger q_y range ($q_y > 0.1 \text{ nm}^{-1}$) for better understanding of the changes associated with the smaller sizes (submicelles < 30 nm) structures.



Figure 2.3:

a) The 2D GIUSAXS scattering pattern of casein micelle thin film measured at BW4, b) log-log plot of the horizontal line cuts from the 2D GIUSAXS signals measured on casein films prepared by incubation in transglutaminase enzyme for different time periods. The time increases from the bottom (no enzyme encubation) to the top (180 minutes incubation) in steps of 20 minutes.

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Crystallinity in thin films of recombinant spider silk protein

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Spider silk protein films have a number of potential applications, such as a scaffold to immobilize enzymes and as wound dressing [1]. Various structural motifs of the spider silk protein including β -sheet, β -turn, α -helix and spacers play an important role for the overall physical properties of the protein film [2]. The goal of our work is to investigate the structural and conformational changes of recombinant spider silk protein films which occur upon chemical treatment.

Cloning strategies [3] were used to produce large quantities of recombinant silk-like proteins. They allow the variation of the sequence of the repetitive part of the protein and in this way to relate the secondary and mesoscopic structure as well as the mechanical properties to the protein sequence. Moreover, films can be cast which are more easy to handle than the threads produced by the spider, and they are accessible to a number of optical and surface scattering methods.

Circular dichroism (CD) spectroscopy obtained from an as-cast immobilized film reveals that the proteins are rich in α -helices [4]. In contrast, the CD spectrum of a chemically treated film is typical for a β -sheet rich structure. This conformational change is paralleled by the transition from a water-soluble to a water-insoluble film.

We have investigated the synthetic spider silk protein [3] derived from the garden spider's (Araneous diadematus) dragline silk protein ADF-4. The protein films were deposited from hexafluoroisopropanol solutions either by casting or by spin coating onto transparent quartz plates or silicon wafers. Subsequently, the films were chemically treated with methanol. We have investigated the secondary structure by FTIR, the surface texture by AFM, and the crystallinity and mesoscopic structure by grazing-incidence X-ray diffraction (GIXRD) and small-angle X-ray scattering (GISAXS). Investigations were carried out both before and after the treatment.



Figure 2.4:

Ellipsometric image of the protein film after methanol treatment (0.4 mm x 0.6 mm). A and B indicate regions of maximum and minimum film thickness, respectively.





Figure 2.5: The fitted amide I spectrum of protein film. (a) Before, (b) after methanol treatment. Methanol treatment leads to a significant enhancement of surface roughness. Figure 2.4 shows an ellipsometric image of the protein film after treatment. The film thickness varies between 2.71 and 2.55 (± 0.04) μ m. From the amide I band observed in FTIR (Figure 2.5), it is seen that in the methanol treated film the content of α -helix and random coil decreases, whereas the content of β -turns and β -sheet increases.



Figure 2.6:

In-plane GIXRD profile of the protein films before and after methanol treatment. The experiment was carried out at BW 2 at HA-SYLAB/DESY.

Figure 2.7:

GISAXS images from thin films of spider silk protein on a silicon wafer cast from 10% solution before (a) and after (b) methanol treatment. The vertical stripe of low intensity in the middle of image is due to the beam stop. The experiment was carried out at BW 4 at HASYLAB/DESY.

Furthermore, methanol treatment leads to an increase in crystalline order, as is evidenced by the increase in peak intensity of the (210) reflection seen in the GIXRD experiment after treatment (Fig. 2.6). This peak is attributed to the presence of β -sheet poly(alanine) crystallites within the treated film. Using the Scherrer equation, the size of these crystallites is estimated to be of the order of 8 nm. Crystallites are also revealed in small-angle scattering: Figure 2.7 shows the 2D GISAXS images of protein films before and after methanol treatment. The images indicate a structural variation upon treatment with the scattering being much more significant after the treatment. We attribute the scattering after treatment to the presence of crystallites in an amorphous matrix.

We conclude that significant structural transformations in the spider silk upon chemical treatment occur. We have identified an increase of surface roughness and in crystallinity.

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3 Biomolecular dynamics

The Effect of Packing on Internal Molecular Motions of Hydrated Myoglobin Observed with Neutron TOF Spectroscopy

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Internal motions in proteins investigated by Quasi Elastic Neutron Scattering

Proteins can be assumed as hetero-polymers composed by a specific amino-acids sequence (primary structure). The chemical characteristic of each of these residues and their positions induce the formation of alpha helix, beta-sheets and turns (secondary structure). The orientation in space of these structures gives a three-dimensional structure to the molecule (tertiary structure). A fourth level of structure can be given by the assembling of several sub-units (quaternary structure). The formation of all of these structures is strongly related to the environment of the protein and, in particular, to the interaction with the solvent. Proteins are essentially close-packed structures, resembling molecular crystals in terms of packing density. Thus, excluded volume interactions in addition to constraints imposed by covalent bonds along the chain strongly restrict the molecular displacements in the protein interior. Two major types of displacements were identified in quasielastic neutron scattering experiments with proteins: rotational transitions, mostly decoupled from the solvent, and water-assisted breathing motions of side chains [1]. Myoglobin has been the object of several dynamic neutron scattering studies and simulations [1,2]. Its biological function is to store oxygen in muscle tissue, by reversible oxidation of the heme iron. The binding site is isolated from the solvent by compact protein structure, which is composed of a-helices and disordered turns. The transfer of ligands across the protein-solvent interface thus needs the assistance of structural fluctuations. The transfer rates depend on the solvent viscosity, as was shown by kinetic experiments [3]. However, internal migration of ligands between vacancies in the protein structure appears to be decoupled from the solvent [3]. The ligand motion between isolated vacancies involves transient channels, formed by rotational displacements of side-chains [4]. In previous investigations we have analysed the solvent-dependent motions, which exhibit a dynamical transition [1], while in this contribution we focus on internal dynamics. Rotation of methyl groups was identified as a major component, contributing to the neutron scattering spectrum [1]. But the distribution of rotational rates due to packing in-homogeneities and the role of the environment are still controversial [1,5,7]. Rotational transitions were observed even in dehydrated myoglobin and myoglobin embedded in a rigid (per-deuterated) glucose matrix [1]. To study the effect of packing density on protein-internal motions, we compare native myoglobin to its partially unfolded state at low hydration, where solvent-induced fluctuations are depressed. Rigorous dehydration using P_2O_5 in contrast to freeze-drying induces structural changes, which are not reversible. The difference between native and partially denatured myoglobin is classified based on the optical spectrum of the heme group in the Soret region.

Results

Figure 3.1 shows the absorption spectra of native, partially- and fully-unfolded myoglobin.

The spectrum of the freeze-dried protein agrees with that of native myoglobin, while further drying leads to significant differences indicating partial unfolding. The extended dehydration induces



Figure 3.1:

Soret-absorption spectra (OD) of native myoglobin and after the following treatments native (dashed), full dehydration using P_2O_5 (dotted) and denatured in 3 M guanidinium-hydrochloride solution (dashed-dotted).

structural changes which are not reversible. The spectrum of P_2O_5 -dehydrated myoglobin is intermediate between those of the native and the completely denatured state. It is thus denoted as partially denatured.

Figure 3.2 shows the scattering functions at fixed angle and q 1.9 $\rm \AA^{-1}$ for the two samples 200 K and 265 K.



Figure 3.2:

Scattering functions of native and partially denatured myoglobin between 200 K and 265 K, and vanadium at fixed angle ($2 \Theta = 114^{\circ}$) corrected for cell scattering and self-absorption. Measurements performed on TOFTOF neutron spectrometer at FRM2.

Almost no quasi-elastic broadening is observed at 200 K. The broadening of the spectrum in the wings of central line results mostly from the vibrations. At 265 K, both spectra of the native and partially denatured form exhibit substantial quasi-elastic scattering. Thus molecular motions occur in this protein even at low degrees of hydration. At h = 0.2 g/g only isolated patches of water molecules exist on the protein surface. Full hydration would require h = 0.35-0.4 g/g. The spectrum of the denatured form is broader in the central energy range, while no differences are observed at high frequencies (above 3 meV) for the vibrations.

Fast molecular motions in a protein at low degrees of hydration were analysed with neutron time-of-flight spectroscopy. The respective quasi-elastic spectrum deviates significantly from a Lorentzian line-shape, which implies a distribution of relaxation rates, either due to a variety of molecular processes or motions of a particular molecular group due to a heterogeneous environment. The spectra of native and partially unfolded myoglobin differ. Partial unfolding can be induced by rigorous drying using P_2O_5 and subsequent re-hydration to h = 0.2 g/g. The unfolded form exhibits the same helix content, but exhibits a lower packing density of side chains. Torsional jumps of methyl groups are assumed to be the major dynamical process. In the native state only 30 % of the methyl groups perform rotational transitions on a time scale of 20 ps, while in the unfolded form 40 % are observed. This result indicates that methyl torsional jump rates depend on the local packing density in the protein structure. A distribution of rates for the methyl groups in lysozyme was observed with NMR [7]. Torsional transitions of internal side-chains contribute to protein function, enabling ligand migration between cavities [4]. The respective inter-cavity transition rates also show distributed kinetics [3].

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Quasi-elastic neutron scattering studies on proteins in different media: the case of β -casein

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To a large majority, in the past, the neutron scattering experiments aimed at studying internal motions of proteins have been performed with the protein in the form of dry or hydrated powders, rather than in solution (which is closer to physiological conditions) [1]. The main advantages of studying proteins in powder form are that on one hand it is not necessary to deal with a significant solvent contribution to the scattering signal and on the other hand the motions of the protein as a whole are inhibited, which avoids the need to deconvolute the scattered signal from those motions,

hence allowing for a direct analysis of the protein internal motions. Proteins were then studied as dry and hydrated powders under the general assumption that once the amount of water was enough to complete the first hydration shell, all the protein internal motions would be active and hence they could be considered to mimic also the internal motions of proteins in solution.

More recently, the quality of new neutron scattering instruments has motivated new attempts to obtain information on the internal motions of proteins in solution and to check the above mentioned assumption [2,3]. For instance in powders, due to molecular proximity and lack of solvent, there are multiple protein-protein interactions which do not exist in solution and which may constrain the protein flexibility.

In the investigations here reported we used the new time-of-flight spectrometer TOFTOF [4] for a comparative study on the rotational motions of the side-chains of the β -casein protein in powder forms and in solution. Such motions occur in time scales of pico-seconds, while the motions of the proteins as a whole have associated times of the order of nano-seconds (though depending, of course, on the spatial range probed and on the molecule size).

Results and discussion

 β -casein was studied, at room temperature (290K) in the form of dry powder (<0.05g D₂O/g protein), hydrated powder (with approximately one hydration shell completed: ~ 0.4 g D₂O/g protein) and D₂O solution (with a protein concentration of 100mg protein/ml solution). The use of D₂O, instead of H₂O, as solvent made it possible to isolate the motions of the protein's non-exchangable hydrogens, taking advantage of the fact that the scattering power of the H atom is much higher than that of the other atoms.

It should also be noted that while the powder spectra result exclusively from the internal dynamics of the protein, the solution spectra, even after proper subtration of the solvent contribution, results from the convolution of the protein internal dynamics with the motions of the protein as a whole. Thus, the quasi-elastic region (-1mev to 1meV) of the powder data has been fitted by

$$S(Q, E) = P(Q) [A_0 . \delta(E) + (1 - A_0) \cdot L_{int}(Q, E) + B(Q)] \otimes S_{res}(Q, E)$$

while the quasi-elastic region of the solution data has been fitred by

$$S(Q, E) = P(Q) \cdot \{L_{dif}(Q, E) \otimes [A_0 \cdot \delta(E) + (1 - A_0) \cdot L_{int}(Q, E) + B(Q)]\} \otimes S_{res}(Q, E)$$

where $S_{res}(Q, E)$ is the resolution function (vanadium measurement), $L_{int}(Q, E)$ and $L_{dif}(Q, E)$ are lorentzians with HWHM w_{int} and w_{dif} , representing the internal and the diffusive motions (both translational and rotational), A_0 is the so called elastic incoherent structure factor and B(Q) is a background due to vibrational motions.

The parameter w_{dif} obtained for the solution data (not plotted) exhibits a linear dependence with Q^2 , leading to an apparent diffussion coefficient consistent with previous PCS results [5]. Also the other parameters exhibit the expected dependences in Q.

Finally, the analysis of the internal dynamics parameters seems, in fact, to point towards a higher flexibility of the protein in solution than in the hydrated state. In addition to being globally larger, the HWHM of the lorentzian also seems to exhibit a dependence with Q that is not observed in the powder forms (figure 3.3). This was also found, by other authors, to be the case for lysozyme and myoglobin in solution [3].



Figure 3.3: HWHM w_{int} of the internal motion Lorentzian obtained for β -casein in dry and hydrated powders and in solution

A more thorough analysis of these results is underway. In addition, similar neutron scattering experiments have already been performed at TOFTOF on other proteins and on the temperature association phenomena of β -casein [5,6]. The results of the former studies allow us to confirm that the main trends of the results obtained are not specific to β -casein. The latter study allowed us to isolate, in solution, the monomer and the micelle states. The analysis of those data should give us better access to the effected of an increase in protein confinement on the internal dynamics of β -casein.

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Microscopic Protein Diffusion at High Concentration

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Diffusion is of enormous importance for any living cell. Nutrition and waste disposal are two striking examples: obviously, it is impossible for the cell to influence the transport of molecules (both, in- and outbound) actively outside the cell membrane – only diffusion safes the cell from starving and suffocation.

However, diffusion is not limited to these cases where a concentration gradient is present. As an example we choose red blood cells. They are responsible for the oxygen transport in vertebrates which need a specialized oxygen-carrier due to their significantly higher metabolic rate compared to non-vertebrates. The carrier for O_2 is the protein *hemoglobin* (see figure 3.4) which is the main organic component (93%) of the red blood cell.



Figure 3.4:

Crystal structure of hemoglobin. Hemoglobin is the essential component of red blood cells and responsible for oxygen transport. It has a radius of gyration $R_g\approx 24$ Å and is almost spherical. The picture is made with PyMol.

Passing the lung, the red blood cell has to absorb O_2 in less than one second. Within this time, as many hemoglobin-molecules as possible have to get to the surface of the blood cell so that they can get in contact with the oxygen-rich environment. This calls for a high hemoglobin concentration: if there are more hemoglobin proteins in the cell, more can carry O_2 . However, the hemoglobins hinder each other's way to the cell's surface. Thus, filling the cell with more and more hemoglobin will not increase the amount of transported oxygen, but indeed even decrease it. There are estimates that the native hemoglobin concentration is near the optimum. However, some diseases change the concentration, for example iron deficiency anemia will decrease the hemoglobin concentration in the red blood cell.

We are interested in the mechanism of diffusion, the effects of concentration changes, and the interaction of hemoglobin molecules. It is only due to the interaction that the diffusion coefficient decreases with increasing concentration. The obtained results are valid generally for concentrated protein solutions as we could show with experiments on myoglobin and lysozyme. The problem of crowding is common to all cells as there is a huge protein concentration in every cell. The only distinct feature of red blood cells is that almost only hemoglobin is present, hereby being a model system.

Diffusive motions are observable with light and neutron scattering. However, light scattering has two disadvantages: first, it is impossible to do light scattering through a cell wall, and second it is probing fluctuations that are on a scale large compared to the proteins. In contrast, it is possible with neutron scattering to get information in situ on the protein motion on an Å scale. As the diffusive motions are very slow, only neutron spin echo and backscattering spectrometers are suitable for measurements. Following earlier low-Q experiments with spin echo [1], now backscattering was employed to access the high-Q region [2]. As the new SPHERES at the FRM II was not yet operational and the ILL was under reconstruction, we used the High Flux Backscattering Spectrometer at the NIST Center for Neutron Research (Maryland, U.S.A.).

This instrument provides an energy resolution as good as $0.8 \,\mu\text{eV}$ covering an energy of $2.08 \,\text{meV} \pm 18 \,\mu\text{eV}$ and a Q-range of $0.25 - 1.75 \,\text{\AA}^{-1}$. The red blood cells and other proteins (myoglobin and lysozyme) were prepared in D₂O to minimize solvent scattering. These solutions and both pure D₂O and Vanadium were measured at room temperature. A typical spectrum can be seen in figure 3.5. The Vanadium measurement gives a line not broadened by diffusion and therefore the resolution.



Figure 3.5:

Backscattering spectra (dots with error bars) of hemoglobin in Red Blood Cells ($\varphi = 0.25$) Q = 0.75 Å⁻¹ respectively 1.51 Å⁻¹. Also shown is the fit to the data (full line, confer to the text) and its two Lorentzian components (dotted and dashed lines) as well as the resolution function (dash-dotted line).

Data analysis was done by subtracting the D_2O measurement which appears as more or less constant background in this narrow energy range and fitting a sum of Lorentzians convoluted with the resolution (vanadium measurement). A Lorentzian is the natural form of diffusion processes. The broad (i. e. fast moving) component is independent from the scattering vector Q, indicating an internal motion. The narrow line shows a very interesting Q-dependence, shown in figure 3.6. For a long-range diffusive motion, the line width should increase linearly with Q². However, as one can see in the figure, this is not the case.



Figure 3.6:

Linewidth (half width at half maximum, HWHM) versus Q^2 of the narrow component of the 2-component fit. The broad (internal) component Γ_{int} is not shown at 10 μ eV. The narrow (translational) component Γ_{diff} is represented by the data points, fits of the Singwi-Sjölander model are also shown.

Clearly, we do not observe normal Fickean diffusion. It is possible to describe this behaviour formally with a jump model that was originally developed by Singwi and Sjölander for water. It assumes that the investigated particle switches back and forth between normal diffusion and local

thermal oscillations. One could think of the protein being stuck in a cage formed of neighbouring proteins or see it as a manifestation of the more general transition from short- to long-time diffusion. However, the observed length scale of only one Å (determined by the wave vector) is much smaller than the inter-protein distance (1 - 2 orders of magnitude).

Thus, we are currently thinking of other explanations for this behaviour. A transition from the ballistic regime to a diffusive motion could explain the evolution of the line width with Q^2 , however we have to analyse whether we are able to see this transition in the time-scale covered by this experiment (nanoseconds). Further analysis – also in the time domain – has to be done. In order to get data with a statistical quality sufficient for Fourier Transformation, subsequent measurements on HFBS are planned.

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4 Bulk polymer structures, solutions and gels

Influence of the block copolymer architecture on the micelle formation in poly(2oxyzoline) copolymers

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Polymeric micelles in aqueous solutions are of interest for a number of applications, such as micellar catalysis, because they are more versatile than low-molecular amphiphiles. In copolymers from poly(2-oxazoline)s, the hydrophobicity can be controlled by the addition of various side groups to the same polymer backbone (Figure 4.1a), and various architectures are accessible. We have studied aqueous solutions of homopolymers of hydrophilic 2-methyl-2-oxazoline (MOx) as well as diblock [1] and triblock copolymers of MOx and hydrophobic 2-*n*-nonyl-2-oxazoline (NOx) [2]. Using fluorescence correlation spectroscopy (FCS), the critical micelle concentration and the hydrodynamic radii of the unimers, i.e. single, dissolved polymers, and of the micelles are accessible. Tracer diffusion measurements with the identical, fluorescence-labeled polymers allowed us to cover a large concentration range $(10^{-8} - 10^{-3} \text{ M})[3]$.



Figure 4.1:

(a) Structure of an oxazoline monomer. Chosing methyl or nonyl for the side group R leads to hydrophilic or hydrophobic monomers PMOx and PNOx, respectively. (b) Hydrodynamic radii of the fluorescence-labeled unimers as a function of overall molar mass. Crosses: the fluorescence dye TRITC, open circles: PMOx homopolymers, filled triangles: diblock copolymers P[NOx₁₀-*b*-MOx₃₂] and P(NOx₇-*b*-MOx₄₀) (the subscripts denote the degree of polymerisation), filled squares: triblock copolymers P(MOx₂₀-*b*-NOx₇-*b*-MOx₁₄) and P(MOx₃₀-*b*-NOx₇-*b*-MOx₂₆).

At low polymer concentrations, only unimers are present. Their hydrodynamic radius depends on the architecture (Figure 4.1b): The presence of NOx monomers in the copolymers results in a less swollen conformation in aqueous solution than in the PMOx homopolymers.

Above the critical micelle concentration, which is detected at concentrations of $10^{-6} - 10^{-5}$ M, an additional signal due to micelles is observed in the FCS correlation curves of diblock and triblock copolymers. The hydrodynamic radii of the micelles formed by the triblock copolymers are

a)

Polymer	Hydrodynamic radii of the micelles [nm]
P[(MOx) ₄₀ - <i>b</i> -(NOx) ₇]	13 ± 2
$P[(NOx)_{10}-b-(MOx)_{32}]$	11.3 ± 0.9
P[(MOx) ₂₀ - <i>b</i> -(NOx) ₇ - <i>b</i> -(MOx) ₁₄]	5.7 ± 0.7
$P[(MOx)_{30}-b-(NOx)_7-b-(MOx)_{26}]$	5.6 ± 0.9



Figure 4.2:

(a) Hydrodynamic radii of the micelles formed by diblock and triblock copolymers. (b) Sketch of the micelles formed by diblock and triblock copolymers. The thick and the thin lines represent the hydrophilic backbone and the *n*-nonyl side groups, respectively. For clarity, a single polymer is shown per micelle, even though they consist of a number of polymers.

roughly half the ones of the micelles formed by the diblock copolymers, independent of the degree of polymerization of the hydrophilic block (Figure 4.2a). The degree of polymerization of the hydrophobic blocks in the triblock copolymers is very similar to the one of the diblock copolymers. The origin of the size reduction is thus two-fold: (i) The additional hindrance imposed by the architecture of the triblock copolymer: In micelles formed by triblock copolymers, both ends of the hydrophobic block are located near the surface of the micellar core, whereas the hydrophobic block stretches from the surface of the micellar core to the center (Figure 4.2b). (ii) The grafting density of hydrophilic blocks at the core surface: In the triblock copolymers, each hydrophobic block is bound to two hydrophilic blocks in triblock copolymers, whereas it is only bound to one hydrophilic block in diblock copolymers. These two effects seem to dominate over the difference of the degrees of polymerization of the hydrophilic blocks of the two triblock copolymers under study.

FCS thus provides detailed information on the hydrodynamic radii of polymeric unimers and micelles in aqueous solution. In this way, information on the packing of the chains into the micelles has been gained.

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Choice of the tracer in fluorescence correlation spectroscopy on polymeric micelles

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Fluorescence correlation spectroscopy (FCS) is a fast and precise method to determine the hydrodynamic radii of micelles formed by amphiphilic block copolymers. However, in many cases, the choice of tracer has been observed to have an influence on the results, especially in the vicinity of the critical micelle concentration, CMC [1]. Instead of a micellar size which is independent of polymer concentration, as predicted by the close-association model, a gradual increase of the hydrodynamic radius of the micelles with polymer concentration has been observed. This increase ranges over several decades of concentration. It is not clear whether this phenomenon is related to the aggregation process of the polymer or whether it is due to the interaction of the tracer with the micelles.

We have studied the micelle formation of a non-charged, amphiphilic poly[(methyl-2oxazoline)₁₀-*b*-(2-*n*-nonyl-2-oxazoline)₃₂], P[NOx₁₀-*b*-MOx₃₂], diblock copolymer (the subcripts denote the degrees of polymerization) in aqueous solution. The hydrodynamic radius of the micelles of this copolymer has been determined using dynamic light scattering (DLS), i.e. without any tracer involved [2]. The result $(11.5 \pm 0.9 \text{ nm})$ does not depend on polymer concentration. We have compared this value with the ones from FCS experiments carried out using two different fluorescent tracers: (i) the identical diblock copolymers being fluorescence-labeled at the hydrophilic block terminus [2] and (ii) a low molar mass fluorescence dye, rhodamine 6G (Rh6G), which is only poorly water-soluble [3].

With the polymeric tracer (i), the same micellar hydrodynamic radius $(11.3 \pm 0.9 \text{ nm})$ was found as in DLS. This value stays constant down to the CMC detected at 2.2×10^{-5} M. Below this concentration, only the diffusion of unimers, i.e. single dissolved polymers, is observed.

With the low molar mass dye Rh6G (ii), only the diffusion of the dye through the aqueous phase is present as a fast decay in the FCS correlation function below a copolymer concentration of 2.0×10^{-5} M (fig. 4.3a). Above this concentration, which corresponds to the CMC of the copolymers, a second, slow decay in the FCS correlation curves is present. We attribute this decay to the diffusion of polymeric micelles carrying a dye molecule. The corresponding hydrodynamic radius of the micelles, however, is not constant as observed in DLS or in FCS with the polymeric tracer (i), but increases from 4.9 nm at the CMC to 9.3 nm two decades above the CMC (fig. 4.3b). We attribute this gradual increase to the finite water-solubility of Rh6G, resulting in a fast exchange of Rh6G between the aqueous phase and the micelle. An average diffusion coefficient is thus measured in the FCS experiment, leading to an underestimated micellar hydrodynamic radius.

We conclude that low molar mass tracers can be used in order to reliably determine the CMC of non-charged, polymeric amphiphiles. However, the hydrodynamic radius of the micelles may be underestimated when using tracers having a finite water-solubility. Using fluorescence-labeled polymers identical to the ones forming micelles results in the most reliable values for the micellar hydrodynamic radius.

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Figure 4.3:

(a) FCS correlation functions of solutions of Rh6G and P[NOx₁₀-*b*-MOx₃₂] at different copolymer concentrations. The curves were normalized by the inverse average number of fluorescent molecules in the detection volume, 1/N. (b) (Apparent) hydrodynamic radii as determined by FCS on P[NOx₁₀-*b*-MOx₃₂] with the identical fluorescence-labeled copolymers as a tracer. Open circles: Solutions containing only labeled copolymers. Filled circles: Solutions containing both, fluorescence-labeled and non-labeled copolymers. Stars: Solutions containing non-labeled copolymers and Rh6G as a tracer.

Multicompartment hydrogels from lipophilic-hydrophilic-fluorophilic triblock copolymers

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Amphiphilic copolymers find numerous applications, e.g. for drug delivery, as gel formers or as nanoreactors. Poly(2-oxazoline) block copolymers constitute a very versatile system [1,2]: The amphiphilicity can be controlled by the choice of side groups (Fig. 4.4), and in aqueous solution, unimers, micelles or micellar hydrogels are formed, depending on the block copolymer architecture [3]. Micellar gels with chemically different types of micelles may be achieved by using triblock copolymers with blocks containing lipophilic, hydrophilic and fluorophilic side groups. Here, the presence of a fluorophilic moiety increases strongly the degree of segregation, and multicompartment gels may be formed even at low degrees of polymerization.

We have used small-angle neutron scattering with contrast matching to study the structures of micellar gels of poly(2-oxazoline)s with the focus on the question whether the two end blocks indeed form separate micelles. In order to uniquely interpret the (complex) scattering curves of the micellar gels formed by concentrated solutions of the poly[(2-n-nonyl-2-oxazoline)₁₂-b-(methyl-2-

 $oxazoline)_{64}$ -b-(perfluorohexyl-2-oxazoline)₉] (PNOx₁₂-b-MOx₆₄-b-FOx₉) triblock copolymers, the sizes and shapes of the micelles formed by P(NOx₁₀-b-MOx₃₂) and P(MOx₄₀-b-FOx₆) diblock copolymers were investigated as well, namely in aqueous solutions of lower concentration. (The subscripts denote the degrees of polymerization.) Furthermore, we verified that aqueous solutions containing both diblock copolymers do not form mixed micelles.



Figure 4.4:

A poly(2-oxazoline) based triblock copolymer with a lipophilic, a hydrophilic and a fluorophilic block.

Upon dissolution in water at room temperature, $P(NOx_{10}-b-MOx_{32})$ diblock copolymers form large aggregates in addition to the expected spherical core-shell micelles. The aggregates - which are presumably due to the strong association via the nonyl side chains of the lipophilic blocks in the bulk state - dissolve upon annealing the solutions at elevated temperatures, and only spherical (equilibrium) micelles remain.

In contrast, $P(MOx_{40}-b-FOx_6)$ diblock copolymers do not form spherical, but slightly elongated micelles (Fig. 4.5). This is possibly due to the steric demands of the fluorophilic side chains forcing the polymer backbones to stretch.



Figure 4.5:

SANS intensity profiles together with the pair distribution functions of (a,b) $P(NOx_{10}-b-MOx_{32})$ and (c,d) $P(MOx_{40}-b-FOx_6)$ diblock copolymers. The SANS curves were obtained from D_2O/H_2O solutions with the MOx-blocks being contrast-matched, i.e. only the micellar core is visible. The pair distribution functions were determined following the method of Glatter [4].

The P(NOx₁₂-*b*-MOx₆₄-*b*-FOx₉) triblock copolymers form gels above polymer concentrations of 10 wt-%. Their scattering can be described by a coexistence of spherical lipophilic and elongated fluorophilic micellar cores, which are linked by the hydrophilic blocks (Fig. 4.6). Thus, the system forms a multicompartment gel.

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Figure 4.6:

SANS intensity profile of a hydrogel of $P(NOx_{12}-b-MOx_{64}-b-FOx_9)$ having a polymer concentration of 20 wt-%. (\circ) experimental data, dotted line: fitting curve of $P(NOx_{10}-b-MOx_{32})$ (spherical micelles), dashed line: fitting curve of $P(MOx_{40}-b-FOx_6)$ (elongated micelles). Solid line: weighted sum of the two fitting curves. Inset: Schematic representation of the structure of the multicompartment hydrogel.

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The structure of macroscopically thick samples investigated by means of grazing incidence X-Ray scattering

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For several decades active fillers like silica or carbon black have been used to improve the properties of elastomers. Meanwhile, it is generally accepted that mainly the filler structure defines the properties of a filler-rubber system. Consequently, analyzing the filler structure is important for understanding the mechanical properties of the composite material. However, on the one hand investigations show [1] that silica can be interpreted as a fractal object with a hierarchical structure, with structure sizes ranging from nanometers up to several micrometers. On the other hand, established methods, e.g. small angle X-ray scattering (SAXS) and ultra small angle X-ray scattering (USAXS) techniques, cover only structure sizes smaller than one micrometer - in other words dont offer the possibility to investigate the entire length scale range necessary, so that the hierarchical structure can not be studied in its entirety. Therefore it is of interest, to apply additional methods to expand the accesible range. Originally developed to investigate surface structures of thin films, grazing incidence small angle X-ray scattering (GISAXS) is a powerful technique, which covers the range of a few nanometers up to several micrometers.

Due to the large length scale accesible, we applied GISAXS to investigate the structure near the surface of macroscopically thick samples. For the very first beginning one has to assure that results obtained from transmission and GISAXS measurements reveal the same information. For this purpose, we used silica loaded rubber, because the primary particles of silica consist of chemically bonded SiO2 molecules, and thus their size and their shape does not depend on the position in the sample. As a consequence such samples are ideally suited to probe the applicability of GISAXS to macroscopically thick samples.

The measurements were performed using beamline BW4 of the DORIS III storage ring at the synchrotron radiation facility HASYLAB/DESY at Hamburg, Germany. The selected wavelength

was 0.138 nm and the sample-detector distance was 2063 mm. Within the utilised reflection geometry, the sample was placed horizontally on a two circle-goniometer attached to a z-translation table with a fixed angle to the incident beam. The complete pathway of the beam was evacuated. A detector with an array of 2048×2048 pixel was used to record the specular intensity as well as the Yoneda peak [3]. From this two-dimensional intensity distribution a vertical cut in the scattering plane (so-called detector cut) and a horizontal cut (so-called out-of-plane cut) were sliced. The position of this q_y -cut, with q_y being the wave vector component parallel to the surface and perpendicular to the scattering plane, was selected according to the critical angle of the filler material SiO₂, so that the structure of filler material would be probed [2].

Figure 4.7 shows the scattered intensity as a function of q_y . The resolution limit is indicated by the dashed line. The intensity decreases with increasing q_y . Several changes in the slope of the intensity values, and thus different crossover points are visible. The radius of gyration of a particle r is related to q_c by means of $q_c = 2\pi/r$. SAXS experiments revealed $q_c = 2.4 \times 10^{-2} \text{ Å}^{-1}$ as indicated by the blue line in figure 4.7. This q_c is very close to the crossover found in the GISAXS experiment.



Figure 4.7:

Horizontal out-of-plane cut of the intensity distribution corresponding to the critical angle of SiO2 oriented perpendicular to the scattering plane as a function of the lateral wave vector q_y . The resolution limit is shown by the dashed line. q_c of crossover point as found by transmission experiments is indicated by the vertical line on the right hand side (blue).

Thus it can be concluded that consistent information can be extracted. We investigated a macroscopically thick sample by means of GISAXS experiments. To avoid differences due to bulk and surface near effects, we analyzed the size of the primary particles only. Due to the stable chemical bonds, the shape and the size of the primary particles not depend on this position in the sample. We found that the data of transmission and reflection experiments is of good consistence. For a first result we obtained very similar values from GISAXS and transmission experiments and thus we conclude GISAXS is suitable to study surface near structures of macroscopically thick samples.

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Development of a tack apparatus for the investigation of pressure sensitive adhesives

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Pressure sensitive adhesives (PSAs) constitute a class of adhesives where only a slight amount of pressure is necessary to establish a bonding between two surfaces. One of the most powerful methods to investigate the adhesive properties of PSAs is the probe tack method. In this mechanical test method a probe (punch) approaches the adhesive material normal to its surface. After applying a distinct contact pressure and holding time the probe is retracted with a given velocity. The full force-distance curve (or based on this, the stress-strain curve) for the debonding process is recorded. In industrial applications the probe tack method often is used with a hemispherical shaped probe. In this case the contact is established regardless of a possible tilt from the orientation normal to the surface. However by using an hemispherical probe the area of contact is ill-defined. Therefore for meaningful and reproducible data the use of a flat ended cylindrical probe is mandatory. In case of transparent samples and the use of a glass slide as the sample support the contact area between probe and adhesive surface can be checked by microscopic observation from underneath the sample. Imaging not only is helpful to align the instrument perfectly, it also gives the opportunity to correlate the course of the stress-strain curve with the micrographs obtained by the optical system of the instrument. Such a tack instrument including an optical system has been successfully developed at E13 earlier [1]. The debonding mechanism of PSAs as for example the cavitation process for acrylate based copolymers has been clarified with this instrument [2].

Now a new tack instrument (figure 4.8) has been developed which adopts the basic tripod concept. Note that only the most important mechanical parts and the actuator and the force sensor are shown in figure 4.8a.



Figure 4.8:

a) Mechanical parts of new developed tack apparatus. b) Software for the online control of the tack experiment.

The optical instrumentation and further electronic equipment is not shown. Samples are attached to the sample holder which is mounted on linear stages allowing for the positioning of the sample in xy-direction. Advances of the new instrument are due to the use of a DC-actuator instead of a conventional stepping motor which leads to smoother motion. The miniature force sensor chosen combines a high sensitivity with an overload capability of 5 times in tension and 10 times in compression allowing for safe handling of the instrument. One objective for the development of the new tack apparatus was the implementation of a user-friendly software. Figure 4.8b shows an example panel for the tack software. The tack software allows for the input of all necessary parameters (e.g. velocity of approaching probe, force for the contact, holding time, velocity for the debonding part of the experiment) controlling the tack experiment. On the panel the position of the probe versus time and the force versus time can be followed during the experiment. For a tack experiment the computer desktop will show the tack software panel neighbored by a second window containing the current image captured by the CCD camera of the optical system.

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5 Liquid dynamics

Dynamics of undercooled liquid Ni

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The study of structure and dynamics in liquid metals is often prevented by a chemical reaction of the high temperature melt with its sample holder. This can be overcome by the use of an electromagnetic levitation apparatus (EML) that allows for a containerless processing of electrically conducting samples. Using an EML design developed at the DLR in Cologne [1], we modified the coil windings and the overall set-up to fulfill the needs for application on the neutron time-of-flight spectrometer ToF-ToF. The absence of a sample holder made it possible to extend the accessible temperature range from more than 200 K above liquidus to more than 230 K of undercooling of the liquid metal.



Figure 5.1:

Electromagnetically levitated liquid Ni droplet at a temperature of 1810 K. The water cooled copper coil is shielded with a neutron absorbing rubber. The radial collimator of Tof-Tof is visible on the right.

The roughly spherical, electrically conductive samples, 6-8 mm in diameter, are levitated within an inhomogeneous electromagnetic radio frequency field. As a result of the RF-field, eddy currents are induced in the specimen. On the one hand, this leads to an inductive heating of the sample which allows melting of the specimen. On the other hand, the interaction of the eddy currents with the inhomogeneous magnetic field of the levitation coil leads to a stabilizing force on the sample towards the direction of low magnetic field strength, compensating gravity. The convective stirring induced by the inductive currents in combination with a large heat conductivity of the sample results in a homogenous sample temperature that is contact-free measured with a two-color pyrometer. The temperature is controlled via the flow of ultrapure cooling gas $(He/4\%H_2)$, which is injected by a nozzle that is installed below the sample. For a picture of the set-up in operation, see Fig. 5.1.

The coil design was modified with respect to [1] to create a larger coil opening of about 8 mm between the upper and the lower part of the coil. This enhanced the visibility of the sample for the incoming beam and for the detectors significantly. In combination with the high flux and the excellent signal-to-noise ratio of the neutron time-of-flight spectrometer ToF-ToF, quasielastic measurements on levitated metallic droplets are now feasible. In a first measurement campaign we
investigated liquid Ni. Figure 5.2 displays the quasielastic signal that is dominated by incoherent scattering below about 2.2 Å⁻¹. The lines are fits with a scaled Lorentz function convoluted with the instrumental energy resolution function. The *q* dependence of the quasielastic signal contains information on the mechanism of atomic transport. Via the width of the quasielastic line the self diffusion coefficient *D* can be derived on an absolute scale with high precision. Over a large temperature range – from more than 200 K above to more than 200 K below the melting point at 1727 K – the temperature dependence of the diffusion coefficients can be described with an Arrhenius law. The change from a liquid in thermodynamical equilibrium to a metastable liquid at large undercoolings is not reflected in its atomic transport.



Figure 5.2:

Quasielastic spectra of liquid Ni (left). Please note the semilogarithmic representation of the scattering law $S(q, \omega)$. Measuring times ranged from 1 h to 3 h. Ni self diffusion coefficients obtained from the width of the quasielastic line (right). The open circles are results from QENS measurements on liquid Ni in an alumina crucible.

With this new sample environment we are now able to study the interplay of structure, dynamics and properties in Ni-based binary alloys, and also to investigate Fe and Ti based melts that form intermetallic phases.

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Collective Excitations in Liquid Ti

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We have used high-resolution IXS spectrometry to measure the coherent dynamical strucure factor $S(Q, \omega)$ in molten titanium at T=2020K ($T_m = 1940$ K) [1]. The melting of the material was

achieved using an aerodynamic levitation setup. Levitation techniques (see also the contribution of Stüber et al. on page 66) have the unique capability of allowing the study of materials with a high melting temperature. The advantages are 1) preventing contamination or oxidation and 2) reducing the number of nucleation sites, which allow the study of liquids in both the equilibrium and supercooled state. The corrected data were analyzed with a fit function for $S(Q, \omega)$ used previously in connection with a generalized hydrodynamic model. This function has the sound dispersion and the half width at half maximum of the sound excitation frequencies as parameters.

The IXS data and the fits are shown in Fig. 5.3 for different Q values. It can be seen that the data show well-defined sound excitations, which still exist at rather high Q-values beyond the first maximum of the structure factor S(Q).



Figure 5.3:

IXS spectra of liquid titanium at T=2023K for different Q values as indicated. The open circles are the data, and the solid lines are the fits, including the empty-cell Ar background. The strong quasi-elastic intensity at low Q is due to the argon atmosphere in the levitation apparatus.

Until now there had been no satisfactory theory for the coherent density fluctuations, including the sound dispersion and attenuation. On the other hand, such a theory exists for the regime near the liquid-glass transition. This is the mode-coupling theory (MCT) [2], which successfully describes the nontrivial relaxation phenomena near the transition. In principle there is no reason, why this theory should not be used away from the glass transition. In fact, light scattering data in liquid Benzene, which does not form a glass, have been successfully described by a schematic MCT model [3]. As the original mode-coupling theory [2] needs as only input data sets the static structure factor S(Q), the temperature and the density, we have solved the mode-coupling equation with two different data sets taken from the literature [4,5]. The results were fitted in the same way as the experimental data.

The dispersion and half width at half maximum obtained in this way is compared with the experimental data in Fig. 5.4 (left). Keeping in mind that the theory has no adjustable parameters (the input is taken from experiment) the agreement between theory and experiment is astonish-



Figure 5.4:

Left: Dispersion and half width at half maximum of the sound excitations in liquid Ti. The solid lines are the MCT calculations using S(Q) of Waseda [4], the dashed lines are the MCT calculations using S(Q) of Lee et al. [5]

Right: Q dependent longitudinal viscosity as evaluated from the experimental data and the two mode-coupling-theory calculations. The value of the shear viscosity is indicated.

ingly good. We conclude firstly that the sound dispersion of longitudinal excitations in this liquid high-melting transition metal is almost as it would be in the glassy amorphous state. Also the low damping of the waves is not very different as it would be in the glass. The difference is the viscosity, which is finite and quite low. From the $S(q, \omega a \text{ longitudinal } Q \text{ dependent viscosity } \eta(Q)$ can be calculated according to the formula $\eta_L(Q) = \pi \rho v_0^2 S(Q, 0) / S(Q)^2$. We have evaluated $\eta(Q)$ from the experimental $S(Q, \omega = 0)$, as well as from the theoretical data. The result is shown in Fig. 5.4 (right). Again the agreement between theory and experiment is rather good. So we conclude that the dynamics of a molten metal is described rather well by mode-coupling theory.

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Preparation and characterization of hydrous silicates

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The structure and dynamics of water-bearing silicate melts is a topic of enormous geological as well as of physical interests. In nature, several weight % water can be thermodynamically stably

dissolved in a silicate melt under high temperature and pressure. Decompressing of these melt during ascent to the Earth's surface constitutes active volcanism, which is governed by the diffusion flux of H_2O from the oversaturated melt into growing bubbles[1,2].

By addition of several weight percent of water in the silicate systems, the viscosity of the melts can be decreased by 5-10 order of magnitudes, while the measurements with neutron diffraction on the glassy state structure show no big change[3]. The relation between viscosity and water species concentration is not yet fully understood and the mass transport mechanism in the melt is not known.

The intrinsic q resolution of quasielastic neutron scattering allows to study the diffusion mechanism in great detail. Pressure up to several kbar is needed to keep the water from leaving the melt. Thus the measurements using in-situ QENS on water bearing silicate melts at high temperature and pressure should be a great step forward towards understanding the transport mechanism in these system.

This year we have successfully prepared the water bearing samples based on sodium trisilicate (NS3) and SiO2 systems at E13 using the new pressure apparatus.



Figure 5.5:

Basic components of the the sample synthesis apparatus. (a) Synthesis furnace (without the outer shell). (b) The furnace mounted on the the autoclave. (c) closed autoclave.

Dry silicate samples were prepared by direct fusion of fine powders at elevated temperature and then drilled into cylinders or milled into fine powder. The glass cylinder or powder were loaded together with proper amount of H_2O or D_2O in Pt capsules and sealed with a microplasma-welder. The capsules were checked for weight loss after heating in an oven at about 114°C for at least 3 hours to eliminate any possible leakage.

Synthesis of the hydrous glass was performed in a high pressure autoclave using a self-made furnace to heat up the samples. The furnace must provide a constant temperature over all the sample which is most important to get a homogenous sample. This is realized by having three heating zones which are powered independently by DC power supplies and monitoring the temperatures with thermocouples at the corresponding positions for each zone. Fig. 5.5 shows the basic components of the apparatus. A 3-folder Eurotherm temperature regulator is used to control the complete furnace. Magnesium oxide is filled between the heating elements and the outer shell of the furnace for thermal isolations. The sample capsules were positioned between the second and the third heating zone. The temperature of sample was monitored with additional thermocouple at the sample position. After closing the autoclave was filled and compressed using Ar gas as pressure medium. The Autoclave was water cooled from outside during the experiments.

Capsules with sample were hold at 1,250 $^{\circ}$ C or 1,400 $^{\circ}$ C and 3 kbar for 4-7 hours depending on the silicate system being prepared to allow complete homogenization of the water. After this the samples were quenched with a quenching rate of 100 K/min programmed by the Eurotherm controller. Special care was taken in order to keep the pressure remaining at 3 kbar during the cooling.



Figure 5.6:

Sample characterization. (a) Capsule after preparation. (b) Sample out of the capsule (c) DSC scans of the sample

The capsules taken out from the autoclave were first checked by weight to ensure no water loss during the preparation. Then the capsules were open and the samples were taken out. The first characterization on the samples was the measurement of the glass transition temperature by DSC for the pieces taken from different positions on one sample. Fig. 5.6 (c) is the DSC result of one NS3 sample with 5 wt% H₂O. It shows the top and the bottom part of the sample have the nearly the same glass transition temperature which is about 207 °C. This means there should be no large gradient of the water in the sample. This glass transition temperature is lower compared with the one of dry NS3 which is located at about 470 °C[4], indicating the water is built in the structure.

Further improvement of the furnace will be embedding a mechanism which is able to drive the samples into a cold zone (below the first heating zone). This allows the samples to be quenched down much fast. The FTIR spectroscopy will be also used to further characterize the water content in the sample and the QENS experiment is in planning.

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Measurements of longitudinal and transverse sound velocity in sodium silicates

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Understanding the hydrodynamics of silicate melts under high pressure and high temperature is of great relevance for processes in Earth's core, mantle and crust like earthquakes and vulcane eruption [1]. In seismic measurements the lateral variation of wave velocity is imaged. For sufficient interpretation of these data, knowledge of material properties like the viscosity η and elastic constants like shear modulus G and elastic modulus E are required. These quantities are related to the longitudinal v_L and transverse v_T sound velocity and the density ρ .

Brillouin light scattering offers an optical method for determining the elastic properties of various materials. Here light interacts with thermal exitations like phonons. These interactions lead to a very small shift in the frequency of the scattered light, which reflects an annihilation (anti-Stokes) or a creation (Stokes) of an exitation. Since longitudinal exitations do not change the polarization of the scattered light, polarized measurement of the Brillouin frequency shift probes the longitudinal sound wave. Exitations of transverse sound waves are accompanied by a rotation of the polarization of the scattered light, which is identified by depolarized measurements.

For detecting the Brillouin lines which are produced by sound waves a Sandercock type six-pass tandem Fabry-Perot interometer was applied. As light source we used the 514 nm line from an argon ion laser from Spectra Physics. From the laser beam a weak reference beam was extracted in order to stabilize the Fabry-Perot while scanning across the elastic line. The remaining beam was polarized and directed by means of mirrors and lenses to the sample. For temperature dependend measurements of the sound velocities a furnace was built, which is able be heat up to 1600 K. During the experiment the temperature was determined by a thermocouple made of a Pt₉₀-Rh₁₀ wire and kept constant within an accurracy of 1K with an Eurotherm conroller. Inside the furnace was a tube of 15 cm length and a diameter of 1.5 cm. The sample, a molten glass droplet hanging in wireloop, was inserted into the tube from the rear side of the furnace. For backscattering experiments light was inserted from the front side of the tube to the sample. Whereas for pseudo-90° (meaning 90° $\pm \Delta \phi$) measurements a second entrance for the laser light on the longitudinal side was drilled.

As example, Brillouin spectra of Na₂O(Si₂)₃ at 1200 K for three different scattering geometries are plottet in Fig.5.7 (left). The strongest signal stems from polarized backscattering (180° VV). Its Brillouin peak at ± 29.5 GHz corresponds to a longitudial acoustic wave propagating with 5054 m/s if we assume a refractive index of n = 1.5. The second spectrum (nominally 90°, VV) represents also scattering at a longitudinal acoustic wave. However, this example shows that the scattering events take place under 80°. In the depolarized third spectrum (nominally 90°, VH) taken under pseudo-90° further Brillouin peaks at ± 12.8 GHz appear. These are related to transverse acoustic waves propagating with 2875 m/s.



Figure 5.7: Left:Brillouin spectra for three different scattering geometries at 1600 K. Right:Longitudinal and transverse sound velocities as a function of temperature

Sound velocities at various temperatures are shown in Fig.5.7 (right). At low temperature the sound velocities are nearly constant with temperature. In contrast the data show clearly a change in temperature dependence above the glass transition temperature near 800 K.

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6 Dynamics of ordered and disordered solids

Interplay of structural instability and lattice dynamics in Ni₂MnAl shape memory alloys

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The interplay of lattice dynamics and structural instability in Ni₂MnAl shape memory alloys has been investigated by inelastic neutron scattering. Acoustic and optical phonon modes have been measured along the high symmetry directions of the cubic B2 phase. The force constants have been fitted to the measured data using the Born-von Karman model. Contrary to the overall behaviour of the phonon branches, the TA₂[$\xi\xi$ 0] phonon branch with the polarisation {110} showed an anomalous softening with decreasing temperature associated with a wiggle in the *q*-range 0.1–0.25 r.l.u. This behaviour indicates low-restoring forces against the sliding of the (110) atomic planes in the [110] direction. Such displacements, associated with atomic shuffles in the (110) planes, constitute basal planes of the close-packed martensite low-temperature phase. The wiggle deepens with decreasing temperature but does not result in any clear minimum down to 10 K. The character of the phonon softening measured in Ni₂MnAl corresponds to the pattern of atomic displacements of the modulations 2M, 10M, 12M and 14M observed in bulk and thin-films of Ni₂MnAl.



Figure 6.1:

Phonon frequencies of the TA₂[$\xi\xi$ 0] branch normalised to the zone boundary phonon frequency ω_{ZB} measured at room temperature in Ni₅₁Mn₁₈Al₃₁ (e/a = 7.29) and in Ni₅₃Mn₂₂Al₂₅ (e/a = 7.59).

The effect of the composition on the lattice instability has been investigated by measuring normal modes of vibration in two different crystals, $Ni_{51}Mn_{18}Al_{31}$ and $Ni_{53}Mn_{22}Al_{25}$, with e/a ratios of 7.29 and 7.59 respectively. The phonon dispersions of the two samples resemble very much each other. In particular, all measured normal modes (apart the TA₂[$\xi\xi$ 0]) scale with the square root of the mass and the lattice parameter. Contrary, phonon frequencies of the TA₂[$\xi\xi$ 0] branch, normalised to the zone boundary phonons, are smaller in Ni₅₃Mn₂₂Al₂₅ (e/a = 7.59). The difference is enhanced up to 20% in the *q*-range where the phonon anomaly is observed

(Fig. 6.1). This behaviour, synonym of increasing lattice instability with increasing e/a, was predicted by *ab-initio* calculations [1]. It provides an explanation on the atomic scale of the DSC measurements and gives a clear evidence of the role played by the number of valence electrons per atom ratio in structural instability.



Figure 6.2:

Temperature dependence of the phonon branches along the [110] direction in Ni₅₁Al₃₁Mn₁₈. Note the anomalous softening of the TA₂[110] in the ξ -range 0.1–0.25 r.l.u.

The stabilisation of a single L2₁ phase in Ni₂MnAl by annealing a Ni₅₁Mn₁₈Al₃₁ single crystal at 673 K during 45 days has been attempted. Despite of the long-time annealing, a single L2₁ phase could not be stabilised because of either a slow diffusion kinetics or the establishment of an equilibrium between the L2₁ and the B2 phases. Phonon measurements of the TA₂[$\xi\xi$ 0] branch in the annealed sample revealed a substantial effect. The wiggle, associated with the anomalous softening, is still present but the degree of softening is smaller below 673 K and changes substantially beyond this temperature which is slightly below the B2 \rightarrow B2+L2₁ order-disorder transition temperature reported in literature. Both ordering effects and precipitates formation can account for this change in the phonon softening. Formation of precipitates, due to the long-time annealing, can lead to changes in the valence electron per atom ratio in the matrix for which the TA₂[$\xi\xi$ 0] phonons are very sensitive.

The investigation of the temperature dependence of the acoustic phonons has been extended to the optical modes which, to our knowledge, has not been reported in any of similar systems investigated up to now. Contrary to the predictions of recent *ab-initio* phonon calculations in L2₁-Ni₂MnAl [2], no anomaly is seen in the optical phonons with the same polarisation as the TA₂[$\xi\xi$ 0] branch. Neither measurements on the as-quenched sample (B2 phase) nor on the long-time annealed sample (B2+L2₁ phase) did reveal any anomalous phonon softening of the optical modes. Indeed, a normal decrease in the frequencies with increasing temperature, presumably due to increasing anharmonicites, is observed (Fig. 6.2). Whether the discrepancy between first-principle calculations and experiment is due to the difference in the atomic ordering itself or to the induced magnetic order can not be concluded here.

The anomalous phonon softening in Ni_2MnAl has been compared to that of other Ni-based alloys (Fig. 6.3). The degree of softening is comparable in different investigated Ni_2MnAl

samples and has the same magnitude as in NiAl and parmagnetic Ni₂MnGa. The only peculiar behaviour is seen in the case of Ni₂MnGa when it orders ferromagnetically where a substantial enhancement of the phonon softening is observed. Despite of the fact that the investigated Ni₂MnAl samples order antiferromagnetically below 300 K, no substantial change in the degree of softening has been observed between the paramagnetic and the antiferromagnetic phases. These results suggest that the magnetization of the sample influences strongly the phonon frequencies through a magnetoelastic coupling.



Figure 6.3:

Temperature dependence of the frequency squared of the soft phonon $TA_2[\xi\xi 0]$ modes in different Ni-based alloys. Note the peculiar behaviour of Ni₂MnGa at the Curie temperature T_c =350 K. The data of Ni₅₄Mn₂₃Al₂₃, Ni_{62.5}Al_{37.5} and Ni₅₂Mn₂₃Ga₂₅ are taken from Refs. [3], [4] and [5] respectively.

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Rotational jump dynamics of ferrocene in two molecular sieves

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The dynamics of guest molecules in zeolitic and related nanoporous hosts continues to be of current interest, as the catalytic and separation properties of zeolites critically depend on guest-molecule diffusion. Moreover, a deeper insight into molecular angular mobility in highly complex channel systems is only possible if the elementary dynamics in simple ordered host structures has been fully understood.

AlPO₄-5, a molecular sieve that possesses straight, parallel, unbranched channels arranged in a hexagonal pattern, can be obtained in large single crystals of high quality. Its channel system is more polar than the one of Si-based molecular sieves. For this reason, the zeosil SSZ-24, which is almost (except for small incommensurate distortions) isostructural to AlPO₄–5 (the channel diametre of both systems amounts to roughly 7.4 Å), presents a rewarding target for a comparative study.



Figure 6.4:

Mössbauer spectrum of ferrocene in SSZ-24 at 178 K, together with Lorentzian fits of two doublets (a,c) and one single line (b).

Nuclear resonant scattering (NRS) of synchrotron radiation, the synchrotron analog of classical Mössbauer spectroscopy (MS), has been proven to yield valuable information about the dynamics in undercooled liquids in various environments, plastic crystals, as well as about slow diffusion in crystals containing Fe and Sn. However, several other experimental techniques, such as quasielastic neutron scattering, NMR, and time-dependent perturbed angular correlation, have been used to elucidate angular jump mechanisms in molecules. In contrast, only some punctual studies have been undertaken using MS, where it was assumed that the electric field gradient, which is parallel to the molecular axis of ferrocene, can only orient along the Cartesian axes [1]. For a system with hexagonal host symmetry, this is clearly not a realistic description.

As NRS offers the possibility to extend the range of applicability of MS both onto small oriented samples and up to higher temperatures, we have attempted to study systematically

- the dependence of powder Mössbauer spectra with respect to various angular jump mechanisms,
- the jump mechanism that probably prevails when ferrocene is introduced into channels of AlPO₄–5 and SSZ-24, and
- the most probably preferential orientation of ferrocene in the channels, from studies using NRS on oriented single crystals of AlPO₄–5.



Figure 6.5:

Sketch of the orientation of the EFG tensor for the six jump models (A: in-plane 3-jump, B: inplane 6-jump, C: $\vartheta = 60^{\circ}$ 3-jump, D: $\vartheta = 60^{\circ}$ 6-jump, E: $\vartheta = 30^{\circ}$ 3-jump, F: $\vartheta = 30^{\circ}$ 6-jump.

The experimental methods used were classical Mössbauer spectroscopy (MS), nuclear forward scattering (NFS) and synchrotron radiation-based perturbed angular correlations (SRPAC). Fig. 6.4 shows a typical Mössbauer spectrum.

The NRS experiments were carried out at the Nuclear Resonance beamline ID18 at the ESRF in 4-bunch mode. A nested high-resolution monochromator yielding an overall energy resolution of 3.5 meV was used.

For the theoretical interpretation, six different discrete jump models (see Fig. 6.5) were studied using the Blume formalism and compared with a novel jump model [2] where the strong-collision model is applied to the azimuthal angle only, assigning a given value to the polar angle, which enters in the shape of the expectation value of the second Legendre polynomial, $\alpha = \langle P_2(\cos \vartheta) \rangle = \langle \frac{1}{2}(3\cos^2 \vartheta - 1) \rangle$, into a modified Blume-type formalism. Pictorially, the EFG reorients on a cone mantle with a given opening angle ϑ . This model, in contrast to the discrete jump models, possesses a closed analytical expression and thus allows for easy data fitting both of Mössbauer and NFS spectra.

We obtain the following results:

First, all models predict that angular jumps lead to asymmetric line broadening, where the stronger broadening is observed towards the centre of the spectrum.

Second, for one mobile species there is never more than one doublet. The experimentally observed four-line spectra (in MS) or two-frequency spectra (using NFS) thus indicate the presence of both a stationary and a mobile species, since one quadrupole doublet/frequency exhibits an almost constant Ω value ("outer" doublet), whereas both shape and effective quadrupole splitting for the mobile species are temperature-dependent ("inner" doublet).

Third, the effective quadrupole splitting of the mobile species approaches a non-zero limiting

value for fast relaxation/high temperature. It is found that this splitting is equal to $\alpha\Omega$, where Ω is the true quadrupole splitting.



Figure 6.6:

Arrhenius plot of relaxation rates for ferrocene/SSZ-24 Mössbauer spectra as obtained with the "cone model".

Fourth, comparing the discrete jump models with the cone model reveals that each spectrum can be perfectly fitted. In other words, to each set of values (λ, α) , where λ is the jump rate as obtained by a fit using the "cone model", there exists another set of values if a special jump model is assumed. We find that the relationship between the relaxation rates of different models is linear if each EFG orientation can be reached from each other orientation with the same jump rate, but that for more complex jump mechanisms the ratio becomes non-linear. Hence, the apparent non-Arrhenius behaviour as observed in SSZ-24 (see Fig. 6.6) may be a hint that another jump mechanism, e. g. one that only allows for jumps between neighbouring orientations on the cone, could provide a more realistic description of the jump behaviour of ferrocene in the channels.

Finally, in order to account for the observation that the intensity ratio between inner and outer doublet is orientation-dependent, we carried out simulations using the SYNFOS program [3]. These studies are still under way.

We can therefore conclude that

- MS and NRS are able to provide us with details about angular jump mechanisms, although the theoretical models are not always unambiguous, i. e. one and the same data set is compatible with more than one jump mechanism,
- we are able to fit our experimental data satisfactorily using the "cone model",
- the jump mechanism may involve only nearest-neighbour angular jumps,
- there is an indication about preferential orientation of ferrocene in the channels of AlPO₄-5, but the data do not yet allow us to conclude definitively which orientation prevails.

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- [2] I. Sergueev, T. Asthalter, U. van Bürck, paper in preparation.
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Synchrotron radiation based perturbed angular correlations from ¹¹⁹Sn.

C. Strohm¹, I. Sergueev², U. van Bürck

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We report the observation of γ - γ -correlations from ¹¹⁹Sn using nuclear resonant scattering of synchrotron radiation. The 23.871 keV M1/E2 $I_g : 1/2 \rightarrow I_e : 3/2$ Mössbauer transition was excited from the ground state, and the time differential correlations between the incident and the scattered photons were recorded for different angles in the plane perpendicular to the incident beam. The experiments were performed on samples of tributyltin-fluoride, which has a very low Lamb-Mössbauer factor already at room temperature. In the time spectra we observed quantum beats from the static perturbation through electric quadrupole interaction.



Figure 6.7: a) Decay scheme. b) Experiment.

Synchrotron radiation based perturbed angular correlations (SRPAC) is a scattering variant of the technique of time differential perturbed angular correlations (TDPAC). In SRPAC, the intermediate state is not populated from a radioactive parent, but excited from the ground state with a pulsed synchrotron beam. Timing and direction of the first γ -quantum in TDPAC are replaced by the time structure and direction of the the synchrotron beam. Contrary to the case of most TDPAC cascades, there are therefore no chemical and electronic after-effects in SRPAC. As in TDPAC, hyperfine interactions of the intermediate state are observed as perturbation of the angular correlations and as quantum beats in the time spectra.

SRPAC was first demonstrated in ${}^{57}Fe$ - [1] and later in ${}^{61}Ni$ -metal [2] for the case of magnetic hyperfine interactions. Hyperfine spectroscopy with PAC-techniques does not depend on the recoilless fraction and SRPAC was used as a unique tool to study glass dynamics using probe molecules [3] and molecular rotations in the rotator phases in plastic crystals [4,5] at vanishing recoilless fractions beyond the possibilities of Mössbauer spectroscopy. Mössbauer spectroscopy with ${}^{119}Sn$ has received considerable interest in general [6], and in particular also in organic compounds with low recoilless fractions [7]. But the dynamics, chemistry and structural properties of soft organotin compounds like polymers, pesticides, antifoulants and amino acid derivatives are interesting especially at ambient or higher temperatures, where Mössbauer spectroscopy becomes

difficult. TDPAC can be performed using a γ - γ -cascade from the ${}^{118m}Sb \rightarrow {}^{118}Sn$ EC decay [8]. A cascade within one and the same element would be more favourable. For instance the 65.2 keV - 23.8 keV cascade from the ${}^{119m}Sn \rightarrow {}^{119}Sn$ (fig. 6.7 a)). γ - γ -correlations from this cascade can however not be exploited due to the high internal conversion ($\alpha = 5300$) of the 65.2 keV transition [9].

But ¹¹⁹Sn is very suitable for the application of SRPAC. Synchrotron sources deliver high fluxes at the transition energy of 23.8 keV and the bunch spacing of the ESRF in 16-bunch mode allows the detection of the decay over nearly 7 lifetmes. The theoretical contrast of the $1/2 \rightarrow 3/2 \rightarrow 1/2$ -transition is high ($2 \cdot A_{22} = 0.5$). The conversion of the transition is low ($\alpha = 5.12$) and all fluorescence lines lie below 4.13 keV and can be easily shielded or discriminated. Organotin compounds often have rather high electric quadrupole interactions. A large number of quantum beat periods can therefore be observed within the time window, allowing for a high sensitivity in the study of dynamics.

Samples of tributyltin-fluoride polymer, $[(C_4H_9)_3SnF]_n$ from Sigma-Aldrich were irradiated with a beam from the premonochromator at the nuclear resonant scattering endstation ID22N at the ESRF in 16-bunch mode (fig 6.7 b)). The experiments were carried out at room temperature. The scattered intensity from the sample was recorded with an avalanche photodiode detector in the time window of 176 ns between the prompt pulses of synchrotron light.



Figure 6.8:

Time spectra from tributyltin-fluoride in the scattering plane perpendicular to the incident beam for different scattering angles. Open cicles: data points, solid lines: fit to the data. a) Original data. b) Anisotropy.

Figure 6.8 a) shows the number of counts as a function of time with respect to the prompt pulse for different angular detector positions in the plane perpendicular to the incident beam. The angles are given with respect to the magnetic polarization vector of the incident photon. The solid lines are fits to the data according to eq. (3) from [3]:

$$I(t,\theta) = I_0 e^{-t/\tau_0} \left[1 - 2 \cdot A_{22}^{exp} \cdot P_2(\cos(\theta)) \cdot G_{22}(t) \right]$$

with the static perturbation factor:

$$G_{22}(t) = \frac{1}{5} + \frac{4}{5} \cdot \cos(\Omega t)$$

where τ_0 is the lifetime, $\hbar\Omega$ the level splitting and A_{22}^{exp} the experimentally observed anisotropy coefficient accounting for a reduction of contrast due to the finite size and distance of the detector, spurious detection of x-ray fluorescence and E2 admixture. The angular dependence is determined by the Legendre-polynomial $P_2(cos(\theta))$. No quantum beats are observed at the particular angle of 54.7°. Figure 6.8 b) shows the anisotropy $A_{22}^{exp} \cdot G_{22}(t)$ for the same data. The observed quantum beat period of 15 ns is equivalent to a quadrupole splitting of 3.47 mm/s (300 K) which is smaller than the value of 3.83 mm/s, measured by Mössbauer spectroscopy at 4.2 K on a sample from the same batch. Figure 6.9 shows the experimentally observed contrast as a function of the detector



Figure 6.9: Points: Experimentally observed contrast $A_{22}^{exp} \cdot P_2(cos(\theta))$. Line: Fit to the data.

angle. The solid line is a fit to $2 \cdot A_{22}^{exp} \cdot P_2(cos(\theta))$.

One may calculate the experimental figure of merit FOM = $5 \cdot \tau_{1/2} \cdot (A_{22}^{exp})^2 \cdot |Q_i|$ as defined in [8] for TDPAC for SRPAC with ¹¹⁹Sn. Using the literature value of $Q_i = 0.094 b$ for the nuclear quadrupole moment of the intermediate state, we obtain a FOM of 0.2 ns \cdot b. If we use $2 \cdot A_{22}^{exp}$ for the contrast to include the effect of polarization of the synchrotron source, we get the value of 0.8 ns \cdot b, which compares favorably to the value of 0.2 ns \cdot b given in [8] for TDPAC from ^{118m}Sb \rightarrow ¹¹⁸Sn.

We would like to thank A. I. Chumakov, U. Ponkratz, S. Stankov and F. E. Wagner for their help.

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Theory of light scattering in disordered solids

B. Schmid, W. Schirmacher

Inelastic light scattering spectra of disordered solids are different from those of crystals. Instead of distinct lines in the light scattering spectra of crystals one observes a continuous spectrum. This is due to the fact that the wavevector conservation rule is not valid any more in disordered solids, so all phonon eigenstates can contribute to light scattering.

Until now mainly two different theories exist for the explanation of the intensity of scattered light. The first one, the one of Shuker and Gammon [1], predicts that the scattering cross section for Stokes scattering is proportional to the density of vibrational states divided by the square of the frequency, evaluated at the frequency downshift of the scattered light. This theory does not agree with experimental data for scattering at acoustic phonons because the theory assumes that the correlation length of the vibrational excitations in the disordered material is shorter than the wavelength of both light and phonon eigenstates, in contradiction to many experimental and theoretical investigations. The second theory, which was developed by Martin and Brenig [2], is derived under the assumption that the dielectric tensor is coupled to the deformations by spatially varying elastooptic constants. The space dependence of these elastooptic constants is known as "electrical disorder", while the "mechanical disorder" is introduced by a very simplified ansatz for the deviation of the phonon eigenstates from plane waves which does not lead to a satisfying agreement with the experimental results either.

We now made use of the fact that mechanical disorder can be described much better by the theory of anomalous vibrations, developed recently in our group [3,4], which is based on classical elasticity theory assuming spatially fluctuating elastic moduli. Using as disorder parameter γ the mean square fluctuation of the shear modulus, the theory correctly predicts the Boson peak which is an excess in the density of vibrational states compared to the result of the Debye model.

In our new theory of light scattering the electrical disorder is incorporated in the same way as in the theory of Martin and Brenig by spatially varying elastooptic constants. The result for the disorder-induced inelastic scattering cross section is a wavenumber integral over the dynamic susceptibility weighted with the Fourier transform $c(\vec{k})$ of the correlation function of the fluctuating elastooptic constants. The dynamic susceptibility can be evaluated using the existing theory [3,4]. For example for depolarized or VH scattering (the polarization of the incoming light is perpendicular to the scattering plane while the detected light has a polarization parallel to the scattering plane) the scattering cross section is proportional to

$$\left(\frac{d\sigma}{d\omega}\right)_{VH} \sim (n(\omega)+1) \int d^3k \ c(\vec{k}) \operatorname{Im}\left(2\chi_L(\omega,\vec{k})+3\chi_T(\omega,\vec{k})\right)$$
(6.1)

where $\chi_L(\omega, \vec{k})$ is the longitudinal, $\chi_T(\omega, \vec{k})$ is the transverse dynamic susceptibility and $n(\omega)$ is the Bose-Einstein occupation number. Assuming $c(\vec{k})$ to be constant in the range where the imaginary part of the dynamic susceptibility is nonzero, the theory simplifies considerably. Fig. 6.10 shows that the experimentally determined scattering cross section can successfully be explained. We are going to improve our theory by selection of a more realistic correlation function for the elastooptic constants and perhaps by consideration of anharmonic effects.

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Figure 6.10:

Reduced intensity of depolarized Raman scattering at glassy As_2S_3 at a Temperature of 8K [5]. The theoretical values were calculated with our new theory with $\gamma = 0.15$.

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7 Teaching and conferences

Lectures, seminars and lab courses

Spring semester 2006

Prof. Dr. Andreas Meyer, Experimentalphysik 2

Prof. Dr. Andreas Meyer, Seminar: Struktur und Dynamik kondensierter Materie

Prof. Dr. Winfried Petry, Physik mit Neutronen 2

Prof. Dr. Christine Papadakis, Angewandte Physik: Polymerphysik 2

Prof. Dr. Christine Papadakis, Prof. Dr. Peter Müller-Buschbaum, Seminar über spezielle Probleme der weichen Materie

PD Dr. Wolfgang Doster, Experimentalphysik 2 für LB (AW/EH/PF)

Prof. Dr. Peter Müller-Buschbaum, Experimentalphysik 2 für LB (BT/ET/MT/EI)

Prof. Dr. Walter Schirmacher, Theoretical Solid State Physic

Fall semester 2006/2007

Prof. Dr. Peter Müller-Buschbaum, Experimentalphysik für Maschinenbauer

Prof. Dr. Peter Müller-Buschbaum, Angewandte Physik: Polymerphysik 1

Prof. Dr. Peter Müller-Buschbaum,

Seminar Struktur und Dynamik kondensierter Materie

Prof. Dr. Christine Papadakis, Experimentalphysik für LB (BT/ET/MT/BI)

Prof. Dr. Christine Papadakis, Prof. Dr. Peter Müller-Buschbaum, Seminar über spezielle Probleme der weichen Materie

PD Dr. Wolfgang Doster, Experimentalphysik 1 für LB (AW/EM/PF)

Prof. Dr. Walter Schirmacher, Theory of liquids and polymer I

Lab cources 2006

Statische und dynamische Lichtstreuung (Biophysikalisches Praktikum) Theoretische und praktische Einführung in AFM (Fortgeschrittenenpraktikum) Thermische Analyse (Fortgeschrittenenpraktikum)

Conferences

EDGAR–LÜSCHER–LECTURES DILLINGEN/DONAU 2006 Thema: Kern- und Elementarteilchenphysik

Datum: Mittwoch, 11. Oktober bis Freitag, 13. Oktober 2006 Tagungsort: Akademie für Lehrerfortbildung Dillingen Veranstalter: Akademie für Lehrerfortbildung Dillingen und TU München wissenschaftliche Leitung: Priv. Doz. Dr. W. Schirmacher und Prof. Dr. S. Paul, Technische Universität München.

PROGRAMM

Prof. Dr. S. Paul, TU München
Einführung
Prof. Dr. Ariane Frey, MPI für Physik, München
Die neuen Collider-Projekte LHC und ILC
Prof. O. Zimmer, TU München
Ultrakalte Neutronen
Dr. Frank Fiedler, Univ. München
Messung der Top-Quark-Masse
Prof. M. Haack, Univ. München
Stringtheorie
Prof. M. Ratz, TU München
Erweiterungen des Standard-Modells
Prof. R. Krücken. TU München
Kernmaterie unter extremen Bedingungen
Dr. Ewald Müller, MPI für Astrophysik, Garching
Supernovae und die Entstehung der Elemente

Lehrerfortbildung an der TU München 2006 Thema:

Physik auf dem Computer

Datum: Samstag, 24. Juni 2006 Tagungsort: Wissenschaftszentrum Weihenstephan der TU München, HS 1 (direkt neben dem "Bräustüberl"") Veranstalter: Zentralinstitut für Lehrerbildung und Lehrerfortbildung der TU M"unchen, Prof. Dr. Wilfried Huber, sowie Physik-Department der TU München. Wissenschaftliche Leitung: Priv.-Doz. Dr. W. Schirmacher, Physik-Department E13, TU München, Anmeldung: wschirma@ph.tum.de

Programm

9.00 - 10.15	PrivDoz. Dr. P. Scherer, TUM: Der Computer als Mikroskop: L"osung klassischer und quantenmechanischer Bewe- gungsgleichungen zur Simulation physikalischer Vorg"ange im molekularen Bereich
10.15 - 10.30	Diskussion
10.30 - 11.45	Prof. Dr. Katharina Krischer, TUM: Simulation nichtlinearer Strukturen an Elektroden-Oberflächen
11.45 - 12.00	Diskussion
12.00 - 13.30	Mittagspause
13.30 - 14.45	Prof. Dr. A. Caldwell, MPI für Physik, München: Analyse von kernphysikalischen Spektren mit extrem geringen Datenmengen
14.45 - 15.00	Diskussion
15.00 - 15.30	Kaffeepause
15.30 - 16.45	Dr. Alex Trellakis, TUM:
	Simulation von Halbleiterbauelementen
16.45 - 17.00	Diskussion
17.00 - 18.15	Prof. Dr. Th. Franosch, LMU München: Molekulardynamik-Simulationen von heterogenen Medien
18.15 - 18.30	Diskussion

RLFB-Tagungsprogramm

30. Edgar-Lüscher-Physikseminar am Gymnasium Zwiesel

Thema: Biophysik und Nanotechnologie

Freitag, 31. März bis Sonntag, 2. April 2006

Veranstalter: Der Ministerialbeauftragte für die Gymnasien in Niederbayern, Ltd. OStD Klaus Drauschke

Wissenschaftliche Leitung: Privatdozent Dr. Walter Schirmacher, Technische Universität München

Org. am Gymnasium Zwiesel: OStD Günther Kratzer, OStR Günther Haller, OStR Wolfgang Achatz

15.30 – 16.00	Begrüßung, Organisatorisches	MB Drauschke, OStD Kratzer, OStR Haller		
16.00 – 17.15	Einführung	Prof. Dr. Martin Stutzmann,		
		Technische Universität München		
17.15 – 18.00	Diskussion und Kaffeepause			
18.00	Kleine Feierstunde	Studienrat Stefan Urlbauer mit der		
		Big-Band des Gymnasiums Zwiesel		

Freitag, 31. März 2006

Samstag, 1. April 2006

Samstay, 1. Api	Samslay, I. April 2000				
9.00 - 10.00	Kleine Laserdioden für die Sensorik	Dr. Markus Ortsiefer,			
	und andere Anwendungen	Vertilas GmbH			
10.15 – 11.00	Diskussion und Kaffeepause				
11.00 – 12.15	Die Physik der Zelle	Prof. Dr. Erich Sackmann,			
		Technische Universität München			
12.15 – 12.30	Diskussion				
15.00 – 16.15	Untersuchung von Nanomaterialien	Dr. Christoph Hugenschmidt			
	mit Positronen	FRM II, Garching			
16.15 – 17.00	Diskussion und Kaffeepause				
17.00 – 18.15	Nano-strukturierte Halbleiter-	Prof. Dr. Gerhard Abstreiter,			
	Bauelemente	Technische Universität München			
18.15 – 18.30	Diskussion				
18.30 – 19.00	Physik im Nanobereich – Physik im	OStR. Friedrich W. Volck			
	Reich der Zwerge	Gymnasium Alzenau			
19.00 - 19.10	Diskussion				

Sonntag, 2. April 2006

9.00 - 10.15	mikroskopische Bodenverunreini-	Prof. Dr. Ingrid Kögel-Knabner,
	gungen	Technische Universität München
10.15 – 11.00	Diskussion und Kaffeepause	
11.00 – 12.15	Nano-strukturierte Polymermate-	Prof. Dr. Peter Müller-Buschbaum,
	rialien	Technische Universität München
12.15 – 13.00	Diskussion; Neues Thema	

Der Ministerialbeauftragte für die Gymnasien in Niederbayern und das Gymnasium Zwiesel danken für finanzielle Unterstützung durch:

Bayerisches Staatsministerium für Unterricht und Kultus, Technische Universität München, Stadt Zwiesel, Zwiesel Kristallglas AG

Kind und Beruf – so funktioniert es

Kolloquium 28.11.06, 17.15 Uhr MW 2250 (Maschinenwesen) TU München, Garching

Sprecherinnen:

Prof. Gudrun Klinker Institut für Informatik

Dr. Joana Rebelo Kornmeier Forschungsreaktor FRM-II

> Dr.-Ing. Alexa Zierl Fa. MVTec

Dr.-Ing. Andrea Bör Institut für Informatik

Eine Initiative der TUM-Frauenbeauftragten des Campus Garching

Berufsbilder für Physikerinnen

Kolloquium 21.06.06, 17.15 h HS 3, Physikdepartment TU München, Garching

Dr. Angelika Hofmann Agfa-Gevaert HealthCare GmbH

See more - do more: Vom Urlaubsfoto zur Röntgendiagnostik - als Physikerin in der Optikentwicklung

Dr. Blanka Zimmerer Deutsches Patent- und Markenamt

Das Deutsche Patent- und Markenamt – an der Schnittstelle zwischen Idee und Realisierung von Innovationen

Dr. Angelika Elhardt Chemieschule Dr. Erwin Elhardt Als Physiklehrerin an einer Berufsfachschule

Dr. Cornelia Engel Infineon Technologies AG Physikerin in der Halbleiterindustrie – Mädchen für (fast) alles

Eine Veranstaltung der Frauenbeauftragten des Physikdepartments, Prof. Christine Papadakis

8 Other activities

Publications

M.A. Ahmed, M.M. Morsi, F. Salman, and E. Metwalli *Electrical properties of some copper containing phosphate glasses.* J. Mater. Sci. Lett 1667 (2006).

M. S. Appavou, S. Busch, W. Doster and T. Unruh *The effect of packing on internal motions of hydrated myoglobin.* MRS Bulletin (2006) in press

T. Asthalter, I. Sergueev, U. van Bürck, R. Dinnebier Identification of a rotator phase of octamethyl ferrocene and correlations between its structural and dynamical properties J. Phys. Chem. Solids **67**, 1416 (2006)

A. Bartsch, K. Rätzke, F. Faupel, A. Meyer
 Appl. Phys. Lett. 89, 121917 (2006)
 Codiffusion of ³²P and ⁵⁷Co in glass forming PdNiCuP alloy and its relation to viscosity

E. Bauer, E. Maurer, T. Mehaddene, S. V. Roth, P. Müller-Buschbaum Flow in confined geometry introduced by dewetting of ultra thin polystyrene films Macromolecules 39, 5087 (2006)

P. Busch, M. Rauscher, D.-M. Smilgies, D. Posselt, C.M. Papadakis Grazing-incidence small-angle X-ray scattering (GISAXS) from thin, nanostructured block copolymer films - The scattering cross-section in the distorted-wave Born approximation J. Appl. Cryst. **39**, 433 (2006)

S. Busch, W. Doster, S. Longeville, V. García Sakai and T. Unruh *Microscopic Protein Diffusion at High Concentration* MRS Bulletin (2006) in press

S. Busch, W. Doster, S. Longeville, V.G. Sakai and T. Unruh *Microscopic protein diffusion at high concentration* MRS Bulletin (Material Research Science) in press (2006)

W. Doster, S Longeville *Microscopic diffusion and hydrodynamic interactions of hemoglobin in red blood cells*, Biophys.J. submitted (2006)

W. Doster

Brownian Oscillator Analysis of Protein Dynamics in 'Neutron Scattering in Biology', Methods and Applications, p. 461-483, Ed. R. Gutberlet, J. Fitter and J. Katsaras, Springer Verlag (2006)

W. Doster Dynamical structural distributions in proteins Physica B **385-386**, 831 (2006) W. Doster, K. Kilimann, R.F. Vogel, C. Hartmann, M.G. Gänzle, *Protection by sucrose against heat-induced lethal and sublethal injury of Lactococcus lactis: an FT-IR study*, Bioch.Biophys.Acta, Proteins and Proteomics**1764**,1188 (2006)

W. Doster, A. Baars, L. Kulisiewicz, R. Gebhardt and A. Delgado, Viscosity and Aggregation of beta-Lactoglobulin under High Pressure Proceedings of the 4th International Symposion on Food Rheology and Structure Kerschensteiner Verlag GmbH (2006) 263-267 ISBN: 3-905609-25-8

R. Gebhardt, W. Doster and J. Friedrich, Size distribution of pressure-decomposed casein micelles studied by dynamic light scattering and AFM, Eur. Biophys. J. **35** 503 (2006).

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Gilles, R., Ostermann, A.. Schanzer, C.. Krimmer, B.. Petry, W. *The concept of the new small-angle scattering instrument SANS-1 at the FRM -II* Proceedings of ICNS 2005', Physica B 385-386, 1174 (2006)

Gilles, R., Ostermann, A., Schanzer, C., Krimmer, B., Petry, W. Optimisation of the new Small-Angle Neutron Scattering instrument SANS-1 at the FRM II by Monte Carlo simulations J. Appl. Cryst. (2006)

Gilles, R., Ostermann, A., Petry, W. Monte Carlo simulations of the new Small-Angle Neutron Scattering instrument SANS-1 at the FRM II J. Appl. Cryst. (2006)

A. Griesche, M.-P. Macht, G. Frohberg, M. M. Koza, S. Mavila Chathoth, A. Meyer Acta Mater (submitted) *Selfdiffusion in Al-Ni-Ce and Al-Ni-La Melts*

J. Horbach, S. K. Das, A. Griesche, G. Frohberg, M.-P. Macht, A. Meyer Phys. Rev. B (submitted) Selfdiffusion and Interdiffusion in Al₈₀Ni₂₀ Melts: Simulation and Experiment

M. Jernenkov, S. Klimko, V. Lauter-Pasyuk, H. Lauter, V. Aksenov, B. Toperverg *Magnetization of magnetic films determined with Larmor pseudo-precession and spin echo* Physica B 385-386, 471-474 (2006)

item[] F. Kargl, A. Meyer, M. M. Koza, H. Schober
Phys. Rev. B 74, 014304 (2006)
Formation of Channels for Fast-Ion Diffusion in Alkali Silicate Melts: A Quasielastic Neutron Scattering Study

T. Komenda, K. Lüdtke, R. Jordan, R. Ivanova, T.B. Bonné, C.M. Papadakis Multicompartment micellar hydrogels from poly(2-oxazoline)s containing fluorophilic, hydrophilic and lipophilic blocks Polym. Prepr. **47**, 197 (2006)

Mehaddene, T., Neuhaus, J., Petry, W., Hradil, K. *Phonon dispersions in NiAlMn shape memory alloy* Material Science and Engineering A (Elsevier Science) submitted, 14 (2006) E. Metwalli, D. Hains, O. Becker, S. Conzone and C.G. Pantano *Surface characterizations of mono, di and tri-aminosilane treated glass substrates* J. Colloid Interface Sci. 298:825 (2006).

A. Meyer, S. Stüber, D. Holland-Moritz, O. Heinen, T. Unruh Phys. Rev. Lett. (submitted) *Quasielastic Neutron Scattering on Levitated Metallic Droplets*

A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto,
J. Korecki, R. Rüffer
Phys. Rev. Lett. 97, 135501 (2006) *Effect of Densification on the Density of Vibrational States of Glasses*

P. Müller-Buschbaum, R. Gebhardt, E. Maurer, E. Bauer, R. Gehrke, W. Doster *Thin casein films as prepared by spin-coating: Influence of film thickness and of pH* Biomacromolecules 7, 1773 (2006)

P. Müller-Buschbaum High-resolution grazing incidence small angle x-ray scattering: Investigation of micrometer sized structured polymer films Prog. Col. Polym. Sci. 132, 23 (2006)

P. Müller-Buschbaum, E. Bauer, E. Maurer, K. Schlögl, S. V. Roth, R. Gehrke *A new route to large-area ordered polymeric nano-channel arrays* Appl. Phys. Lett. 88, 083114 (2006)

P. Müller-Buschbaum, E. Bauer, S. Pfister, S. V. Roth, M. Burghammer, C. Riekel, C. David, U. Thiele *Creation of multi-scale stripe-like patterns in thin polymer blend films*Europhys. Lett. 73, 35 (2006)

P. Müller-Buschbaum, E. Bauer, E. Maurer, R. Cubitt *Fast swelling kinetics of thin polystyrene films* Physica B 385-386, 703 (2006)

P. Müller-Buschbaum, E. Maurer, E. Bauer, R. Cubitt Surface versus confinement induced morphology transition in triblock copolymer films: A GISANS investigation Langmuir 22, 9295 (2006)

Palancher, H., Martin, P., Sabathier, C., Dubois, S., Valot, C., Wieschalla, N., Röhrmoser, A., Petry, W., Jarousse, C., Grasse, M., Tucoulou, R. *Heavy Ion Irradiation as a Method to Discriminate Research Reactor Fuels*Proceedings on the 'International Conference on Research Reactor Fuel Management RRFM 2006', May 04, 2006, Sofia (2006)

C.M. Papadakis, R. Ivanova, K. Lüdtke, K. Mortensen, P.K. Pranzas, R. Jordan *Micellar structure of amphiphilic poly(2-oxazoline) diblock copolymers* J. Appl. Cryst. **40** (2007) (Supplement)submitted 2006

I. I. Potemkin, P. Busch, D.-M. Smilgies, D. Posselt, C.M. Papadakis Effect of the Molecular Weight of AB Diblock Copolymers on the Lamellar Orientation in Thin Films: Theory and Experiment Macromolecular Rapid Communications, accepted (2006)

R.J. Redkar, N.A. Schultz, V. Scheumann, L.A. Burzio, E. Metwalli, O. Becker and S. Conzone *Signal and sensitivity enhancement through optical interference coating for DNA and*

protein microarray applications. Biomolecular techniques 17:122 (2006).

S. V. Roth, H. Walter, M. Burghammer, C. Riekel, B. Lengeler, C. Schroer, M. Kuhlmann, T. Walther, R. Domnick, P. Müller-Buschbaum *Combinatorial investigation of the isolated nanoparticle to coalescent layer transition in a gradient sputtered gold nanoparticle multilayer* Appl. Phys. Lett. 88, 021910 (2006)

S. V. Roth, R. Döhrmann, M. Dommach, M. Kuhlmann, I. Kröger, R. Gehrke, H. Walter, C. Schroer, B. Lengeler, P. Müller-Buschbaum *The small-angle options of the upgraded USAXS beamline BW4 at HASYLAB* Rev. Sci. Instr. 77, 085106 (2006)

Sergueev, I., van Bürck, U., Chumakov, AI., Asthalter, T., Smirnov, GV., Franz, H., Rüffer. R., Petry, W.

Synchrotron-radiation-based perturbed angular correlations used in the investigation of rotational dynamics in soft matter Physical Review B73, 024203-1-12 (2006)

I. Sergueev, U. van Bürck, A.I. Chumakov, T. Asthalter, G.V. Smirnov, H. Franz, R. Rüffer, W. Petry

Synchrotron-radiation-based perturbed angular correlations used in the investigation of rotational dynamics in soft matter Phys. Rev. B **73**, 024203 (2006)

Smirnov,G.V., van Bürck, U., Franz, A., Asthalter,T., Leupold, O., Schreier, E., Petry, W. *Nuclear gamma resonance time-domain interferometry: Quantum beat and radiative coupling regimes compared in revealing quasielastic scattering* Physical Review B 73, 184126-1-9 (2006)

G.V. Smirnov, U. van Bürck, H. Franz, T. Asthalter, O. Leupold, E. Schreier, W. Petry Nuclear γ resonance time-domain interferometry: Quantum beat and radiative coupling regimes compared in revealing quasielastic scattering Phys. Rev. B **73**, 184126 (2006)

Unruh, T., Meyer, A., Neuhaus, J., Petry, W. *The Time-of-flight Spectrometer TOFTOF* Neutron News

V.V. Ustinov, M.A. Milayev, L.N. Romashev, T.P. Krinitsina, A.M. Burkhanov, V. Lauter-Pasyuk, H.J. Lauter Multiple spin-flip transitions and stairs-like GMR in Fe/Cr superlattices with uniaxial inplane anisotropy J. Magn. Mater. 300, e281-e283 (2006) V.V. Ustinov, M.A. Milayev, L.N. Romashev, T.P. Krinitsina, A.M. Burkhanov, V. Lauter-Pasyuk, H.J. Lauter *Multi-stepwise GMR and layers magnetic reversal in uniaxial Fe/Cr superlattices* Physica Status Solidi (c) 3, 1249-1256 (2006)

G. Wellenreuther, H. Franz, U. van Bürck, I. Sergueev *Rotational dynamics in anisotropic confinement* Hyperfine Interact. http://dx.doi.org/10.1007/s10751-006-9257-x

Wieschalla, N., Bergmaier, A., Böni, P., Bñing, K., Dollinger, G., Gro ssmann, R., Petry, W., Röhrmoser, A., Schneider, J. *Heavy ion irradiation of U-Mo/Al dispersion fuel*Journal of Nuclear Materials 357, Issues 1-3, 191-197 (2006)

Zeitelhack, K., Schanzer, C., Kastenmüller, A., Röhrmoser A., Daniel, C., Franke, J., Gutsmiedl, E., Kudryashov, V., Maier, D., Päthe, D., Petry, W., Schöffel, T., Schreckenbach, K., Urban, A., Wildgruber, U. *Measurement of neutron flux and beam divergence at the cold neutron guide system of the new Munich research reactor FRM-II* Nuclear Instruments and Methods in Physics Research A 560, 444-453 (2006)

Talks given by members of E13

C. Darko

COST P12 Conference, 'Crystallisation and Structure Formation of Polymers', Mittelwihr Center, France *Thin films of crystalline blockcopolymers* 9.10.-11.10. 06

Z. Di

Workshop for neutron scattering from biological and soft matter interfaces, FRM-II Transient states during vapor treatment of thin diblock copolymer films: An in-situ GISAXS study 22.09.06

W. Doster, NIST, Gaithersburg, USA, *Protein-water displacement distributions* 7.3.06

W. Doster, NIST, Gaithersburg, USA, *Elastic resolution spectroscopy* 8.3.06

W. Doster, Bioneutron 2006 in Taormina, Italy, invited talk *The dynamical transition of proteins, concepts and misconceptions*

W. Doster, Symposion on NMR-based Research in Ulm, 13.10.0613.10.06 invited talk *Anomalous diffusion from polymer reptation to protein diffusion in cells* 13.10.06

W. Doster, Colloquium of Biomolecular Structure and Dynamics in Freising, *Pressure tuning of biomolecular complexes ass Transport in Silicate Melts* 12.12.06

W. Doster, Workshop for chemistry of biological processes created by water and biomolecules, in Okazaki, Japan, invited talk: *Protein-water dynamics from neutron scattering experiments* 8.1.06

V. Lauter-Pasyuk, invited talk at the 3rd International Workshop on Dynamics in Confinement - CONFIT 2006, March 23 to 26, 2006, Grenoble, France *Interfacial frozen capillary waves in diblock copolymer multilayer*

V. Lauter-Pasyuk, invited seminar at Halle University Highly ordered self-organized copolymer-nanoparticle composite films studied by complete neutron reflectometry
30. 06. 2006

V. Lauter-Pasyuk, invited lecture at the International Summer School on Neutron techniques in molecular magnetism, September 1 to 9, 2006, Jaca, Spain Internal Structure in Magnetic Nanosystems studied by Neutron Reflectometry

E. Maurer, S. Loi, D. Wulff, N. Willenbacher, M. Ruckpaul, P. Müller-Buschbaum, DPG Frühjahrstagung in Dresden *Structure creation in pressure sensitive adhesives* 27.-31. 3. 2006

A. Meyer

IInd Workshop on Dynamics in Viscous Liquids, 11. April 2006 in Mainz *Mechanism of Ionic Transport in Viscous Sodium Borate Melts*

A. Meyer ILL Millenium Symposium, 28. April 2006 in Grenoble, Frankreich *A Microscopic View on M*

A. Meyer Institut für Werkstoffforschung Dresden, 11. Mai 2006 A Microscopic View on Mass Transport in Metallic Melts

A. Meyer Institut für Materialphysik, Universität Wien, 23. Mai 2006 Struktur-Eigenschafts-Beziehungen in zähen Flüssigkeiten

A. Meyer Institut für Materialphysik, Universität Göttingen, 8. Juni 2006 Struktur-Eigenschafts-Beziehungen in zähen Flüssigkeiten

A. Meyer Universität Mainz, 19. Juni 2006 Addressing Soft Matter Issues with Neutron Scattering on Liquid Metals

P. Müller-Buschbaum, Satellite meeting - status and perspectives of SAXS/WAXS/GISAXS in Hamburg *High-resolution GISAXS - probing large scale structures in thin polymer films* 26. 1. 2006

P. Müller-Buschbaum, BASF Seminar in Ludwigshafen *Structure determination in the thin film geometry using GISAXS*14. 2. 2006

 P. Müller-Buschbaum, 30. Edgar-Lüscher-Physikseminar zur Lehrerfortbildung in Zwiesel Nano-strukturierte Polymermaterialien
 1.-2. 4. 2006

P. Müller-Buschbaum, E. Bauer, V. Körstgens, J. Wiedersich, S. V. Roth, V. Lauter-Pasyuk, W. Petry, Workshop on Nanocompoistes in Montpellier (France) *Magnetic particles in supported polymer nano-structures* 5.-7. 4. 2006

P. Müller-Buschbaum, E. Bauer, E. Maurer, R. Cubitt, ILL Millenium Symposium in Grenoble (France) *Surface induced morphology transition in triblock copolymer films* 27.-30. 4. 2006

P. Müller-Buschbaum, 1st micro-SAXS/ WAXS beamline workshop for PETRA III in Hamburg *Micro-beam experiments probing local surface structures* 9.-10. 5. 2006

P. Müller-Buschbaum, Seminar des Insitut de Science et d'Ingenierie Supramoleculaires (ISIS) in Strassbourg *Grazing Incidence Small Angle Scattering - An Advanced Characterization Technique for Structured Polymer Films* 8. 6. 2006

P. Müller-Buschbaum, Diskussionstreffen Industrieklebstoffe in Düsseldorf *Possible extension to classical probe-tack measurements* 12. 6. 2006

P. Müller-Buschbaum, International Small Angle Scattering conference SAS2006 in Kyoto (Japan) *Grazing Incidence Small Angle Scattering - An Advanced Characterization Technique for Structured Polymer Films* 9.-14. 7. 2006

P. Müller-Buschbaum, Diskussionstreffen Industrieklebstoffe in Salzburg (Austria) *Possible* extension to classical probe-tack measurements
28. 7. 2006

P. Müller-Buschbaum, 5th PSI Summer School on Condensed Matter Research in Zuoz (Schweiz) *Grazing Incidence Small Angle Scattering* 20.-26. 8. 2006

P. Müller-Buschbaum, Diskussionstreffen Industrieklebstoffe in Darmstadt *Possible extension to classical probe-tack measurements* 8.-10. 9. 2006

P. Müller-Buschbaum, 1st REFSANS workshop in München Surface versus confinement induced transition in thin diblock copolymer films
22. 9. 2006 P. Müller-Buschbaum, Diskussionstreffen Mikrofluidik in Dresden *New pathways to microfluidics utilizing microbeam scattering experiments* 12.-15. 10. 2006

P. Müller-Buschbaum, Kolloquium der Materialwissenschaften der Technischen Universität in Darmstadt *Nano-structured polymer films - relation between structure and function* 14. 11. 2006

P. Müller-Buschbaum, internationale Tagung SoftILL in Grenoble (France) *Status and perspectives of GISANS*

22.-24. 11. 2006

P. Müller-Buschbaum, BASF Seminar in Ludwigshafen *Structural characterisation of adhesive surfaces*18. 12. 2006

C.M. Papadakis

Wissenschaftszentrum Weihenstephan, TU München Aggregationsverhalten amphiphiler Diblockcopolymere - Fluoreszenz-Korrelations-Spektroskopie in den Materialwissenschaften 10.01.06

C.M. Papadakis

Satellite meeting of the HASYLAB User Meeting DORIS III: (GI)SAXS/WAXS Experiments - Status and Perspectives' *Investigations of thin block copolymer films with a crystalline block.* 26.01.06

C.M. Papadakis, T.B. Bonné, R. Ivanova, P. Štěpánek, K. Lüdtke, R. Jordan Annual Meeting of the German Physical Society, Dresden *Micelle formation of amphiphilic poly(2-alkyl-2-oxazoline) block copolymers* 27.03.06

C.M. Papadakis Annual Meeting of the German Physical Society, Dresden *Thin films of crystallisable diblock copolymers* 29.03.06

C.M. Papadakis Universität Göttingen Structure and stability of thin block copolymer films 20.04.06

C.M. Papadakis XIII International Conference on Small-Angle Scattering, Kyoto Amphiphilic block copolymers of poly(2-oxazoline): Promising candidates for multicompartment hydrogels 11.07.06

C.M. Papadakis The 232nd ACS National Meeting, San Francisco, CA Amphiphilic block copolymers of poly(2-oxazoline): Promising candidates for multicompartment hydrogels 10.09.06

C.M. Papadakis SONS/Polyamphi Workshop 'Structure and prophesis of self-organized amphiphilic copolymers', Prague *Fluorescence correlation spectroscopy in polymer science* 04.10.06

C.M. Papadakis Deutsche Physikerinnentagung, Berlin Nanostrukturierte Blockcopolymerfilme:Matrizen für die Nanotechnologie 05.11.06

C.M. Papadakis Universität Regensburg Struktur und Stabilität von Blockcopolymerfilmen 16.11.06

J. Perlich, Treffen des AK Funktionsmaterialien im SPP 1181 NanoMat, Institut für Physikalische Chemie und Elektrochemie Hannover Nanostructured Films of Selfencapsulating Inorganic-Organic Hybrid Materials 06.10.06

W. Petry

Neujahrsempfang des KKW Unterwesel Licht im Dunkeln - Neutronen für Wissenschaft, Technik und Medizin 21.01.06

W. Petry

Symposium von Bayern Innovativ "Material Innovativ", Universität Bayreuth Neutronen zum Design neuer Materialien 29.03.06

W. Petry

10th International Topical Meeting on Research Reactor Fuel Management (RRFM), Sofia Heavy Ion Irradiation as a Method to Discriminate Research Reactor Fuels 30.04.06

W. Petry

"Themen-Forum-Odeon" im Bayerischen Staatsministerium des Inneren Licht im Dunkeln, Neutronen für Wissenschaft, Medizin und Industrie 12.05.06

W. Petry

IPP Kolloquium Max-Planck-Institut in Garching Brilliant Neutrons in the Immediate Neighbourhood of the IPP, so what? 19.05.06 W. Petry

Farewell Colloquium for Professor Gernot Kostarz ETH Zürich, Schweiz FRM II a brilliant new Neutron Source for Material Science 31.05.06

W. Petry

Kerntechnisches Kolloquium der RWTH Aachen Neutronen für Wissenschaft, Technik und Medizin - der FRM II in München 13.06.06

W. Petry

INI.TUM Kolloquium, AUDI Forum, Ingolstadt Neutronen für Wissenschaft, Technik und Medizin - der neue Forschungsreaktor in Garching 20.06.06

W. Petry

Physikalisches Kolloquium der Universtät Duisburg-Essen Licht im Dunkeln, die neue deutsche Neutronenquelle FRM II für Wissenschaft, Medizin und Industrie 21.06.06

W. Petry

International Symposium on HEU Minimization in the Civilian Sector, Oslo *Reduced Enrichment for FRM II* 17.06.06

W. Petry

Bayerische Vertretung bei der EU in Brüssel in Anwesenheit von Staatsminister Dr. A. Goppel

The New Source Heinz-Meier-Leibnitz- contribution to strengthen the European Research Area

26.06.06

W. Petry

Journee Scientifique du Laboratoire Leon Brillouin, CEA Saclay, lors de son 25 ème Anniversaire

Utilisation des Neutrons pour Industrie, Activite au FRM II de Munich 05.07.06

W. Petry

IAEA Seminar on the Installation of a New Research Reactor, Hanoi *Requirements for a successful Research Reactor Projekt*14.08.06 *Design and Construction Phase of a New Research Reactor Project: Example of the FRM II Project*15.08.06 *Operation of a New Research Reactor: Experience of the Operation and Utilisation of FRM II*16.08.06

W. Petry Ferienakademie TUM Sarntal, Südtirol *Neutron Source* 17-19.09.06

W. Petry

Magnus-Haus der Deutschen Physikalischen Gesellschaft in Berlin Neutronen sind wunderbar; Anwendungen in Grundlagenforschung, Industrie und Medizin 24.10.06

W. Petry Forum Mobil (Informationskreis Kernenergie), Aachen Licht im Dunkeln - Die Forschungsneutronenquelle FRM II 06.11.06

W. Petry Invited Talk at TOKAI (JAEA) Japan *The Prensent Status of FRM II* 10.11.06

W. Petry

The US-China Workshop Series of Neutron Scattering Science and Technology. The Inaugurating Meeting: November 15 2006, Beijing *FRM II - a New brilliant Neutron Source* 15.11.06

W. Petry

RETR 2006 Cape Town, Southafrica - Talk in the framework of the International Fuel Development Working Group IRIS-TUM paltes Irradiation in OSIRIS 2005/06 02.11.06

W. Schirmacher, Seminar Talk at the Università "La Sapienza" Rome Anomalous Vibrational and Thermal Properties of Disordered Solids 21. 2. 2006

 W. Schirmacher, Invited talk at the International Seminar on Quantum Disordered Systems, Glassy Low-Temperature Physics and Physics at the Glass Transition, Dresden *Thermal Conductivity of Disordered Solids and the Boson Peak* 15. 3. 2006

W. Schirmacher, Frühjahrstagung der DPG*Thermal Conductivity of Glasses and the Boson Peak*27. 3. 2006

W. Schirmacher, Festkörper-Seminar, Forschungszentrum Jülich Vibrational and Thermal Anomalies in Disordered Solids
30. 6. 2006

W. Schirmacher, Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Grossgeräten, Hamburg

Collective Excitations in Simple Liquids: Inelastic X-Ray Scattering and Mode-Coupling Theory 7. 10. 2006

W. Schirmacher, Kolliquium zur Physik der kondensierten Materie, Universität Freiburg Anomale Schwingungs- und thermische Eigenschaften ungeordneter Festkörper
23. 11. 2006

W. Schirmacher, Seminar über Neutronenstreuung in Rothenfels (Main) Anomalous Vibrational Properties of Disordered Solids 21. 7. 2006

W. Schirmacher, invited lecture series at the Advanced Photon Source, Argonne National Laboratory Dynamics of Liquids and Disordered Solids

17. - 26. 9. 2006

S. Stüber, Frühjahrstagung des Arbeitskreises Festkörperphysik, Deutsche Physikalische Gesellschaft, Dresden
Inelastic Neutron Scattering on AlNi melts
28. 3. 2006

S. Stüber, Arbeitskreis intermetallische Verbindungen, Deutsche Gesellschaft für Kristallwachstum und Kristallzüchtung, Garching
 Neutronen-Untersuchungen an metallischen Schmelzen
 28. 9. 2006

Poster

detector

V. Aksenov, T. Enik, M. Jernenkov, V. Lauter-Pasyuk, H.J. Lauter, E. Litvinenko, A. Petrenko, V. Proglyado *First GISANS measurements in time-of-flight on REMUR with new 2D position sensitive*

IBR-2 User meeting June 2006, Dubna, Russia

M. S. Appavou, S. Busch, W. Doster and T. Unruh Dynamics of Partially Unfolded Myoglobin The Eighth International Conference on Quasi-Elastic Neutron Scattering (QENS 2006) Bloomington (Indiana, USA) 14. - 17. 6. 2006

M. S. Appavou, S. Busch, W. Doster and T. Unruh Protein internal molecular dynamics investigated by quasi-elastic neutron scattering: effect of packing on methyl group rotation in myoglobin Neutron Scattering Highlights on Biological Systems (Bioneutron 2006) Taormina (Sicily) 7. - 10. 10. 2006

M. S. Appavou, S. Busch, W. Doster and T. Unruh Dynamique molulaire interne étudi par diffusion quasi-élastique de neutron: influence du repliement sur la rotation des groupes m hyles dans la myoglobine ECOLE L'EAU DANS LES MILIEUX BIOLOGIQUES Roscoff (Bretagne, FRANCE) 25. - 28. 10. 2006
T. Asthalter, I. Sergueev, U. van Bürck, S. Klingelhöfer, P. Behrens, J. Kornatowski 3rd Int. Workshop on Dynamics in Confinement, ILL Grenoble (France) *Dynamics of ferrocene in two zeotypic hosts as studied by nuclear resonant scattering* 23.-26. 03. 2006

T. Asthalter, I. Sergueev, U. van Bürck, S. Klingelhöfer, P. Behrens, J. Kornatowski Bunsentagung 2006, Erlangen Anisotrope Rotationsdynamik von Ferrocen in polaren und unpolaren Wirtsgittern 25.-27. 05. 2006

T. Asthalter, U. van Bürck, F.E. Wagner, V. Rabe, S. Laschat 6th Seeheim Workshop on Mössbauer Spectroscopy, Seeheim *In situ Mössbauer studies of novel Gif-type oxidation catalysts* 07.-11. 06. 2006

T. Asthalter, U. van Bürck, F.E. Wagner, I. Sergueev, S. Klingelhöfer, P. Behrens, J. Kornatowski, P. Härter 6th Seeheim Workshop on Mössbauer Spectroscopy, Seeheim

Anisotropic Rotational Dynamics of Ferrocene ${}^{57}Fe(C_5H_5)_2$ Confined in Polar and Nonpolar Host Lattices 09. 06. 2006

S. Busch, W. Doster, S. Longeville, V. García Sakai, T. Unruh *Protein Diffusion in Crowded Environments* 5th PSI Summer School on Condensed Matter Research, 19. – 26. 8. 2006

C. Darko, I. Botiz, G. Reiter, S.V. Roth, D.-M. Smilgies, C.M. Papadakis
Deutsche Tagung für Forschung mit Synchrotronenstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2006, Hamburg
Dünne Filme aus kristallinen Diblockcopolymeren
04.-06.10.06

C. Darko, I. Botiz, G. Reiter, D.W. Breiby, S.V. Roth, C.M. Papadakis DPG-Tagung Dresden *Thin films of crystallisable diblock copolymers* 27.03.-31.03.06

C. Darko, I. Botiz, G. Reiter, D.W. Breiby, S.V. Roth, C.M. Papadakis HASYLAB User Meeting, *Thin films of crystalline diblock copolymers* 27.01.06

Z. Di, C.M. Papadakis, D.-M. Smilgies, D. Posselt
5th PSI Summer School on Condensed Matter Research 'Neutron, X-ray and Muon Studies of Nano Scale Structures', Zuoz, Switzerland *Transient states during vapor treatment of thin, lamellar diblock copolymer films*19.-26.08.06

R. Ivanova, T. Bonné, C.M. Papadakis, K. Lüdtke, T. Komenda, R. Jordan Makromolekulares Kolloquium, Freiburg *Aggregation behavior of amphiphilic, poly(2-alkyl-2-oxazoline)-based copolymers* 23.02.-25.02.06 R. Ivanova, T.B. Bonné, K. Lüdtke, T. Komenda, R. Jordan, K. Mortensen, P.K. Pranzas, C.M. Papadakis

Deutsche Tagung für Forschung mit Synchrotronenstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2006, Hamburg

Multicompartment-Hydrogele aus amphiphilen Poly(2-oxazolin) Triblockcopolymeren 04.-06.10.06

R. Kampmann, U. Tietze, H.J. Lauter, V.V. Lauter-Pasyuk, B. P. Toperverg *Larmor encoding and Fourier reconstruction for wavelength dispersive reflectometry* PNCMI 2006: Polarised neutrons for condenced matter investigations 25. - 28. 09. 2006, Berlin, Germany

V. Lauter-Pasyuk, P. Müller-Buschbaum, W. Petry, M. Jernenkov, B. Toperverg, H. Lauter *Self-organized complex nano-composites studied at the nano-scale* Millenium Symposium ILL, 27 - 29.12. 2006, Grenoble, France

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

Self-assembled copolymer-nanoparticle multilayers studied by specular and off-specular scattering

SAS 2006: XIII International Conference on Small-angle Scattering 9 - 13. 07. 2006, Kyoto, Japan

V. Lauter-Pasyuk, H. Lauter, M. Jernenkov, B. Toperverg, P. Müller-Buschbaum, W. Petry Highly ordered self-organized copolymer-nanoparticle composite films studied by specular reflectometry and off-specular neutron scattering

SNI 2006: Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Großen, 4. - 6.10. 2006, Hamburg, Germany

T. Mehaddene, J. Neuhaus and W. Petry

Interplay of magnetism and vibrational degrees of freedom in magnetic shape memory alloys Kick-off meeting of the SPP1239 "Magnetic field induced modification of microstructure and form of solid materials"

18.- 19. 10 2006 IFW, Dresden.

E. Metwalli, U. Slotta, C. Darko, T. Scheibel, C.M. Papadakis
HASYLAB User Meeting,
Structural investigations of recombinant spider silk protein films using grazing-incidence small-angle X-ray scattering.
27.01.06

E. Metwalli, U. Slotta, T. Scheibel, C.M. Papadakis DPG-Tagung Dresden Structural characterization of recombinant spider silk protein films immobilized to solid surface 27.03.-31.03.06

E. Metwalli, U. Slotta, S.V. Roth, T. Scheibel, C.M. Papadakis PETRA III Workshop: 'First MicroSAXS/WAXS Beamline Workshop at DESY' *X-ray scattering study of protein films immobilized to solid surfaces* 09.05.-10.05.06 E. Metwalli, C. Darko, U. Slotta, T. Scheibel, S.V. Roth, C.M. Papadakis Deutsche Tagung für Forschung mit Synchrotronenstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2006, Hamburg Dünne Filme aus rekombinant hergestellter Spinnenseide untersucht mit Röntgenstreuung unter streifendem Einfall 04.-06.10.06

J.-F. Moulin, P. Müller-Buschbaum and S. V. Roth. *Probing polymer thin film by GISAXS and GIUSAXS* SNI2006 Hamburg, 04 - 06. 10. 2006

J.-F. Moulin, P. Müller-Buschbaum and S. V. Roth. *GIUSAXS study of polymer films prepared under flow conditions* PSI Summer School on Condensed Matter Research, Suoz 19 -26. 08. 2006

P Müller-Buschbaum, E. Bauer, V. Körstgens, J. Wiedersich, S. V. Roth, R. Gehrke, HA-SYLAB User Meeting in Hamburg *High-resolution grazing incidence small angle x-ray scattering - investigation of micrometer sized structured polymer films* 27. 1. 2006

P Müller-Buschbaum, S. V. Roth, R. Cubitt, M. Burghammer, C. Riekel, SNI2006 in Hamburg *Probing thin polymer films: A comparative GISAXS and GISANS investigation* 4.-6. 10. 2006

C.M. Papadakis, P. Michelberger, C. Darko, E. Metwalli, S.V. Roth, D. Posselt, D.-M. Smilgies

HASYLAB User Meeting,

Perpendicular lamellae in thin films of poly(styrene-b-butadiene) diblock copolymers 27.01.06

C.M. Papadakis, R. Ivanova, T.B. Bonné, P.K. Pranzas, K. Mortensen, R. Jordan, K. Lüdtke, T. Komenda

JCNS Symposium, Jülich Multicompartment micellar gels of amphiphilic poly(2-alkyl-2-oxazoline) triblock copolymers 16.02.-17.02.06

C.M. Papadakis, D.-M. Smilgies, D. Posselt DPG-Tagung Dresden *Transient states during vapor treatment of thin, lamellar diblock copolymer films* 27.03.-31.03.06

C.M. Papadakis, R. Ivanova, T. Bonné, K. Pranzas, K. Mortensen, K. Lüdtke, T. Komenda, R. Jordan

DPG-Tagung Dresden

Multicompartment micellar gels of amphiphilic poly(2-oxazoline) *triblock copolymers* 27.03.-31.03.06

C.M. Papadakis, D.-M. Smilgies, D. Posselt XIII International Conference on Small-Angle Scattering, Kyoto *Transient states during vapor treatment of thin, lamellar diblock copolymer films* 09.07.-13.07.06 C.M. Papadakis, D. Posselt, D.-M. Smilgies

Deutsche Tagung für Forschung mit Synchrotronenstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2006, Hamburg Instabilitäten während der Dampfbehandlung dünner Diblockcopolymerfilme: Zeitaufgelöste Röntgenkleinwinkelstreuung unter streifendem Einfall

04.-06.10.06

C.M. Papadakis, P. Busch, M. Rauscher, D.-M. Smilgies, D. Posselt Deutsche Tagung für Forschung mit Synchrotronenstrahlung, Neutronen und Ionenstrahlen an Großgeräten 2006, Hamburg

Röntgenkleinwinkelstreuung unter streifendem Einfall von dünnen, lamellaren Diblockcopolymerfilmen in der Bornschen Näherung mit gestörten Wellen 04.-06.10.06

J. Perlich, Y. Cheng, M. Memesa, J. S. Gutmann, S. V. Roth, P. MÎler-Buschbaum GISAXS investigation of sol-gel templated nanocomposite films Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Großen 2006, Universität Hamburg, 04. - 06. 10. 2006

W. Potzel, A.L. Kholmetskii, U. van Bürck, R. Röhlsberger, E. Gerdau Neutrino 2006, Santa Fe (USA) *Experiment for Discrimination between Special Relativity Theory and Covariant Ether Theories*

13.-19.06.2006

W. Schirmacher, 2nd International Workshop on Dynamics in Viscous Liquids, Mainz, 9. -12. 4. 2006 Dynamics of Less Viscous Liquids as Described by Mode-Coupling Theory

W. Schirmacher, Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an Grossgeräten, Hamburg, 4. - 6. 10. 2006 Acoustic Attenuation in Glasses and its Relation to the Boson Peak

W. Schirmacher, IV. Workshop on Non-Equilibrium Phenomena in Supercooled Flueds, Glasses and Amorphous Materials, Pisa, 17. - 22. 9. 2006 Acoustic Attenuation in Glasses and its Relation to the Boson Peak

R. Schützhold, U. van Bürck, D. Habs ELI Workshops, MPQ-LMU Garching Nuclear multi-exciton states: theory and experiments 13.-14. 11. 2006

I. Sergueev, U. van Bürck, A.I. Chumakov, T. Asthalter, R. Rüffer 2nd Int. Workshop on Dynamics in Viscous Liquids, Mainz *The non-translational origin of the slow* β *relaxation* 10. 04. 2006

I. Sergueev, T. Asthalter, U. van Bürck, A.I. Chumakov, C. Strohm, R. Rüffer, G.V. Smirnov, W. Petry SNI2006, Hamburg *SRPAC: Basic Features and First Applications* 04.-06. 10. 2006 S. Stüber, S. Mavila Chathoth, A. Meyer, J. Horbach, M. M. Koza Influence of chemical short-range order on atomic diffusion in Al-Ni melts JCNS Symposium and European User Meeting Forschungszentrum Jülich 16. - 17. 2. 2006

S. Stüber, A. Meyer, T. Unruh
Diffusion in Al₄Ni melts, by inelastic neutron scattering
Deutsche Tagung für Forschung mit Synchrotronstrahlung, Neutronen und Ionenstrahlen an
Großgeräten Hamburg 4. - 6. 10. 2006

U. van Bürck, F.E. Wagner 6th Seeheim Workshop on Mössbauer Spectroscopy, Seeheim *Mössbauer spectroscopy on subfossil oak* 07.-11. 06. 2006

Invited talks at E13

Dr. Katharina Vollmeyer-Lee, Universität Göttingen Collective single-particle jumps below the glass transition: a computer

Fan Zhirong, Universität Halle *Thermal isomerisation of alternating maliec acid copolymer*

Dr. Dimitri Khoshtariya, Universität Erlangen Local hydrogen-bonded structures in bulk water under variable temperature and pressure and at the protein surface from NIR/IR spectroscopic studies

Hussein Akbari, Technische Universität Kiel Correlation between morphologie and composition in fine compounds

Dr. Petr Stephanek, Institute of Macromolecular Chemistry Prag Self-organized nanostructure in multicomponent polymer systems: structure and dynamic properties

Prof. Dr. L. Dubrovinsky, Bayerisches Geoinstitut, Universität Bayreuth Chemistry at extreme conditions: from geosciences to synthesis of new materials

Prof. Dr. Alfons Schulte, University of Central Florida, Orlando Waveguide structures as subtrates and guiding layers for evanescent wave raman spectroscopy of bacteriorhodopsin

Sahid Ullah Uhan, Universität Kiel *TiO*₂ nanostructures

Dr. Jean-Francois Moulin, CNR Instituto per lo Studio degli Materiali Nanostrutturati Organic semiconductor thin films: growth and pattering

N. Shingue, Universität Halle Crystalization of PVDF in 2 D confinement

A. Chumakov, Everything you always wanted to know about vibrational dynamics of glasses Gunar Kaune, Universität Chemnitz Indium-thin oxide films as prepared by sputtering

Prof. Ralf Stannarius, Otto-von-Guericke-Universität Magdeburg Stucture and dynamics of free standing liquid crystalline films

Prof. Günter Reiter, Universität Mulhouse Morphologies of polymer crystals in thin films

Weinan Wang, PSI Villingen Adhäsion enhancment between polymer films and inert metal by low energy ion treatment

A. Kloke, ETH Zürich Single crystals of functionalized acenes

Dr. Gabi Cantea, Universtät Bayreuth Shear-induced alignment in block copolymer solution

Jun Quian, Ruhr-Universität Bochum Preperation of carbon fibers by chemical vapor deposition

Zhenyu Di, Universtät Giessen Development and application of an Otho-Time of Flight Mass Spectrum Meter for the Shiptrap exotic nuclei mass measurement

Funding

Deutsche Forschungsgemeinschaft

Untersuchung des Einflusses der atomaren Dynamik auf Materietransport, Segregation und Erstarrung mehrkomponentiger Schmelzen Förderkennzeichen: Me 1958/2-2, Folgeprojekt ME 1958/2-3 Leiter: Prof. Andreas Meyer

Inelastische Neutronenstreuung bei hohen Temperaturen und Drücken zur Aufklärung der Lösungs- und Transportmechanismen von Wasser in wasserhaltigen Silikatschmelzen Förderkennzeichen: ME 1958/8-2 Leiter: Prof. Andreas Meyer

Im Rahmen des SFB 533 "Lichtinduzierte Dynamik von Biopolymeren": *Zeitaufgelöste Kalorimetrie an lichtinduzierten Prozessen in Proteinen* Förderkennzeichen: SFB533 - 3001748 Leiter: PD Wolfgang Doster

Im Rahmen des DFG priority program SPP 1164: Non-equilibrium flow in nanoscale geometrics: Influence of confinement and surface functionality Förderkennzeichen MU 1487/2-1 Leiter: Prof. Peter Müller-Buschbaum Im Rahmen des DFG priority program SPP 1164: Non-equilibrium flow at gradient surface: multi-component fluids" Förderkennzeichen: MU 1487/2-2 Leiter: Prof. Peter Müller-Buschbaum

Quellverhalten von dünnen Polymerfilmen: Struktur, Kinetik und Dynamik Förderkennzeichen: MU 1487/4-2 Leiter: Prof. Peter Müller-Buschbaum

Im Rahmen des DFG priority program SPP 1164: Nanostrukturierte Filme aus selbstkapselnden anorganisch-organischen Hybridmaterialien Förderkennzeichen: MU 1487/5-1 Leiter: Prof. Peter Müller-Buschbaum

Im Rahmen des DFG priority program SPP 1259: *Struktur und Kinetik stimuli-responsiver, dünner Hydrogenfilme aus amphiphilen Block copolymern* Förderkennzeichen: MU 1487/8-1 Leiter: Prof. Peter Müller-Buschbaum

Einfluss von Grenzflächeneffekten auf die Adhäsion weicher Polymere Förderkennzeichen: MU 1487/6-1 Leiter: Prof. Peter Müller-Buschbaum

In the SFB 563 'Bioorganische Funktionssysteme auf Festkörperoberflächen': Untersuchung der Struktur und des Wachstums von Proteinfibrillen immobilisiert auf Festkörperoberflächen Förderkennzeichen: SFB 563 TP A10 Leiter: Prof. Christine Papadakis

Thin films of crystalline diblock copolymers: Crystalline and mesoscopic structures and their macroscopic alignment Förderkennzeichen: Pa 771/3-2 Leiter: Prof. Christine Papadakis

In the DFG priority program: SPP1259 'Intelligente Hydrogele' Struktur und Kinetik stimuli-responsiver, dünner Hydrogelfilme aus amphiphilen Blockcopolymeren Förderkennzeichen: Pa 771/4-1 Leiter: Prof. Christine Papadakis

Im Graduiertenkolleg 'Materials Science of Complex Interfaces': *Strukturelle Änderungen in nanostrukturierten Blockcopolymerfilmen* Leiter: Prof. Christine Papadakis

Magnetic, magnetoelastic and dynamical properties of martensitic Heusler alloys - Teilprojekt Neuhaus-Förderkennzeichen: NE 1405/1-1 Leiter: Dr. Jürgen Neuhaus

Steigerung der Berechnungsgenauigkeit der Eigenspannungsverteilung im Aluminiumformguss mittels Neutronendiffraktometrie Förderkennzeichen: PE 580/6-2 Leiter: Dr. Michael Hofmann

Bundesministerium für Bildung und Forschung

ESRF: Methodische Entwicklungen zum SRPAC Spektrometer: Gestörte Winkelkorrelationen mit Synchrotronstrahlung Förderkennzeichen 05KS1WOC/3 Leiter: Dr. Uwe van Bürck, Prof. Andreas Meyer

Wechselwirkung von Polymermatrizen mit magnetischen Nanostrukturen und Studium der magnetischen Eigenschaften Förderkennzeichen 03DU03MU Leiter: Prof. Peter Müller-Buschbaum

Bau eines thermischen Dreiachsenspektrometers am FRM-II Förderkennzeichen 03EC5SRM/1 Leiterin: Dr. Claudia Hradil

Others:

FuE-Vertrag mit der Henkel KGaA: Konstruktion einer Messapparatur und Entwicklung einer Methode zur Bestimmung spezifischer Haftklebeeigenschaften von Klebebändern Leiter: Prof. Peter Müller-Buschbaum

9 The chair

Diploma and PhD thesis

Accomplished diploma thesis

Leander Schulz Magnetische Nanopartikel in dünnen Polymerfilmen

Accomplished PhD thesis

Panteleimon Panagiotou Selbstorganisation und Strukturbildung multiskaliger Polymermischungsfilme November 2006

Staff and guests

Chair: Univ.-Prof. Dr. Winfried Petry

Head: Prof. Dr. Andreas Meyer (until August 2006) Head: Prof. Dr. Peter Müller-Buschbaum (from September 2006)

Fellows

Dr. Ezzeldin Metwalli Ali PD Dr. Wolfgang Doster Dr. Ana Gaspar Dr. Ruzha Ivanova Dr. Volker Körstgens Dr. Valeria Lauter-Pasyuk (ILL) Dr. Emmanuel Longueteau PD Dr. Peter Müller-Buschbaum Dr. Jürgen Neuhaus (FRM II) Prof. Dr. Christine Papadakis PD Dr. Walter Schirmacher Dr. Cornelius Strohm Dr. Tobias Unruh (FRM-II) Dr. Uwe van Bürck

PhD students

Mottakin Abul Kashem Tune Bonne Charles Darko Zhenyu Di Ronald Gebhardt Florian Kargl Tarik Mehaddene Andreas Meier-Koll Panteleimon Panagiotou Jan Perlich Sebastian Stüber Weinan Wang Fan Yang

Diploma students

Sebastian Busch Matthias Ruderer Bernhard Schmid Leander Schulz

Students assistants

Stefan Aschauer Katharina Diller Rosemarie Hengstler Christina Loose Martin Niedermeier

Technical/administrative staff

Ricarda Baumhoer Joachim Dörbecker Elke Fehsenfeld (August 2006) Reinhold Funer Josef Kaplonski Dieter Müller Jandal Ringe (FRM-II) Cornelia Simon Max Wittich (Juli 2006) Lukas Hein (September 2006)

Guests

Prof. Dr. Gennadi Smirnov, Russian Research Center Kurchatov Institute (August-September 2006)

Prof. Dr. Alfons Schulte, University of Central Florida (June 2006)