Annual Report 2007

Chair of Experimental Physics Prof. Dr. Winfried Petry



Physik-Department E13

Technische Universität München

Prof. Dr. Winfried Petry Chair of experimental physics IV Physik-Department E13

Deputy chairman for Prof. Petry: Prof. Dr. Peter Müller-Buschbaum

Physik-Department E13 Technische Universität München James-Franck-Straße 1 85747 Garching

Sekretariat: Petra Douglas

Tel.: 089 289 12452 Fax: 089 289 12473

Email: peter.mueller-buschbaum@ph.tum.de Petra.Douglas@ph.tum.de http://www.e13.ph.tum.de

Title picture:

The tandem Fabry-Perot experiment is getting its first light just before the end of the year after a major upgrade over the last couple of months. Due to old age, the Ar laser had to be replaced by a solid state Nd:YAG laser and the chance was taken to overhaul the whole instrument as well (see reports 6.2 and 6.3). The center of the image shows the new sample cell during testing.

Preface

It is a great pleasure to present the 2007 annual report of the chair E13 at the Physics Department of TU München. Our research activities cover a broad range from soft matter physics to instrumental and methodical developments. We examine the physical fundamentals of material properties using, among others, scattering methods (neutron, x-ray and light scattering). The general goal of our research is to understand the functional characteristics of condensed matter from the knowledge of the microscopic dynamics and structure.

In 2007 we extended our research activities to cover the fields of water-based polymer systems, polymer thin films, polymer hybrid systems, biopolymers and solid state dynamics in the soft matter area. Accompanied with this extension was an increase in funding, instrumentation and chair members. In 2007 the chair E13 comprised 17 fellows, 15 PhD students, 4 diploma students, 1 bachelor student, 7 student assistants and 11 administrative and technical staff members. Newly obtained instruments were a white-light interferometer, a second imaging ellipsometer coupled with a second atomic force microscope and an home-built highpressure and high-temperature cell. In the last quarter of 2007 the refurbishment of the E13 light scattering laboratory was started by Dr. Johannes Wiedersich who is newly heading this laboratory. In addition to the activities in the E13 laboratories, the instrument TOF-TOF at the research reactor FRM-II was operated and upgraded.

Several scientific workshops and symposia were organized by E13 members in 2007. Prof. Schirmacher organized the 31th Edgar-Lüscher-Seminar in Zwiesel as well as vocational training in Dillingen. Prof. Papadakis organized an information lecture for female scientists. In the framework of the spring meeting of the Division Condensed Matter of the Deutsche Physikalische Gesellschaft (DPG) Prof. Müller-Buschbaum organized a special symposium on "Bio-inspired Materials" together with Prof. Dr. Eduard Arzt (MPI für Metallforschung Stuttgart) and Prof. Dr. Peter Fratzl (MPI Potsdam) and a second special symposium on "Scattering experiments on soft-condensed matter systems – new techniques and experimental possibilities" together with Prof. Dr. Thomas Thurn-Albrecht (Universität Halle) in Regensburg. Moreover, he organized jointly with Dr. Stephan Roth (HASYLAB) and Dr. Rainer Gehrke (HASYLAB) the second workshop on "GISAXS – an advanced scattering method" in Hamburg and a first Bilateral Colloquium TUM- HASYLAB entitled "The polymer-metal interface (Real-time observation of metal-on-polymer deposition kinetics)" at the TU München. All E13 members were very active at conferences and workshops, participating with talks and posters.

Regarding teaching activities of E13 we covered a large part of the export lectures: mechanical engineering (Prof. Müller-Buschbaum), teaching at colleges BT / ET / MT / EI (Prof. Papadakis) and teaching at colleges AW / EH / PF (PD Doster). Prof. Papadakis was the women's representative of the Physics Department.

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 2008.

Contents

1	Water-based polymer systems					
	1.1	Influence of polymer architecture of amphiphilic poly(2-oxazoline) copolymers on the aggregation and aggregate structure	7			
	1.2	Role of the tracer in characterizing the aggregation behavior of aqueous block				
		copolymer solutions using fluorescence correlation spectroscopy	9			
	1.3	Micellar structures of hydrophilic-lipophilic and hydrophilic-fluorophilic poly(2-oxazoline) diblock copolymers in water	11			
	1.4	Multicompartment hydrogels from lipophilic-hydrophilic-fluorophilic triblock copolymers	13			
	1.3	hydrophilic block	14			
	1.6 1.7	Stimuli-sensitive self-organized triblock copolymer micelles	16			
		carbonate	18			
2	Polymer thin films 21					
	2.1	Surface enrichment in statistical copolymer films	21			
	2.2	Pressure sensitive adhesive blend films for low tack applications	23			
	2.3	Nanostructuring of thin semiconducting polymer films for photovoltaic appli- cations	25			
	2.4	In-situ neutron reflectometry probing competitive swelling and de-swelling of thin polystyrene films	27			
	2.5	Structural changes of thin block copolymer films during solvent vapor treatment	29			
	2.6	Distinct kinetic regimes in a lamellar diblock copolymer thin film during solvent vapor uptake	31			
	2.7	Improving the lateral long-range order in block copolymer films by thermal annealing	34			
	2.8	Thin films of diblock copolymers having one crystalline block	36			
	2.9	Break-away crystallization in thin films of cylinder-forming PI- <i>b</i> -PEO diblock	• •			
	2.10	copolymers Structured organic solar cells	38 40			
3	Polymer hybrid systems 42					
U	3.1	Influence of maghemite nanoparticles on the microphase separated nanostruc-				
		tures in cylinder forming P(S-b-MMA) copolymer films	42			
	3.2	Magnetic properties of magnetic nanoparticles in a copolymer matrix	44			
	3.3	In-situ observation of nanoparticle ordering at the air-water-substrate bound-				
		ary in colloidal solutions using X-ray nanobeams	47			
	3.4	In situ GISAXS study of gold sputtering onto a polymer template	49			
	3.5	Structure of gold films as contact material in organic photovoltaic devices	51			
	3.6	Combinatorial investigation of nanostructures formed in a titanium dioxide based nanocomposite film on top of fluor-doped tin oxide layers	53			
	0.7	nanocomposite films	56			

4	Bio-	polymers	59		
	4.1	The influence of medium pressure on global and internal dynamics of human			
		hemoglobin: observation by quasielastic neutron scattering	59		
	4.2	Separation of coherent and spin-incoherent neutron scattering from protein			
		samples by polarization analysis	60		
	4.3	Water vapour induced swelling of thin casein films	63		
	4.4	Micellar structure of casein investigated by μ GISAXS	65		
	4.5 4.6	Effect of calcium concentration on the structure of casein micelles in thin films . Dynamics of phospholipids in stabilizing monolayers investigated by	67		
	4.7	Water-uptake in biocompatible hydrogel films: Neutron reflectivity study	70		
	4.8	Conformational and structural changes of thin films from recombinant spider silk proteins upon post-treatment with methanol	72		
5	Solid state dynamics 75				
	5.1	Mode-coupling description of the dynamics of simple liquids	75		
	5.2	Vibrational excitations in systems with correlated disorder	77		
	5.3	Theory of low-frequency Raman scattering in disordered solids	78		
	5.4	Low-frequency vibrational excitations in niobium-phosphate glasses for Ra-			
		man gain application	81		
	5.5	Rotational dynamics of methyl groups in pentafluorotoluene and pentafluo-	0.0		
	- (83		
	5.6	Self-diffusion measurements of medium-chain molecules at IOFIOF	85		
	5./ E 0	Structure and dynamics in Ni Zr	87 80		
	5.0 5.0	Structure and dynamics in $N_{36} Zr_{64}$	09		
	5.9	fields	91		
	5.10	Mößbauer spectroscopy and nuclear inelastic scattering studies on a polynu-	1		
	0.10	clear oxo-bridged iron catalyst - first results	93		
6	Inst	rumental and methodical developments	97		
	6.1	Status of the instrumentation at the Forschungsneutronenquelle Heinz Maier-			
		Leibnitz (FRM II)	97		
	6.2	Upgrade of the tandem Fabry-Perot interferometer	98		
	6.3	Characterisation of the upgraded Fabry-Perot interferometer	100		
	6.4	Implementation and testing of a GISAXS fluidic cell	102		
	6.5	Time-of flight grazing incidence small angle neutron scattering	104		
	6.6	Spectral fluence rates of the fast neutron beam MEDAPP at FRM II	106		
	6.7	Heavy ion bombardment of UMo/Al dispersionn fuel	109		
	0.ð	Influence of microstructural parameters on macro residual stress analysis	110		
	0.9	Manufacturing of monolithic U-Mo test fuel plates by cathode erosion	112		
7	Outreach 115				
	7.1	Electronic repository of student's problems	115		
	7.2	Report of the women's representative of the Physics Department	117		

6 Physik-Department E13 Annual Report 2007

8	Teaching and conferences					
	8.1	Lectures, seminars and lab courses	118			
	8.2	Conferences	119			
9	Publications, talks and funding					
	9.1	Publications	146			
	9.2	Talks given by members of E13	150			
	9.3	Poster	159			
	9.4	Invited talks at E13	164			
	9.5	Funding	165			
10	The	chair	168			
	10.1	Graduations	168			
	10.2	Staff	168			
	10.3	Guests	169			

1 Water-based polymer systems

1.1 Influence of polymer architecture of amphiphilic poly(2-oxazoline) copolymers on the aggregation and aggregate structure

T. B. Bonné, K. Lüdtke¹, R. Jordan¹, P. Štěpánek², C. M. Papadakis

- ¹ Lehrstuhl für Makromolekulare Stoffe, Department Chemie, TU München
- ² Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague

Micelle formation is frequently encountered in amphiphilic block copolymers in aqueous solution [1]. The critical micelle concentrations (CMC's) are typically low $(10^{-8} - 10^{-2} \text{ M})$, and above this concentration, micelles of core-shell type are formed. The architecture of the block copolymers (e.g. diblock, triblock or random copolymers) has a strong influence on the size and structure of the micelles because the polymers tend to optimize both, the hydrophobic interaction and the entropic contributions related to stretching or coiling.



Figure 1.1:

(a) Structure of a 2-oxazoline monomer. Chosing methyl or *n*-nonyl for the side group *R* leads to hydrophilic or hydrophobic monomers MOx and NOx, respectively. (b) Normalized FCS intensity autocorrelation functions of aqueous solutions of the triblock copolymer P(MOx₂₀-*b*-NOx₇-*b*-MOx₁₄) (the subscripts denote the degrees of polymerizations) at polymer concentrations 1×10^{-8} M (\blacktriangle), 1×10^{-6} M (\bigtriangleup), 1×10^{-5} M (\blacktriangledown), and 6×10^{-4} M (\bigtriangledown).

We have studied poly(2-oxazoline) copolymers which offer the possibility to tailor amphiphilic polymers of comparable composition but different polymer architecture (Fig. 1.1a). For poly(2-alkyl-2-oxazoline)s, the water solubility can be controlled by altering the nature of the substitution in the 2-position. In case of long alkyl chains such as *n*-nonyl, the monomer unit is of amphiphilic nature with the structure of a non-ionic polysoap with at polar backbone and a water-insoluble side group. The aggregation behavior of copolymers containing both, water-soluble and soap-like monomers, is thus expected to be more complex than the one of the usual copolymers with water-soluble and water-insoluble monomers.

We present here results from aqueous solutions of ABA triblock copolymers, P(MOx-*b*-NOx-*b*-MOx) (MOx and NOx stand for 2-methyl-2-oxazoline and 2-*n*-nonyl-2-oxazoline, respectively), AB diblock copolymers, P(MOx-*b*-NOx), and a gradient copolymer, P(NOx-*g*-MOx), with the focus on the CMC and the hydrodynamic radii of the solubilized unimers and the aggregates [2,3]. The polymers were synthesized using living cationic polymerization. All copolymers were of low molar mass (4000 - 6300 g/mol) and had similar volume fractions of

NOx (0.27-0.43). A fraction of these polymers had been fluorescence-labeled with tetramethylrhodamine isocyanate (TRITC). This enabled us to carry out tracer diffusion measurements with fluorescence correlation spectroscopy (FCS) using the identical, fluorescence-labeled polymers as tracers. In this way, a large concentration range could be covered $(10^{-8} - 10^{-3} M)$.



Figure 1.2:

Sketch of the micelles formed by (a) diblock, (b) triblock and (c) gradient copolymers. The circles indicate the surfaces of the micellar core and the micellar shell, respectively. The thick gray lines repesent the hydrophilic backbone and the thin black lines the *n*-nonyl side groups. For clarity, only a single polymer is shown per micelle, even though they consist of a number of polymers.

We have found that the aggregation behavior of di- and triblock copolymers is very similar: The FCS intensity autocorrelation functions show a single, fast decay below the CMC – in this case $3 \pm 2 \times 10^{-6}$ M – and an additional slower decay above (Fig. 1.1b). As expected, the CMC of a triblock copolymer with identical NOx block, but longer hydrophilic MOx blocks, P(MOx₃₀-*b*-NOx₇-*b*-MOx₂₆) is, within the uncertainty, the same: The CMC largely depends on the degree of polymerization of the hydrophobic block. From the diffusion times deduced from the autocorrelation functions, the hydrodynamic radii of the unimers and the micelles were found to be ~ 1 nm and ~ 6 nm, respectively, for both triblock copolymers. As expected from the steric demands, the micelles are a factor of two smaller the ones formed by diblock copolymers having similar block molar masses [2] (Fig. 1.2a,b).

A P(MOx₄₀-*g*-NOx₆) gradient copolymer shows a distinct CMC as well – $8 \pm 3 \times 10^{-6}$ M – and aggregates having a hydrodynamic radius of ~ 5 nm, i.e. much smaller than the ones formed by the corresponding diblock copolymers. We suggest that these micelles are not of coreshell type, but rather the *n*-nonyl side groups aggregate with the polymer backbone partly wrapping around (Fig. 1.2c). The relatively high value of the CMC points to a stabilization of the unimers, possibly due to intramolecular aggregation of the *n*-nonyl side groups.

We conclude that FCS is a sensitive method which allows to characterize the aggregation behavior of amphiphilic polymers in dependence of polymer architecture. The use of fluorescence-labeled polymers being identical to the ones under study allows the reliable determination of very low CMC's and to determine hydrodynamic radii of unimers and aggregates.

This project was funded by DFG (Pa 771/2-1).

- [1] P. Alexandridis, B. Lindman (Eds.): *Amphiphilic block copolymers: Self-assembly and applications*, Elsevier, Amsterdam (2000)
- [2] T. B. Bonné, K. Lüdtke, R. Jordan, P. Štěpánek and C. M. Papadakis, Coll. Polym. Sci. 282, 833 (2004)
- [3] T. B. Bonné, K. Lüdtke, R. Jordan and C. M. Papadakis, Macromol. Chem. Phys. 208, 1402 (2007)

1.2 Role of the tracer in characterizing the aggregation behavior of aqueous block copolymer solutions using fluorescence correlation spectroscopy

T. B. Bonné, K. Lüdtke¹, R. Jordan¹, C. M. Papadakis

¹ Lehrstuhl für Makromolekulare Stoffe, Department Chemie, TU München

Fluorescence correlation spectroscopy (FCS) allows the determination of diffusion coefficients of fluorescent molecules in solution by measuring their average diffusion times through the detection volume, which is as small as $\sim 1 \,\mu m^3$ [1]. By means of the Stokes-Einstein equation, the hydrodynamic radii of the molecules or their aggregates can be determined. To maximize the relative intensity fluctuations, low concentrations of the fluorescent molecules (below $\sim 1 \,\mu M$) are required. In solutions of amphiphilic copolymers, however, a concentration range over several orders of magnitude needs to be investigated to characterize their complex phase behavior, e.g. the unimer-to-micelle transition and gel formation. This can be realized by carrying out tracer experiments with fluorescence-labeled molecules as tracers in a solution of non-labeled polymers.

We focus here on the choice of the tracer. Commercially available, low-molecular fluorescent dyes, which are poorly water-soluble, have previously been used as tracers for determining the critical micelle concentration (CMC) and micellar hydrodynamic radius of amphiphilic block copolymers in solution [2]. However, when increasing the polymer concentration from the unimer to the micellar regime, instead of the usually observed sharp CMC a broad transition range was observed with the micellar size increasing with polymer concentration.



Figure 1.3: Structures of Rh6G (a) and of P(NOx₁₀-*b*-MOx₃₂)-TRITC (b).

In order to clarify the role of the tracer, we have used as tracers both, a low-molecular fluorescent dye and an amphiphilic diblock copolymer identical to the one under study, which was fluorescence-labeled at the hydrophilic terminus. In our previous detailed study on an amphiphilic diblock copolymer [3], poly((*n*-nonyl-2-oxazoline)₇-*b*-(2-methyl-2-oxazoline)₄₀), P(NOx₇-*b*-MOx₄₀), in aqueous solution using the identical, fluorescence-labeled diblock copolymer as a tracer, we have found a sharp CMC. Above the CMC, micelles having a concentration-independent hydrodynamic radius were observed using FCS, which was identical to the one found in dynamic light scattering (DLS) experiments on the non-labeled polymers. This system is thus an ideal model system to determine the role of the tracer.

The system chosen was a poly((*n*-nonyl-2-oxazoline)₁₀-*b*-(2-methyl-2-oxazoline)₃₂), P(NOx₁₀*b*-MOx₃₂), diblock copolymer in aqueous solution in a concentration range of $10^{-8} - 10^{-2}$ M [4]. In analogy with P(NOx₇-*b*-MOx₄₀), P(NOx₁₀-*b*-MOx₃₂) is expected to show a sharp unimer-to-micelle transition at the critical micelle concentration (CMC). As a low molar mass tracer, rhodamine 6G (Rh6G) was chosen (Fig. 1.3a). The Rh6G concentration in the polymer solutions was kept below 10^{-8} M. As a polymeric tracer, P(NOx₁₀-*b*-MOx₃₂) labeled with tetramethylrhodamine isocyanate (TRITC) was used, i.e. P(NOx₁₀-*b*-MOx₃₂)-TRITC (Fig. 1.3b). Its concentration in the polymer solution was kept below 10^{-6} M.



Figure 1.4:

(Apparent) hydrodynamic radii as a function of polymer concentration as determined by FCS on $P(NOx_{10}-b-MOx_{32})$ using different tracers. (\circ) Solutions containing only labeled copolymers. (\bullet Solutions containing both non-labeled and labeled copolymers. (\star) Solutions containing non-labeled copolymers and Rh6G. (\bigstar) DLS results on non-labeled copolymers.

The (apparent) resulting hydrodynamic radii of the unimers and micelles are given in Fig. 1.4. Using the polymeric tracer, unimers of a size of 1.3 ± 0.2 nm are observed below a concentration of $(11 \pm 7) \times 10^{-6}$ M, the CMC. Above, micelles are present as well, having a concentration-independent hydrodynamic radius of 11.3 ± 0.9 nm. These results are in line with the ones obtained with P(NOx₇-*b*-MOx₄₀). Using Rh6G as a tracer, it is found that only monomeric Rh6G is present below the CMC. Above, micelles are observed as well, but their hydrodynamic radius apparently increases and reaches the value determined with the labeled copolymers and with DLS only ~ 2 decades above the CMC.

Since this increase is neither observed with the polymeric tracers nor with DLS on non-labeled copolymers, it must be related to the nature of the low-molecular dye. We attribute the apparent increase of the micellar size to the fast exchange of the dye between the micelle and the aqueous surrounding: During the diffusion of the micelle through the FCS detection volume, the dye is attached to the micelle only for a certain fraction of time and it is free for the remaining time fraction. In a concentration range just above the CMC, the probability that the dye is attached to a micelle is decreased because the number of micelles is low.

We conclude that by means of commercially available, low-molecular dyes, the CMC can be determined reliably, however, the micellar size is only recovered far above the CMC. This project was funded by DFG (Pa 771/2-1).

- R. Rigler, E. Elson (Eds.): *Fluorescence correlation spectroscopy. Theory and applications*, Springer, Berlin (2000) S.T. Hess, S. Huang, A.A. Heikal, W.W. Webb, Biochemistry 41, 697 (2002)
- [2] H. Schuch, J. Klingler, P. Rossmanith, T. Frechen, M. Gerst, J. Feldthusen, A.H.E. Müller, Macromolecules 33, 1734 (2000). K. Loos, A. Böker, H. Zettl, M. Zhang, G. Krausch, Macromolecules 38, 873 (2005)
- [3] T. B. Bonné, K. Lüdtke, R. Jordan, P. Štěpánek and C. M. Papadakis, Coll. Polym. Sci. 282, 833 (2004)
- [4] T. B. Bonné, C. M. Papadakis, K. Lüdtke, R. Jordan, Coll. Polym. Sci. 285, 491 (2007)

1.3 Micellar structures of hydrophilic-lipophilic and hydrophilic-fluorophilic poly(2-oxazoline) diblock copolymers in water

R. Ivanova, T. B. Bonné, T. Komenda¹, K. Lüdtke¹, R. Jordan¹, K. Mortensen², P. K. Pranzas³ and C. M. Papadakis

- ¹ Department Chemie, TU München
- ² Department of Natural Sciences/Biophysics, Copenhagen University, Denmark
- ³ Institut für Werkstoffforschung, GKSS-Forschungszentrum Geesthacht

Amphiphilic block copolymers associate in aqueous solution reversibly into micelles, similar to low molar mass amphiphiles (e.g. [1]). Whereas the aggregation behavior of hydrophilic-hydrophobic copolymers is well studied, reports on amphiphilic polymers containing fluorophilic moieties are still rare. What is more, the presence of fluorophilic moieties in the polymer structure offers the possibility to achieve the superstrong-segregation regime at low degrees of polymerization, which is of fundamental as well as practical interest, e.g. in designing multicompartment micelles or gels. Poly(2-oxazoline)s are a very versatile system to study the aggregation behavior as a function of the polymer architecture and the hydrophilic-lipophilic balance since a broad variety of tailored copolymers with diverse architectures and block solubilities can be synthesized by varying the substitution in the 2- position of the 2-oxazoline monomer unit [2].

We have studied in detail the micellar structure in aqueous solutions of two poly(2oxazoline) diblock copolymers, a lipophilic-hydrophilic poly[(2-*n*-nonyl-2-oxazoline)₁₀-*b*-(methyl-2-oxazoline)₃₂], P(NOx₁₀-*b*-MOx₃₂), and a hydrophilic-fluorophilic poly[(2-(methyl-2-oxazoline)₄₀-*b*-(2-(1'H,1'H,2'H,2'H-perfluorohexyl)-2-oxazoline)₆)], P(MOx₄₀-*b*-FOx₆). The subscripts denote the number-average degrees of polymerization of the blocks. These copolymers have almost identical block lengths, and differ only in the chemical nature of the hydrophobic segment, thus enabling the study of the influence of the perfluorinated side chains on the internal structure of the equilibrium micelles. By means of small angle neutron scattering (SANS) using mixtures of D₂O and H₂O in order to contrast-match either block, we have determined the size and the shape of the micellar core and corona separately. In addition, the micelles formed by P(MOx₄₀-*b*-FOx₆) were visualized using transmission electron microscopy (TEM).

Upon dissolution in water at room temperature, $P(NOx_{10}-b-MOx_{32})$ diblock copolymer forms large aggregates (hydrodynamic radius of ~ 140 nm) in addition to the micelles confirming our previous fluorescence correlation spectroscopy (FCS) and photon correlation spectroscopy (PCS) results [3]. 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 equilibrium micelles (hydrodynamic radius of 11-13 nm) remain. The equilibrium micelles are of core- shell type and have a spherical shape as evidenced by the symmetric shape of the distance distribution function [4] (Fig. 1.5).

Comparing the core radius determined to 2.6 nm to the estimated fully stretched backbone length of the NOx_n block (3.7 nm) and to the unperturbed radius of gyration (1.2 nm), we conclude that the core NOx_n block is stretched. The corona thickness of 3.9 nm is significantly lower than the fully stretched MOx₃₂ backbone length of 12.2 nm, which means that the MOx₃₂ block is rather coiled than stretched. Therefore, the brush model of grafted, flexible, neutral polymer chains in good solvent by Alexander and de Gennes [5] is more suitable to describe the conformation of the corona blocks. Indeed, the thickness of the polymer brush



Figure 1.5:

SANS intensity profiles together with the distance 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 distance distribution functions were calculated following the method of Glatter [4].

estimated to 3.8 nm is very close to the corona thickness, which indicates that the MOx_n blocks adopt a polymer brush conformation.

The chain stretching of the core block is due to the sterically demanding *n*-nonyl side groups and hence, the large conformational asymmetry of the diblock copolymer. The NOx_n block is stiff due to its bulky *n*-nonyl side chains, whereas the MOx_n block is much more flexible. Hence, the MOx_n block will tend to coil and the NOx_n block has to stretch to meet the geometrical limits.

In contrast to $P(NOx_{10}-b-MOx_{32})$, the core-shell micelles formed by the hydrophilic-fluorophilic $P(MOx_{40}-b-FOx_6)$ diblock copolymer are elongated as evidenced by the asymmetric shape of the pair distribution functions (Fig. 1.5). This is possibly due to the higher stiffness of the perfluorinated side chains forcing the FOx_n backbone to strongly stretch. Another possibility is the strong segregation of the FOx_n block from the environment, i.e. the transition into the superstrong- segregation regime, where non-spherical micelles have been theoretically predicted.

The radius and the length of the FOx_6 core amount to 3.7 nm and 13 nm. The micellar core radius is thus relatively large, indicating strong backbone stretching of the fluorophilic core block. The corona thickness is 1.5 nm, which is significantly smaller than the 6.9 nm estimated for a brush formed by the MOx₄₀ corona block. We attribute this discrepancy to the strong

swelling of the corona blocks which is not well described by the hitherto used core-shell model with a sharp corona-solvent interface. The elongated shape of the $P(MOx_{40}-b-FOx_6)$ micelles as well as the core dimensions were confirmed by TEM micrographs.

We conclude that the structure of micelles from diblock copolymers containing a fluorinated hydrophobic block are more complex than the ones formed by diblock copolymers containing a lipophilic block.

This project was funded by DFG (Pa 771/2-1).

- I. W. Hamley, *The Physics of Block Copolymers*, Oxford Science Publications, Oxford (1998), Ch. 3, p. 131-220.
- [2] T. Komenda, R. Jordan, Polymer Preprints 44, 986 (2003).
- [3] T.B. Bonné, K. Lüdtke, R. Jordan, P. Štěpánek, C.M. Papadakis, Coll. Polym. Sci. 282, 833 (2004).
 T.B. Bonné, K. Lüdtke, R. Jordan, P. Štěpánek, C.M. Papadakis, Coll. Polym. Sci. 285, 491 (2007).
- [4] O. Glatter, J. Appl. Cryst. 10, 425 (1977) and 13, 577 (1980).
- [5] S. J. Alexander, Phys. Paris 38, 983 (1977). P. G. de Gennes, Macromolecules 13, 1069 (1980).

1.4 Multicompartment hydrogels from lipophilic-hydrophilic-fluorophilic triblock copolymers

R. Ivanova, T. Komenda¹, T. B. Bonné, R. Jordan¹, K. Mortensen², P. K. Pranzas³ and C. M. Papadakis

- ¹ Department Chemie, TU München
- ² Department of Natural Sciences/Biophysics, Copenhagen University, Denmark
- ³ Institut für Werkstoffforschung, GKSS-Forschungszentrum Geesthacht

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]: The amphiphilicity can be controlled by the choice of side groups (Fig. 1.6), and in aqueous solution, unimers, micelles or micellar hydrogels are formed, depending on the block copolymer architecture [2]. 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.



Figure 1.6:

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

We have used small-angle neutron scattering with contrast matching to study the structures of poly(2-oxazoline)-based micellar gels 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*-(2-(1'H,1'H,2'H,2'Hperfluorohexyl)-2-oxazoline)₉], P(NOx₁₂-*b*-MOx₆₄-*b*-FOx₉), triblock copolymers, the sizes



Figure 1.7:

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.

and shapes of the micelles formed by $P(NOx_{10}-b-MOx_{32})$ and $P(MOx_{40}-b-FOx_6)$ diblock copolymers in aqueous solutions of lower concentration were investigated (see previous report).

Furthermore, experiments on mixtures of micellar solutions of $P(NOx_{10}-b-MOx_{32})$ and $P(MOx_{40}-b-FOx_6)$ showed that the micelles formed by the two block copolymers do not mix but coexist as micelles with pure lipophilic or fluorophilic cores.

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. 1.7). Thus, the system forms a multicompartment gel.

This project was financially supported by the DFG (Pa 771/2-1).

- R. Jordan, K. Martin, H. J. R\u00e4dler, K. K. Unger, Macromolecules 38, 8858 (2001). T. Komenda, R. Jordan, Polymer Preprints 44, 986 (2003).
- [2] T.B. Bonné, K. Lüdtke, R. Jordan, P. Štěpánek, C.M. Papadakis, Coll. Polym. Sci. 282, 833 (2004).

1.5 The collapse transition of amphiphilic diblock copolymers with a responsive hydrophilic block

K. Troll, A. Kulkarni, W. Wang, C. Darko, A.M.Bivigou Koumba¹, A. Laschewsky¹, P. Müller-Buschbaum, C.M. Papadakis

¹ Institut für Chemie, Universität Potsdam

The collapse transition of polymers with lower critical solution temperature (LCST) behavior is of great interest for a number of purposes where a strong and fast change of volume is desired even for small changes of temperature, such as valves in microfluidics, but also for the release of drugs in the body or as sensors. A polymer which is a promising candidate in this context is poly(*N*-ispropylacrylamide), PNIPAM [1]. It exhibits a lower critical solution temperature (LCST) of about 32°C that is due to alterations in the hydrogen-bonding interactions of the amide group. Traditionally, chemically cross-linked hydrogels have been



Figure 1.8:

(a) Structure of P(S-*b*-NIPAM). (b) Hydrodynamic radii of (\circ) unimers and (\bullet) micelles from FCS as a function of polymer concentration in aqueous solution. (c) Thermogram of an aqueous solution having a concentration of 1.0 mg/ml, heating rate 0.5 K/min.





prepared which show significant macroscopic volume changes accompanied by the uptake and release of water [2].

However, the response times of such thermosensitive hydrogels decrease strongly with increasing size of the gel [3] and become too long for some applications. A recent trend in creating responsive, polymeric hydrogels is thus to decrease the size of the responsive units. For instance, the micelles formed by block copolymers from PNIPAM and one or two hydrophobic blocks constitute building blocks for responsive hydrogels which are only of the order of ~ 10 nm [4].

We present here a study of the self-assembly and the thermal behavior of a diblock copolymer from polystyrene (PS) as the hydrophobic block and PNIPAM as the responsive, hydrophilic block (Fig. 1.8a, Ref. 5). The molar masses of the PS and the PNIPAM block are 5000 and 18000 g/mol, the weight fraction of PNIPAM is thus 78 %. The critical micelle concentration (CMC) has been detected at 0.029 mg/ml (Fig. 1.8b): Below, unimers having a hydrodynamic radius of 1.0 nm are present in aqueous solution, whereas above, they coexist with micelles of a hydrodynamic radius of 40 nm. Using microcalorimetry, the LCST of the PNIPAM block in the micelle was found at 31.4°C (Fig. 1.8c), it is thus unchanged from the unimer state.

The mesoscopic processes following the LCST of the PNIPAM blocks have been characterized using DLS. The collapse transition of the micelles was recovered (Fig. 1.9a), and it was additionally found that, at temperatures above 40°C, clusters formed by the collapsed – and thus water-insoluble – micelles are present as well. The interaction between collapsed micelles far above the LCST is also revealed in the SAXS curves (Fig. 1.9b): Whereas up to 30°C, the curves are indicative of polydisperse micelles, above, a correlation peak together with forward scattering is observed. The sphere radius below the LCST is 19 nm, as estimated from a Guinier analysis. Above the LCST, the average distance between collapsed micelles is 20 nm, pointing to a collapsed micellar radius of 10 nm. The polymer behaves similar to the diblock copolymer described by Nuopponen et al. [4] having block molar masses of 8000 and 13600 g/mol for PS and PNIPAM, respectively, even though the latter has a lower PNIPAM weight fraction than our copolymer.

Knowledge of the thermal behavior of the single micelle is paramount for the understanding of the micellar gels formed at higher concentration.

This project was funded by DFG (Pa 771/4-1) within the priority progam SPP 1259 'Intelligente Hydrogele'.

- [1] H.G. Schild, Prog. Polym. Sci. 17, 163 (1992)
- [2] E. Sato, T. Tanaka, J. Chem. Phys. 89 1695 (1988). M. Shibayama, T. Tanaka, C.C. Han, J. Chem. Phys. 97, 6829 (1992)
- [3] T. Tanaka, E. Sato, Y. Hirokawa, S. Hirotsu, J. Peetermans, Phys. Rev. Lett. 55 2455 (1985)
- [4] M. Nuopponen, J. Ojala, H. Tenhu, Polymer 45, 3643 (2004). W. Zhang, X. Zhou, H. Li, Y. Fang, G. Zhang, Macromolecules 38 909 (2005)
- [5] K. Troll, A. Kulkarni, W. Wang, C. Darko, A.M. Bivigou Koumba, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis, Coll. Polym. Sci., accepted

1.6 Stimuli-sensitive self-organized triblock copolymer micelles

A. Kulkarni, K. Troll, W. Wang, C. Darko, S. Funari¹, A.M. Bivigou Koumba², A. Laschewsky², P. Müller-Buschbaum, C. M. Papadakis

- ¹ HASYLAB at DESY, Hamburg
- ² Institut für Chemie, Universität Potsdam

Stimuli-responsive polymers react strongly to even weak changes of their environment and are therefore of interest for a number of applications, such as drug delivery systems, sensors and micromechanics [1]. In many applications, chemically connected polymer networks have been used [2], which, however, have the disadvantage that the response time depends on the network size and may be too long. An alternative approach is based on physically connected (micellar) gels from amphiphilic block copolymers with a responsive hydrophilic block and a hydrophobic block [3]. They have the advantage that the micelles are much smaller than usual chemically connected microgels and that the gels can easily be reshaped.

Three triblock copolymers with polystyrene (PS) end blocks of molar mass 2 300 g/mol and a poly(*N*-isopropylacrylamide) (PNIPAM) middle block having different molar masses (20000 - 40000 g/mol) were studied. These polymers are water-soluble, hence micellar solutions and gels could be prepared by dissolving the polymers in deionized water (pH = 6). PNIPAM homopolymers shows lower critical solution (LCST) behavior and has an LCST temperature of 32°C. The solutions were investigated by dynamic light scattering (DLS), fluorescence correlation spectroscopy and synchrotron small-angle X-ray scattering (SAXS) at beamline A2 at HASYLAB, DESY.





The critical micelle concentration and the micellar size were determined using fluorescence correlation spectroscopy and dynamic light scattering, respectively. The triblock copolymer gels show the lower critical solution temperature (LCST) at 32°C with micellar sizes of ~25 nm below. In figure 1.10, SAXS curves from three different triblock copolymer solutions (all at 1 wt.%) are shown. All triblock copolymers show the micellar form factor at low temperature, the LCST at 32°C and the formation of clusters above the LCST. The Guinier analysis below the LCST lead to $R_g = 6.6$ nm, thus sphere radii of R = 8.6 nm. Due to the difference in chain architecture, these micelles are smaller than the ones formed by the diblock copolymers [4]. In summary, the micelles formed by the triblock copolymers show the collapse of the PNIPAM shell at 32°C. We could determine the size of the swollen micelles. Above the LCST, the collapsed micelles form clusters due to physical crosslinking.

This project was funded by DFG (Pa 771/4-1) within the priority progam SPP 1259 'Intelligente Hydrogele'.

- M. Shibayama *et. al.*, J. Chem. Phys, **97**, 6829 (2002). D. Kuckling *et. al.*, Macromol. Mater. Eng, **288**, 144 (2003). J.E. Chung J. Controlled Release , **62**, 115(1999).
- [2] T. Tanaka, E. Sato, Y. Hirokawa, S. Hirotsu, J. Peetermans, Phys. Rev. Lett. 55 2455 (1985).
- [3] F.M. Winnik, A.R. Davidson, G.K. Hamer, H. Kitano, Macromolecules 25, 1876 (1992).
- [4] K. Troll, A. Kulkarni, W. Wang, C. Darko, A.M. Bivigou Koumba, A. Laschewsky, P. Müller-Buschbaum, C.M. Papadakis, Coll. Polym. Sci., accepted.

1.7 Thin films of poly(N-isopropylacrylamide) end-capped with *n*-butyltrithiocarbonate

W. Wang, K. Troll, K. Skrabania¹, A. Laschewsky¹, C. M. Papadakis, P. Müller-Buschbaum

¹ Potsdam Universität, Inst. Chemie, Potsdam-Golm, Germany

Responsive hydrogels are water-based cross-linked polymer networks that can be switched between a collapsed and an extended chain conformation by means of various external stimuli such as temperature, pH, liquid composition, electric stimulation [1, 2]. Poly(Nisopropylacrylamide) (PNIPAM) is one of the prominent temperature-sensitive hydrogels because it has a relatively low collapse transition temperature at 32°C [3] and thus slightly less than body temperature, which makes PNIPAM a representative of environmental-sensitive polymers studies for biomedical applications [4]. As pure PNIPAM homopolymer films miss the possibility of internal cross-links to build up a gel, the addition of hydrophobic chain ends (e.g. polystyrene, PS) is a simple way to overcome this problem. However, with increasing glassy, hydrophobic block length the ability to swell decreases. In case of the triblock copolymer P(S-b-NIPAM-b-S) bulk compositions with spherical PS domains and a PNIPAM continuous phase swelled very well in water, whereas composition resulting in cylindrical PS domains or in the bicontinous gyroid structure in bulk swelled only by a factor of 3 to 5, respectively. Finally, lamellar compositions did not show any swelling. Along this line short hydrophobically end-capped PNIPAM chains might be expected to exhibit the strongest swelling thereby maintaining the gel character.

Within the present work we focus on hydrophobically end-capped PNIPAM to address the question if end-capped PNIPAM in thin films undergoes micro-phase separation and creats an internal structure. At each chain end a very short hydrophobic end group, *n*butyltrithocarbonate, was chosen (denoted nbc-PNIPAM). A series of films with thickness ranging from 2 nm to 240 nm were prepared by spin-coating on pre-cleaned glass slides. The film thicknesses were measured by X-ray reflectivity. The structural investigation is based on X-ray reflectivity, atomic force microscopy and micro-beam grazing incidence small-angle X-ray scattering (μ GISAX). Thus the surface and the inner film structure can be accessed.

With AFM, the surfaces of the nbc-PNIPAM thin films appear smooth and continuous. Fig. 1.11 shows the example of topography data on a scan size of $1\mu m \times 1\mu m$ to emphasize on local surface structures for film thickness of 10, 46 and 240 nm. All films have a surface structure on the nanometer scale, which is caused by the micelle structure of the nbc-PNIPAM. For 10 nm film thickness (Fig. 1.11a) the presence of the micelles as building blocks for the hydrogel film is best seen. With increasing film thickness the surface structures coarsen laterally, but decease in height (peak-to-valley amplitude) from 0.8 nm to 0.3 nm. At larger film thickness the attractive surface interaction is weaker for the topmost nbc-PNIPAM micelles, and a larger

number of micelles is stacked which allows for an improved space filling with polydisperse spherical soft objects.



Figure 1.11:

AFM micrographs show a scan size of $1\mu m \times 1\mu m$ to emphasize on local surfaces for film thickness of a) 10, b) 46 and c) 240 nm.





Line cuts from the μ GISAX 2d data for a representative selection of different film thickness (5, 7, 8, 22, 35, 74, 154 and 241 nm from bottom to top). a) Detector scans shown as a function of the detector angle $\alpha_i + \alpha_f$ and b) out-of plane scans shown as a function of the q_y component of the scattering vector. The solid lines are fits to the data. The resolution limit is shown with the dashed line. From bottom to top the film thickness increases and the curves are shifted along the y-axis for clarity

In contrast to AFM, μ GISAX is not limited to the sample surface, but structures inside the film are probed. It is well suited to investigate structures parallel to the surface, so called lateral structures and long ranged correlation. μ GISAX was carried out at the beam-line BW4 of the DORIS III storage ring at HASYLAB (DESY, Hamburg). Fig. 1.12a shows the detector scans. In addition to the Yoneda peaks, strong modulations in the intensity are detected. These modulations are caused by a partial phase coherence of X-ray waves diffusely scattered from different interfaces which hints a roughness correlation between the SiO_x surface and the nbc-PNIPAM surface. From the out-of-plane cuts made at the q_z-value of the critical angle of PNIPAM and showed in Fig. 1.12b, none of the scattering curves exhibits a strong

intensity peak. Instead, a weak and broad intensity peak at large q_y values is present and the intensity rises towards smaller q_u values. Thus the thin nbc-PNIPAM films exhibit an internal structure, which differs from a well defined micro-phase separation. The presence of a weak broad, instead of a strong sharp peak, is due to an increased deviation in the nearest neighbor distances from its mean value, typically expressed with a Gaussian-type distribution with an increased full-width half-maximum. Therefore, in the investigated films the mean distance between adjacent regions of hydrophobic *n*-butyltrithiocarbonate end groups is more broadly distributed than in systems with long end groups. A reason can be the broad distribution of the micellar size in the solution. The out-of plane cuts are fitted with a simplified model. This model accounts for a structure factor due to the distance between neighboring domains of hydrophobic chain ends in the PNIPAM matrix (denoted structure factor 1). Moreover, it includes a structure factor due to the presence of large heterogeneities (denoted structure factor 2) and takes the experimental resolution into account. Both structure factors are distributed with a Gaussian-type. The form factor (spherical shape of the micelles) is omitted due to the polydispersity of the micelles as probed in solution and due to the gelation of the micelles in the thin film. The solid lines in figure 1.12b show the corresponding fits to the out-of plane scans. The resulting mean distance between domains of chain ends is 25 nm. Comparing this value with the micellar size detected in solution shows that the micelles are indeed bridged and entangled inside the film. The resulting distance corresponding to structure factor 2 decreases from 600 nm to 400 nm with increasing film thickness. In addition, for films with thicknesses lower than 30 nm, structure factor 1 is more pronounced than structure factor 2 while for thicker films, the situation is opposite. Thus the heterogeneities are denser populated in thicker films, or in other words, thicker films are less perfect with respect to the inner structure. The nature of the heterogeneities remains undetermined, however, errors in the positioning of hydrophobic domains, such as merging of two or more domains, are quite likely. A possible reason is the increased concentration, which was used in spin-coating film with increased film thicknesses. At high concentrations, already in solution larger, entangled associates of core-shell type micelles might have formed, which embedded in the thin film cause large-scale density inhomogeneities.

As a conclution, thin nbc-PNIPAM films are successfully prepared on SiOx surfaces using spin-coating. The very short end groups can be regarded as degrarded hydrophobic blocks of a ABA-type block copolymer (A denoting a hydrophobic and B a thermoseneitive block). The nbc-PNIPAM films exhibit an internal structure due to the micro-phase separation of the hydrophilic and hydrophobic segments. The structure is expected in the analogy to triblock copolymer films and consists of small spherical domains of hydrophobic chain ends randomly distribute in a matrix of PNIPAM.

- [1] Tanaka, T. Phys. ReV. Lett. 40, 820 (1978).
- [2] Tanaka, T.; Nishio, I.; Sun, S. T.; Ueno-Nishio, S. Science 218, 67, (1982). Stimuli-Responsive Water Soluble and Amphiphilic Polymers; McCormick, C. L., Ed.; ACS Symposium Series 780; The American Chemical Society: Washington, DC, 2001
- [3] A. Nykanen, M. Nuopponen, A. Laukkanen, S. -P. Hirvonen, M. Rytela, O. Turunen, H. Tenhu, R. Mezzenga, O. Ikkala, and J. Ruokolainen, Macromolecules 40, 5827 (2007)
- [4] Huber, D. L.; Manginell, R. P.; Samara, M. A.; Kim, B. I.; Bunker, B. C. Science 301, 352-354 (2003)

2 Polymer thin films

2.1 Surface enrichment in statistical copolymer films

A. Diethert, P. Müller-Buschbaum

Pressure sensitive adhesives (PSA) are used for many different applications, such as for example adhesive foils or binding materials. A prominent class of PSA films is based on statistical copolymers [1-4]. Typically, two or three different monomers are combined in the statistical copolymer to balance the different requests of the PSA [5, 6]. The adhesive properties of the PSA films are mainly determined by surface-near regions. With x-ray reflectivity (XRR) the density profile perpendicular to the PSA surface is probed.



Figure 2.1: four different possibilities of plotting the XRR data to emphasize the existence of a surface layer

We focus on PSA model systems and investigate the dependence on different monomers of the copolymer [4]. Because the data analysis is still in progress, we here restrict to one statistical copolymer consisting of 90% ethylhexylacrylate (PEHA) and 10% maleic acid anhydride (PMSA) [5, 6]. The copolymer films were prepared from a toluene solution by solution casting on a pre-cleaned glass substrate. By measuring the weight of the sample we estimate a total film thickness of approximately 50 μm . From a naive point of view one would now expect a homogenous film, but the XRR experiment shows that one monomer component is enriched

at the surface.

The XRR measurements were performed with a Siemens D5000 diffractometer at E21 in the physics department using a wavelength of 1.54 Å. For the data analysis we used Parratt32, a simulation tool for neutron and x-ray reflectivity.

Figure 2.1 shows the reflected intensity over q_z normalized to 1. Different axes are chosen to pronounce different features of the curve. Figure 2.1c is the classical plot on a logarithmic scale. On a double-logarithmic scale in figure 2.1a one can see that the critical angle of total reflection coincides with the critical angle of the majority component PEHA which is marked with the left vertical line. Furthermore modulations in the curve which prove the existence of enrichment layers become visible. In figures 2.1b and 2.1d the intensity is multiplied by q_z^4 and in 2.1d also the background is substracted. With these two curves one can better judge the quality of the fit which is diplayed with the black solid line.



Figure 2.2:

density profile perpendicular to the sample surface, the solid horizontal lines are guides to the eye to emphasize the two components (PEHA and PMSA) of the copolymer (PEHA-PMSA)

To analyse the data we assume that our sample consists of bulk material and an enrichment on top. From the fitted density profile shown in figure 2.2 the reflectivity is calculated. In figure 2.2 the real part of the refractive index δ is plotted over z which is perpendicular to the sample surface (z = 0).

A homogenous film would have the constant refractive index $\delta = 3.38 \cdot 10^{-6}$ which is marked with the middle horizontal line. But the plot shows a shoulder at around z = 10 Å at the refractive index of PEHA which indicates an enrichment of PEHA at the surface. The curve reaches its maximum at z = 57 Å, here we have 53% PEHA and 47% PMSA. For higher *z*values the contribution of PMSA decreases and for z > 140 Å we reach the homogenous bulk material.

To find out if there are even lateral structures in the enriched layers grazing incidence small angle x-ray scattering experiments were performed. Concerning this, data analysis is still ongoing and more information about the sample system is expected.

- [1] K. R. Brown, C. Creton, Eur. Phys. J E, 9, 35-40 (2002)
- [2] A. Chiche, P. Pareige, C. Creton, C. R. Acad. Sci. Paris, 1, 1197-1204 (2000)
- [3] A. J. Crosby, K. R. Shull, J. Polym. Sci. B Polym. Phys., 37, 3455-3472 (1999)
- [4] A. Falsafi, M. Tyrell, A. V. Pocius, Langmuir, 16, 1816-1824 (2000)
- [5] D. W. Schubert, V. Abetz, M. Stamm, T. Hack, W. Siol, Macromolecules, 28, 2519 (1995)
- [6] S. Bunker, C. Staller, N. Willenbacher, R. Wool, Int. J. Adhesion and Adhesives, 28, 29-38 (2003)

2.2 Pressure sensitive adhesive blend films for low tack applications

P. Müller-Buschbaum, T. Ittner, E. Maurer, V. Körstgens, W. Petry

Pressure sensitive adhesives (PSA) mark one class of adhesives which is characterized by the presence of re-openable bonds. Typical PSA applications from daily life are stick-on notes, scotch tape, labels and re-usable packages. Thus PSA offer the opportunity to connect extremely different materials such as paper, metals, glasses, ceramics and polymers in a re-useable way. The adhesive properties of PSA strongly depend on the way the bonding was created. Typical parameters to quantify this history of bond formation are the applied pressure and the time it was applied. De-bonding becomes possible by applying a distinct force. Typically the performance of PSA is measured in different probe test geometries like the peel or tack test.



Figure 2.3:

a) Optical micrograph picturing the cavitation structure present between punch and PSA film at a position in the plateau of the force-distance curve in case of a PnBA rich blend. The dark areas represent polymeric material surrounding the cavities shown in white. The bar represents a length of 500 μm . A circular shaped rim separates the flat PSA film from the surface area which was in contact with the punch. b) Schematic sketch of a horizontal cut through the polygonal polymer structure surrounding the macroscopic cavities. Due to the high level of magnification the optically invisible nano-bubbles are visible. The differences in the real part of the refractive index as detected with the X-ray scattering are sketched with the chosen gray scale. Taken from [4].

A special class of PSA applications strengthens the idea of an easy de-bonding. These low tack materials, e.g. masking tapes, are commonly used to avoid damage of the material the PSA is bonded with by requiring only very small forces for the de-bonding. In other applications low-adhesion provides the possibility to position or relocate the adhesive product. One way of achieving such a characteristic behavior is the addition of a non-tacky component in order to limit the contact area between the PSA system and the bonded surface. For example inorganic solid particles like glass beads or calcium carbonate are distributed over the surface of the PSA or dispersed throughout the volume of the PSA. Within the present investigation we follow the idea of mixing tacky and non-adhesive components to reduce the force necessary for the de-bonding. Instead of using inorganic filler materials a second polymer is blended. Blending of incompatible polymers adds the possibility to create marked structures in the mixed film. Thus our model system consists of a tacky polymer component, typically characterized by a glass transition temperature below room temperature, and a second glassy polymer component, with a glass transition temperature significantly above room temperature. In more detail, our model system comprises of two blended homopolymers. The one, poly-n-butylacrylate (PnBA), promotes adhesion. The second, polystyrene (PS), increases cohesion and yields structured films, due to the incompatibility with PnBA. The tacky component, PnBA, was used in several investigations in the past. The non-adhesive component, PS, was chosen as a standard polymer with well characterized physical parameters, including the polymer-polymer interaction parameter with PnBA, which characterizes the incompatibility. In the blend system PnBA:PS the majority component forms a matrix embedding the minority component. Thus the blend PnBA:PS seems to be a promising candidate with respect to the desired low tack application.

As well known from other blend systems [1] due to the immiscibility of both components, PnBA and PS, a marked structure results from a phase separation process. Recent scanning probe experiments utilizing pulsed force mode on thin PnBA:PS blend films determined the chemical composition and the surface structure due to the related mechanical differences [2]. The majority component forms a matrix embedding the minority component as disperse objects. The size of these objects decreases with decreasing amount of the minority component. Up to a blending ratio of 5:5 PnBA forms a tacky matrix with rigid PS islands inside. As a consequence, we restricted our mechanical tack experiments to films with a majority of PnBA as compared to PS, including the symmetric blend with PnBA:PS= 5:5.

Whereas macroscopic structures in the blend PSA deviate from standard filler systems and cause a more complex macroscopic behavior, its effect on the microscopic structure is revealed with x-ray scattering. n-situ during the de-bonding with USAXS information is detected on length scales, which is not accessible with optical methods [3]. Due to the necessity to perform these experiments at a synchrotron and the limited synchrotron beamtime available in general, we concentrate on two blending ratios. We selected PnBA:PS= 9:1 and 7:3 to cover a regime which is well within the regime having a well defined force curve with a force maximum present as well as having a certain amount of non tacky homopolymer added [4]. To address structures in the vertically expanded state, the USAXS measurements were performed at quantized distances during the de-bonding. To work out numbers, the USAXS data are modelled with a model assuming cylindrically shaped nano-bubbles, which was successfully applied for the explanation of the USAXS data measured at pure PnBA [3]. Fig. 2.3 sketches the applied model. With optical techniques only the well known large cavities are visible (see Fig. 2.3a). Due to the reflection of light from the punch surface, the cavities appear in white and the polygonal polymer structure separating the cavities in black. The untouched PSA film surface appears in white as well. With increasing amount of PS added to the blend, in these transmission micrographs the phase separation structures yield lateral fluctuations of the refractive index. Due to the low magnification the lateral phase separation structures are not resolved and as a consequence the pure PSA film only appears less white. However, the tacked surface area is strongly modified from the presence of the cavities and in addition easily detected from the presence of a circularly shaped rim of polymer separating both, untouched film and tacked film.

The observed size of the nano-bubbles fits well into the regime which is below the critical radius of growth reported in case of other adhesive systems. In case of small sized cavities a certain activation energy barrier needs to be overcome to enable a cavity growth. As the stress increases, this energetic gap decreases. Cavity growth depends on the initial size of the cavities and the available elastic energy. Thus perhaps the nano-bubbles are a precursor of the optically observable macroscopic cavities which form out of some of the nano-bubbles by overcoming the activation energy barrier.

With respect to the aim of low tack materials, the added PS works perfectly comparable to an inert filler on the microscopic scale. Interesting for applications is the absence of the non-tacky component in the vertically expanded material during de-bonding. As a consequence, the

added non-tacky PS is not transferred to the material in contact with the blend PSA. Only the tacky component, PnBA in the presented work, is transferred. Thus the behavior is identical to the pure adhesive system, but with a tailored reduced tack.

- [1] G. Krausch, Mat. Sci. Eng. Rep 14, 1 (1995)
- [2] M. Stenert et al., e-Polymers 15, 1 (2004)
- [3] P. Müller-Buschbaum et al., Europhys. Lett. 66, 513 (2004)
- [4] P. Müller-Buschbaum et al., Macromol. Mat. Eng. 292, 793 (2007)

2.3 Nanostructuring of thin semiconducting polymer films for photovoltaic applications

M. Ruderer, S. V. Roth¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

Conducting polymers have shown to be interesting candidates for photovoltaics due to their high absorption coefficient, easy processibility, mechanical flexibility and low costs. Furthermore the possibility to tune the properties of the polymers make broad-ranged applications feasible. Nevertheless there are stringent constraints in device fabrication due to the short exciton diffusion length, i.e. the charge carrier separation has to occur in this length scale. Therefore the structure of the polymer film is crucial. It was shown that a blended structure compared to a layered structure increases the efficiency. [1]

The blended structure is strongly depending on the blending ratio of the polymers. Two different polymers phase separate normally whereas one polymer is embedded in the matrix of the other polymer. At a critical ratio the polymer blend forms an interpenetrating network, the so called bicontinuous structure. Adapted from the Flory-Huggins theory one can approximately calculate the critical blending ratio ϕ_c for bulk systems with

$$\phi_c = \frac{1}{\sqrt{N_2/N_1} + 1} \tag{2.1}$$

The binary polymer blend of MEH-PPV (poly(1-methoxy-4-(2-ethylhexyloxy)-pphenylenevinylene)) and P3HT (poly(3-hexylthiophene-2,5-diyl) was investigated. The critical blending ratio for the used system was calculated to $\phi_{MEH-PPV} = 11\%$. Both homopolymers are soluble in chloroform and were dissolved with different blending ratios. Thus solutions with the MEH-PPV to P3TH ratio of 100% to 0% were obtained. Thin films with a constant thickness of 39 nm were prepared via spin-coating on glass slides.

Optical absorption spectra were obtained by using a Perkin-Elmer Lambda 35 spectrometer (UV/ Vis) in transmission geometry. We measured in the range of 300 to 1100 nm with a scan velocity of 120 nm/min and a step size of 0.1 nm. With the FT-IR spectrometer IFS 55 EQUINOX (Bruker Optik GmbH) the degradation of the pure polymer films due to ambient influences like heat and light was investigated.

Both homopolymers absorb mainly light in the range of 300 to 700 nm. By integrating the absorption spectra and normalisation to the different film thicknesses the integrated absorption coefficients α of the pure homopolymers were obtained. For the range of 300 to 1100 nm $\alpha_{MEH-PPV} = (3.08 \pm 0.08) \text{ nm}^{-1}$ and $\alpha_{P3HT} = (3.46 \pm 0.05) \text{ nm}^{-1}$ were determined. The



Figure 2.4:

(a) Wavelength dependence of the absorption coefficients of MEH-PPV:P3HT films for different blending ratios $\phi_{MEH-PPV}$. (b) The integrated absorption coefficients for different blending ratios $\phi_{MEH-PPV}$. The integration was performed in the range from 300 to 1100 nm. [3]



Figure 2.5:

Out-of-plane cuts (dots) with fits (lines) of the 2d-GISAXS- (a) and GIUSAXS- (b) pattern of a series of MEH-PPV:P3HT blended films with different blending ratios. The ratio of MEH-PPV to P3HT is increasing from 0% to 100% in steps of 10% from the bottom to the top curve. The fitted structure peaks are highlighted with the arrows A - D. The dashed line gives the resolution limit. The curves are shifted in the direction of the y-axis for clarity. (c) Composition dependence of the lateral structure size (A (black solid triangles), C (red open squares)). [3]

absorption spectra of the blended films show a superposition of the pure spectra. The integrated absorption spectra are nearly independent of the blending ratio of the polymers (see Fig. 2.4).

Films stored at 160 °C show a clear decrease of the integrated absorption coefficient whereas the effect on MEH-PPV is stronger than on P3HT. Under light exposition there is only a small change of the spectra for P3HT observable. However the decrease of the absorption of MEH-

PPV due to light degradation is comparable to the heat exposition. The FT-IR spectra of the heat and light exposed MEH-PPV films show degradation of the molecular structure whereas mainly oxidation of the carbon double bonds occurs. Thus a decrease of the conductivity of the polymer is expected. There was no change in the FT-IR spectra of aged P3HT visible. The inner structure of the blended polymer films was investigated via grazing incidence (ultra) small angle x-ray scattering (GI(U)SAXS) at the beamline BW4 of HASYLAB at DESY. The sample-detector distance defines the resolution of the measurement. The experiments were carried out with a sample-detector distance of 2 m (GISAXS) and of 12 m (GIUSAXS). [2] In Fig. 2.5a the out-of-plane cuts (dots) with fits (lines) of the GISAXS measurements and in Fig. 2.5b of the GIUSAXS measurements are shown. The data was fitted by a model which includes a resolution peak and two structure peaks. The structure peaks are highlighted by arrows A - D. It was possible to fit the curves by changing one structure peak with the second peak fixed at a constant value. The structures are in-plane information. The determined values are for B 30 nm and for D 750 nm. The value of A and C are equal within the experimental errors and shown in Fig. 2.5c.

At the blending ratio $\phi_{MEH-PPV} = 10\%$ a minimal structure size of $\Lambda = 300$ nm was determined. Thus we expect the bicontinuous structure at this blending ratio which agrees with the theoretical value of the critical blending ratio. [3]

- [1] S. V. Chasteen et al., J. Appl. Phys., 99, 033709 (2006)
- [2] P. Müller-Buschbaum, Anal. Bioanal. Chem., 376, 3 (2003)
- [3] M. Ruderer et al., to be published

2.4 In-situ neutron reflectometry probing competitive swelling and de-swelling of thin polystyrene films

P. Müller-Buschbaum, E. Bauer, E. Maurer, A. Nelson¹, R. Cubitt²

- ¹ Bragg Institute at ANSTO, Menai, Australia
- ² ILL, Grenoble, France

Thin polymer films on solid supports are used in many daily life and technical applications, as for example in microelectronics through lithographic processes or as dielectric layers. Typically, these films are exposed to a gas atmosphere and molecules from this atmosphere are incorporated inside the thin polymer film. Penetration of a micromolecular species into an initially dry polymer film is driven by a chemical potential gradient [1, 2]. It is normally accompanied by swelling and plasticization of the polymer. The penetrant may be a solvent or a non-solvent of the particular polymer, depending on the thermodynamic properties of the polymer-penetrant pair. A significant body of work has examined experimental and the-oretical characteristics of swelling and dissolution of glassy polymer films by single organic solvent molecules. In most of these investigations the polymer film is in contact with an atmosphere close to saturation of the penetrating species.

Less attention has been paid to the swelling of thin polymer films in undersaturated atmospheres, particularly those consisting of several different molecules. In this investigation we select the model system of deuterated polystyrene (dPS) in contact with an unsaturated vapor of toluene in air. Thus the present work addresses melts/glasses and not cross-linked films. Toluene is a good solvent of dPS and the combination of dPS and toluene a well investigated



Figure 2.6:

Top) Solvent penetration and (bottom) film thickness (filled symbols) and normalized diffusely scattered intensity (open symbols) shown on a logarithmic time axis to account for the different time constants of the swelling and deswelling. Taken from [4].

model system in terms of swelling and dissolution. Consequently, it is well suited for the investigation of competitive penetration of different micromolecular species into an initially dry polymer film.

The addition of the toluene marks the starting point of the kinetic swelling investigation (time t=0). After equilibrium was reached, the toluene addition to the air atmosphere is removed by an exchange of air surrounding the swollen dPS film. Finally de-swelling occurs and the dPS film relaxes back.

Neutron reflectometry was used (D17 reflectometer of ILL, Grenoble, in time-of-flight (TOF) mode [3, 4]) to trace small changes in the dPS film thickness upon exposure to the undersaturated toluene atmosphere. Kinetic changes were probed by performing reflectivity scans every 30 s.

In a saturated atmosphere the introduction of a thermodynamically compatible solvent vapor (toluene) to a polymer film (dPS) leads to a continuous absorption of the solvent into the polymer film, at undersaturation the increase in film thickness is very limited. For the presented example it increases from 49.8 to 58.8 nm (instead of 101.4 nm close to saturation [3]). The driving force given by the difference in the chemical potential of the vapor and the swelling polymer film is small.

The swelling rate is linear with time with v = 0.03 nm s⁻¹ after an initiation time of typically 140 s (Fig. 2.6). Such behavior has been reported for case II diffusion with bulky material and thick films, were the absorption of a high activity solvent vapor follows two steps: initiation and linear increase with time [1, 2]. The difference between Fickian and Case II behavior is the concentration profile of the solvent in the polymer that increases as \sqrt{t} and t for Fickian and Case II diffusion, respectively. Sorption of small molecules in glassy polymers, such as toluene in dPS, that is instantaneously introduced, shows non-Fickian behavior (Case II). The Case II diffusion can be described in terms of a moving boundary of nearly constant concentration [2]. However, such a front was not observed in the neutron data, which might motivate a new mechanism caused by the small thickness of the dPS film.

Upon removal of solvent the film de-swells. However, de-swelling is significantly slower than the swelling process with a de-swelling rate of $v = 7.67 \cdot 10^{-4}$ nm s⁻¹. Again, in the neutron data no sign of a moving front was observed. Notably, the initial film thickness is not attained

due to the finite volume of the vapor chamber - the toluene molecules leaving the dPS film enrich in the air volume of the cell. To extract all incorporated toluene the vapor chamber has to be opened completely, thereby allowing for a back relaxation of the dPS film. [4]

- [1] C.Y. Hui et al., J. Appl. Phys. 61, 5129 (1987)
- [2] T.P. Gall et al., Polymer 32, 265 (1991)
- [3] P. Müller-Buschbaum et al., Physica B 385-386, 703 (2006)
- [4] P. Müller-Buschbaum et al., phys.stat.sol. (RRL) 1, 68 (2007)

2.5 Structural changes of thin block copolymer films during solvent vapor treatment

Z. Di, C. M. Papadakis, D. Posselt¹, D.-M. Smilgies², A. Timmann³

- ¹ IMFUFA, Department of Science, Systems and Models, Roskilde University, Denmark
- ² Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA
- ³ HASYLAB at DESY, Hamburg

Diblock copolymer thin films are of interest for a range of applications requiring nanostructured surfaces. However, the lack of long-range order of the self-assembled structures may be a hindrance for some purposes. Treatment with solvent vapor has been known to be an efficient way to improve long-range order [1]. However, the processes taking place during vapor treatment are still largely unknown.



Figure 2.7:

AFM (a) and GISAXS (b) images of a spin-coated film from a sample having 215.8 kg/mol. (c) Lateral cut at the q_z -value of the Yoneda peak of the polymer. (d-f) Same results after storage in saturated toluene vapor for 18 h.

We have investigated thin films of lamellar poly(styrene-*b*-butadiene), P(S-*b*-B), having low (22.1 kg/mol) and high molar mass (215.8 kg/mol). We have chosen this system because, in thin film geometry, the lamellar interfaces are parallel or perpendicular to the film surface, and this lamellar orientation can be controlled by the block copolymer molar mass [2]. We have carried out ex-situ and in-situ studies of the film surface by atomic force microscopy (AFM) and of the inner film structure by grazing-incidence small-angle X-ray scattering (GISAXS) at BW 4 at HASYLAB and at D-line at CHESS. We have investigated (i) a



Figure 2.8:

Results from a spin-coated film from a sample with 22.1 kg/mol during treatment with cyclohexane vapor. (a) GISAXS image before vapor treatment. (b) Intensity profiles along q_z through one of the Bragg rods vs. time during treatment. (c) Thicknesses of the (•) parallel and (\circ) lamellae. The line indicates the bulk lamellar thickness.

high molar mass film having the perpendicular lamellar orientation in the vapor of the nonselective solvent toluene and (ii) a low molar mass film having initially a mixed lamellar orientation in the vapor of cyclohexane, a solvent slightly selective for the PB block.

A thin film of a high molar mass P(S-*b*-B) diblock copolymer was prepared by spin-coating from toluene solution onto a silicon wafer. Then, the film was stored in saturated toluene vapor for 18 hours. The long-range lamellar order at the film surface improved significantly after vapor treatment (figure 2.7a,d). This improvement takes place not only at the surface but in the entire film, as reflected in the appearance of higher-order Bragg rods in the GISAXS images (figure 2.7b,e and c,f). In addition, both AFM and GISAXS reveal that vapor treatment leads to an increase of the lamellar thickness by 20%.

In order to elucidate the processes *during* vapor treatment, we have carried out in-situ GISAXS experiments. A thin film from a low molar mass P(S-b-B) diblock copolymer was prepared in the same way as described above, which resulted in a film thickness of 1010 Å. In dry state, the GISAXS image shows both, a Bragg sheet and a ring of high intensity which is enhanced at the q_z -value of the Yoneda peak of P(S-*b*-B) (figure 2.8a). This out-of-plane scattering is overlaid by intensity oscillations reflecting the correlated roughness of the film suface and the film/substrate interface. These observations point to a predominantly parallel orientation together with a fraction of tilted lamellae. The GISAXS images recorded after injection of cyclohexane into the cell, which leads to saturated vapor, allowed us to follow the fast dynamics during the first 30 min. The swelling of the film is reflected in changes of the width of the intensity oscillations (figure 2.8b). The film thickness increases during the first ~ 5 min and levels off after ~ 20 min. Converting the q_z -positions of the Bragg sheets and the lateral (q_y) positions of the Bragg rods into lamellar thicknesses as a function of treatment time allows us to characterize the swelling of the parallel and the perpendicular lamellae separately (figure 2.8c). Two time regimes can be discerned for the swelling of the perpendicular lamellae (open circles): an incubation time of ~ 5 min, followed by the swelling to an equilibrium value, which is 4.2% higher than the one in the dry state. Meanwhile, the behavior of the parallel lamellae is more complex: Three time regimes are distinguished (filled circles): A decrease during the first few minutes, then strong swelling (by 14%), and finally a decrease to the same degree of swelling as the perpendicular lamellae. These complex processes show that the changes of the chain conformation upon solvent uptake and the resulting changes of the lamellar thickness are partially hindered by the space restrictions in thin film geometry.

We conclude that the absorption of solvent vapor not only leads to swelling of the block copolymer films but also to changes of the internal nanostructure. A significant improvement of the lateral correlation in a film containing perpendicular lamellae could be achieved using a non-selective solvent. Treatment of a thin film containing initially both parallel and tilted lamellae with a selective solvent revealed complex processes.

This project has been funded by the Graduate School 'Materials Science of Complex Interfaces'.

- K. Fukunaga, H. Elbs et al. Macromolecules 33, 947 (2000). K. A. Cavicchi and T. P. Russell Macromolecules 40, 1181 (2007).
- P. Busch, D. Posselt, D.-M. Smilgies, C.M. Papadakis et al. Macromolecules 36, 8717 (2003).
 C.M. Papadakis, P. Busch, D. Posselt, D.-M. Smilgies, Adv. Solid State Phys. 44, 327 (2004).
 P. Busch, D. Posselt, D.-M. Smilgies, M. Rauscher, C.M. Papadakis, Macromolecules 40, 630 (2007).

2.6 Distinct kinetic regimes in a lamellar diblock copolymer thin film during solvent vapor uptake

C. M. Papadakis, Z. Di, D. Posselt¹, D.-M. Smilgies²

- ¹ IMFUFA, Department of Science, Systems and Models, Roskilde University, Denmark
- ² Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA

Thin block copolymer films are of interest for the preparation of nanoporous films and nanostructured templates [1]. An important issue is control of the defect density. Solvent annealing offers a simple and flexible method with a potentially high degree of controllability through choice of solvent. However, the molecular mechanisms and mesoscopic rearrangements involved in solvent annealing are still largely unexplored.

Here we address the immediate response of the lamellar mesophase to exposure to solvent vapor. Real-time, in-situ grazing-incidence small-angle X-ray scattering (GISAXS) with a time resolution of a few seconds [2] was used to investigate the structural re-arrangements in a thin, supported film of lamellae-forming poly(styrene-*b*-butadiene), P(S-*b*-B), diblock copolymers consisting initially of ~ 13 stacked lamellae. The films were prepared by spin-casting from toluene solution on Si wafers terminated with a native oxide layer and by subsequent thermal annealing. In-situ GISAXS experiments were performed in saturated toluene vapor – a good and non-selective solvent – at CHESS beamline D1 with a time resolution of 10 s.

Before vapor treatment, the lamellae in the film were parallel to the film surface, as revealed by diffuse Bragg sheets (DBS) appearing along the film normal, q_z , and extending along q_y , the scattering vector component in the film plane (Fig. 2.9a). During the first 3 min of solvent vapor exposure, the DBSs moved downwards and became more intense. After 3 min, the DBSs spread out along q_y and curved downwards, this effect being strongest after 5 min. Moreover, side peaks at finite q_y appeared next to the DBSs in this time regime. These changes were transient, even though the environmental conditions were not altered. Then, the DBSs moved again towards larger q_z -values, their lateral width decreased, and the side peaks vanished. After 8 min, the 2D image looked very similar to the one in the initial, dry state.



Figure 2.9:

(a) 2D GISAXS maps before and during vapor treatment. Logarithmic intensity scale. The horizontal arrows mark the tails of the DBSs. The times after injection of toluene are indicated. (b) Suggested scenario. Toluene molecules are represented by circles, voids are white. See text for explanation.



Figure 2.10:

Structural changes along the film normal: (a) lamellar thickness, (b) integrated intensity of the DBS and (c) height of the correlated lamellar stack. (d) Lateral length scale obtained from the side peak. The vertical lines delineate the three time regimes identified.

Three distinct time regimes were identified from an analysis of the q_z position, and the intensity and widths along q_z and q_y of the DBS at ~ 0.6 nm⁻¹. During the first time regime, the lamellar thickness increased linearly until the lamellar thickness had increased by 16% (Fig. 2.10a). The integrated intensity of the DBS increased more than a factor of 4 during the first time regime (Fig. 2.10b). The average height of the stack of correlated lamellae, H, as deduced from the FWHM of the DBS along q_z increased from 100 nm to 240 nm, a value close to the film thickness (Fig. 2.10c). The situation suddenly reversed after 3.4 min as marked by a maximum in the lamellar thickness and the DBS intensity together with a maximum in the correlated stack height of ~ 130 nm. In the lateral direction, the DBSs spread out along q_y and curved downwards (Fig. 2.9a). Side peaks at finite q_y appeared and were present during the entire second time regime (Fig. 2.10d). The second time regime ended 5-6 min after injection, as suggested by the 2nd maximum of the intensity of the DBS and of the stack height as well

as the disappearance of the side peaks. During the third time regime, the lamellar thickness and the intensity of the DBS, the width along q_y decreased again and the stack height all decreased. 8 min after the injection, a lamellar thickness similar to the lamellar thickness before treatment was reached.

We attribute this complex behavior to the changes of chain conformation upon solvent vapor uptake. In dry state, the blocks are stretched normal to the interface, whereas they assume a more globular conformation in the solvent-swollen state [3]. The swollen chains require a higher interfacial area which leads to an increase of the distance between the chains at the interface. In a thin film consisting of stacked lamellae this is not easily accomodated by diffusion of the copolymers along the interfaces alone. Moreover, the solvent vapor is expected to raise the polymer mobility. We thus attribute our findings to the scenario depicted in Fig. 2.9b: First, the solvent distributes homogeneously into the PS and the PB layers which leads to swelling of the lamellae and annealing of defects. Due to the lateral constraints in the extended lamellae in thin film geometry, the lamellae swell uniaxially normal to the lamellar interface. In the second time regime, the blocks relax towards more globular conformations, which leads to a de-swelling of the lamellae [4]. However, this situation is unstable because of the increased interfacial area required by the two blocks. The lamellar interfaces therefore form ripples with characteristic lateral length scales down to $\approx 2D_{\text{lam}}^{\text{film}}$. This is evident from the lateral widening of the DBSs [5] and the appearance of the side peaks. The decrease of the correlated stack height indicates a major reconstruction of the polymer film. Copolymers diffuse normal to the lamellar interfaces and form additional domains between the existing lamellae. These added domains may also be at the origin of the curvature of the DBSs [6]. During the third time regime, the height of the correlated lamellar stack reaches again the film thickness, and eventually, the film consists of more lamellae than in the dry sample with swollen and less stretched blocks.

We conclude that exposure of a lamellar block copolymer film to a good and non-selective solvent leads to distinct processes and abrupt changes during the first minutes, including swelling and subsequent deswelling of the lamellae as well as roughening of the lamellar interfaces and the formation of additional lamellae. The occurrence of transient states on a time-scale of a few minutes was previously unknown and indicates that thin film polymer kinetics needs to be probed in-situ and in real time.

This project has been funded by the Graduate School 'Materials Science of Complex Interfaces'.

- [1] R.A. Segalman, Mat. Sci. Eng.: R: Reports 48, 191 (2005)
- [2] D.-M. Smilgies, P. Busch, C.M. Papadakis, D. Posselt, Synchr. Rad. News 15, 35 (2002). S.H. Kim, M.J. Misner, T. Xu, M. Kimura, T.P. Russell, Adv. Mater. 16, 226 (2004). C.M. Papadakis, Z. Di, D. Posselt, D.-M. Smilgies, submitted
- [3] R.J. Albalak, M.S. Capel, E.L. Thomas, Polymer 39, 1647 (1998)
- [4] M. Shibayama, T. Hashimoto, H. Kawai, Macromolecules 16, 1434 (1983)
- [5] J.S. Gutmann, P. Müller-Buschbaum, D.W. Schubert, N. Stribeck, D. Smilgies, M. Stamm, Physica B 283, 40 (2000)
- [6] D.R. Lee, K. Shin, O.H. Seeck, H. Kim, Y.-S. Seo, M. Tolan, M.H. Rafailovich, J. Sokolov, S.K. Sinha, Phys. Rev. Lett. 90, 185503 (2003)

2.7 Improving the lateral long-range order in block copolymer films by thermal annealing

Z. Di, C. Darko, D. Posselt¹, D.-M. Smilgies², A. Timmann³, M.N. Groves⁴, M.A. Singh⁴, C.M. Papadakis

- ¹ Department of Sciences, Systems and Models (IMFUFA), Roskilde University, Denmark
- ² Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, USA
- ³ HASYLAB at DESY, Hamburg
- ⁴ Department of Physics, Queen's University, Kingston, Ontario, Canada

Diblock copolymer thin films are prominent candidates for a range of applications requiring nanostructured surfaces, such as the creation of nanoporous films or nanowires [1] because they self-assemble into regular nanostructures on the length scale of 10 - 100 nm. We have been studying thin films of lamellar poly(styrene-*b*-butadiene), P(S-*b*-B), and have found that for high block copolymer molar masses (above ~ 90 kg/mol), the lamellae are perpendicular to the surface [2], which is especially interesting for the above mentioned applications .

We focus here on the possibilities to improve the long-range order in the perpendicular lamellar orientation by thermal annealing [3]. It may be anticipated that the choice of the annealing temperature with respect to the highest glass transition temperature, T_g , of the block copolymer is important. Annealing above T_g enables long-range diffusion of the copolymers, whereas below T_g , only local rearrangements are possible. We have therefore chosen annealing temperatures below and above the T_g of the PS block, which is 100°C. GISAXS allowed us to investigate the changes of the lateral correlation of the lamellae as well as to detect an influence of the surface roughness. We correlate these results to the ones obtained by atomic force microscopy (AFM) and X-ray reflectometry (XR). Scattering experiments were performed at D-line at the Cornell High Energy Synchrotron Source (CHESS) and at BW 4 at HASYLAB.



Figure 2.11:

XR (a) and GISAXS (b-d) on a film with $\overline{M}_n = 183 \text{ kg/mol}$ at 35°C, i.e. before annealing (b), at 150°C, i.e. during annealing (c) and at 45°C, i.e. after annealing (d). Logarithmic intensity scale. The white lines indicate the positions of the Bragg rods.

In-situ results from a thin film annealed at 150°C are compiled in Figure 2.11. The film was placed in the X-ray beam in a heatable cell which was constantly flushed with He gas [4]. In this way, the probability of cross-linking the PB block was reduced. The X-ray reflectivity curve at 35°C, i.e. before annealing (Fig. 2.11a) does not display Kiessig fringes, i.e. the film thickness is inhomogeneous. The large number of well-pronounced Kiessig fringes observed at 150°C reveals that large-scale heterogeneities flatten out and the film thickness becomes

more well-defined. A GISAXS image taken before annealing shows straight Bragg rods (Fig. 2.11b). Upon heating the sample in the beam to 150° C, the image changes drastically: The straight Bragg rods transform into a ring of high intensity centered around the specularly reflected beam (Fig. 2.11c), i.e. the lamellae tilt away from the perpendicular orientation, resulting in a certain distribution of tilt angles. This ring persists upon cooling down to 45° C (Fig. 2.11d), but is then superimposed by straight Bragg rods which extend towards high q_z . We conclude that a certain fraction of the lamellae regain their original perpendicular orientation orientation upon cooling, whereas the remainder stays tilted.



Figure 2.12:

AFM phase images of a film with $M_n = 215.8$ kg/mol before (a) and after (b) thermal treatment at 60°C in air for 18 h. Image size 3 μ m × 3 μ m. (c, d) Corresponding GISAXS images. Logarithmic intensity scale. The grey region in the center indicates the beamstop. The vertical lines indicate the first and second-order Bragg rods.

The effect of thermal annealing below T_g is shown in Fig. 2.12. The resulting AFM height images do not reflect any improvement of the long-range correlation at the film surface (Fig. 2.12a,b). The GISAXS image before annealing (Fig. 2.12c) displays Bragg rods, i.e. the lamellar interfaces are perpendicular to the substrate surface. The most striking change upon thermal annealing is the shape of the intensity along the film normal, q_z (Fig. 2.12d): The intensity oscillations reflect the correlated roughness between the substrate surface and the film surface. Laterally extended oscillations indicate that the (flat) substrate surface is replicated by the film surface down to small length scales, i.e. thermal annealing results in a flattening of the film surface.

We conclude that whereas annealing above T_g of the PS block leads to deterioration of the perpendicular lamellar orientation and tilting of the lamellae – presumably related to an incipient dewetting process, annealing below T_g results in a local improvement of the lateral correlation of the lamellar interfaces as well as to a flattening of the film surface.

This project has funded by the Graduate School 'Materials Science of Complex Interfaces'.

- I.W. Hamley, Nanotechnology 14, R39 (2003). M. Lazzari, M.A. Lopez-Quintela, Adv. Mater. 15, 1583 (2003).
- [2] P. Busch, D. Posselt, D.-M. Smilgies, B. Rheinländer, F. Kremer, C.M. Papadakis, Macromolecules 36, 8717 (2003). C.M. Papadakis, P. Busch, D. Posselt, D.-M. Smilgies, Adv. Solid State Phys. 44, 327 (2004). P. Busch, D. Posselt, D.-M. Smilgies, M. Rauscher, C.M. Papadakis, Macromolecules 40, 630 (2007).

- [3] C.M. Papadakis, Z. Di, C. Darko, D. Posselt, D.-M. Smilgies, M.A. Singh, Lecture Notes in Physics, in the press.
- [4] M.N. Groves, M.A. Singh et al., J. Appl. Cryst. 39, 120 (2006) and Rev. Sci. Instrum. 78, 113910 (2007).

2.8 Thin films of diblock copolymers having one crystalline block

C. Darko, I. Botiz¹, G. Reiter¹, D. W. Breiby², J. W. Andreasen³, D.-M. Smilgies⁴, S. V. Roth⁵, C. M. Papadakis

- ¹ Institut de Chimie de Surfaces et Interfaces, CNRS, Mulhouse, France
- ² Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway
- ³ Danish Polymer Centre, Risø National Laboratory, Technical University of Denmark
- ⁴ Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA
- ⁵ HASYLAB at DESY, Hamburg

In thin films of diblock copolymers having one amorphous and one (semi-)crystalline block, the final structure formed depends on the competition between three transitions: the orderto-disorder transition of the diblock copolymer, the crystallization of the crystallizable block, and the vitrification of the amorphous block [1]. 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 various parameters contributing to the structure formation. We have investigated a lamellae-forming poly(styrene-bethyleneoxide), P(S-b-EO), diblock copolymer with the blocks having molar masses of 3 000 g/mol. Thin films were prepared by spin-coating from toluene solution onto Si wafers and crystallization was performed at different temperatures, T_x . The film thickness was ~ 760 Å. The mesoscopic lamellar structure was determined using GISAXS at BW4 [2]. The orientation of the PEO crystallites and the degree of crystallinity was investigated by GIWAXS at Risø National Laboratory, Roskilde, Denmark and at BW2, HASYLAB.

The surface morpholgy (Fig. 2.13) depends significantly on T_x . At 25°C (Fig. 2.13a), crystallization results in a weakly textured morphology, whereas at $T_x = 50$ °C, large terraces having a height of 110 ± 5 Å are formed (Fig. 2.13b). The 2D GISAXS maps give insight into the lamellar orientation and thickness (Fig. 2.13c,d). The diffuse Bragg sheets are located at the positions consistent with the prediction from the distorted-wave Born approximation for parallel lamellae [3] of thickness 160 ± 5 Å for $T_x = 25$ °C and 210 ± 5 Å for $T_x = 50$ °C.

The 2D GIWAXS images show a clear distinction of the crystalline texture in the two films (Fig. 2.14a, b). At $T_x = 25^{\circ}$ C, two strong and rather isotropic rings are observed (Fig. 2.14a): The first is due to the 120 reflection, whereas the second consists of the 032, -132, -212, and 112. For films crystallized at 50°C (Fig. 2.14b), two peaks with a significantly narrower distribution were observed, which were assigned to the 120 and 032 reflections. Fig. 2.14c,d shows simulated 2D GIWAXS images for films crystallized at 25°C and at 50°C. These images were obtained using the bulk monoclinic unit cell for the PEO crystals [4] and by varying both, the orientation angle of the *c*-axis with respect to the film normal and the width of the crystallite orientation. At $T_x = 50^{\circ}$ C, the best fit is obtained for the *c*-axis of the unit cell parallel to the film normal, whereas at $T_x = 25^{\circ}$ C, it is on average tilted by an angle of 35° with a wide


Figure 2.13:

AFM topography images of PS-*b*-PEO thin films crystallized at $T_x = 25^{\circ}$ C (a) and 50° C (b). 2D GISAXS images measured at $\alpha_i = 0.39^{\circ}$ for the same films (c,d). The grey rectangles in the GISAXS images mark the rod-like beamstop. The first two arrows (from the bottom) mark the positions of the Yoneda peak and the specularly reflected beam, respectively, followed by arrows indicating the positions of the diffuse Bragg sheets.





(a,b) Experimental 2D GIWAXS images from thin films of lamellar P(S-*b*-EO) crystallized at $T_x = 25^{\circ}$ C and 50°C, respectively. (c,d) Simulated 2D GIWAXS images for the films shown in (a,b). (e) GIWAXS in-plane intensity profiles for P(S-*b*-EO) thin films crystallized at $T_x = 25^{\circ}$ C (•) and at 50°C (•). The lines are guides to the eye.

distribution. We note that the asymmetry in the intensities of Fig. 2.14b is due to the large size of the crystalline domains (Fig. 2.13b). The dependence of the tilt angle on T_x explains the change of repeat distances found using GISAXS.

The degree of crystallinity was estimated from the high-resolution intensity profiles obtained at BW2. The percentage of crystalline domains in the films was found to be 62 and 98 % for $T_x = 25$ and 50°C, respectively, which suggest a more perfect PEO chain attachment at $T_x = 50$ °C than at 25°C. These findings are in consistency with the AFM images.

In summary, we have demonstrated that crystalline lamellae preferentially orient parallel to the film substrate both for strong and weak supercooling, but the lamellar repeat distance increases with T_x . At $T_x = 25^{\circ}$ C, the orientation of the PEO chain stems fluctuates around an average inclination angle of 35° with respect to the film normal, which is at the origin of the roughness of the film surface. For films crystallized at $T_x = 50^{\circ}$ C, the chain stems are mainly perpendicular to the film surface, promoting flat and terraced surfaces.

This work has been financially supported by DFG (Pa771/3) and the Incentive Fund for Research Collaborations between TU München and the Danish Technical University.

- [1] G. Reiter, G. Castelein, P. Hoerner, G. Riess, A. Blumen, J. -U. Sommer, and G. Floudas, Eur. Phys. J. E., 2, 319 (2000). L. Zhu, P. Huang, W. Y. Cheng, Q. Ge, R. P. Quirk, and S. Z. D. Cheng, Macromolecules 35, 3553 (2002).
- [2] S. V. Roth, R. Döhrmann, M. Dommach, M. Kuhlmann, I. Kröger, R. Gehrke, H. Walter, C. Schroer, B. Lengeler, P. Müller-Buschbaum, Rev. Sci. Instr. 77, 085106 (2006).
- [3] P. Busch, M. Rauscher, D. -M. Smilgies, D. Posselt, C. M. Papadakis, J. Appl. Cryst. 39, 433 (2006).
- [4] Y. Takahashi and H. Takadoro, Macromolecules 6, 672 (1978)

2.9 Break-away crystallization in thin films of cylinder-forming PI-b-PEO diblock copolymers

C. Darko, K. Troll, Z. Di, D.-M. Smilgies¹, A. Timmann², S. Förster³, C. M. Papadakis

- ¹ Cornell High-Energy Synchrotron Source (CHESS), Cornell University, USA
- ² HASYLAB at DESY, Hamburg
- ³ Department Chemie, Universität Hamburg

Crystallization is a widely studied phenomenon which imparts important physical properties to polymeric materials. In thin films of semicrystalline diblock copolymers, depending on the order-to-disorder-transition temperature, the melting temperature of the crystallizable block, and the glass transition temperature of the amorphous block, both unconfined and confined crystallization have been observed [1]. In bulk studies of the hexagonal cylindrical phase, crystallization of the block forming the cylinders was observed to destroy the microphase-separated hexagonal structure and to transform it into less ordered lamellae, i.e. crystalline lamellae within an amorphous matrix [2].

In the present study, we combine surface investigations by optical microscopy with scattering techniques to study the crystallization in thin films of cylinder-forming poly(isoprene-*b*ethyleneoxide) (PI-*b*-PEO) diblock copolymers. The blocks have molar masses of 2100 and 1100 g/mol, respectively.

Samples were prepared by spin-coating from toluene solution onto Si wafers. The film thickness is ~ 140 nm. The samples were annealed at 62° C for a few minutes, i.e. above the melting point of PEO, and were then quenched to room temperature. The crystallization of the PEO block was monitored using optical microscopy for several days until no more changes occured. The orientation of the PEO crystallites was studied by GIWAXS at BW2, HASYLAB, and the mesoscopic structures were investigated by GISAXS at BW4, HASYLAB [3].

From the optical micrographs (Fig. 2.15a), we observed that the thin film surface was smooth with holes. After 41 days at room temperature (Fig. 2.15b), we observed growing PEO crystals. The crystalline domains grew radially leading to a circular shape. Near the growth front, the films are thicker. The crystallization of the entire film was completed after 148 days (Fig. 2.15c).



Figure 2.15:

Optical micrographs of a PI-*b*-PEO thin film right after spin-coating (a), after 41 days at room temperature (b), and after completion of the crystallization after 148 days (c). The lighter, the higher the film thickness.



Figure 2.16:

2D GISAXS images of a PI-*b*-PEO thin film right after spin-coating (a) and of a completely crystallized film after 148 days (b). The arrows indicate the positions of the Bragg reflections from the hexagonal lattice. (c) GIWAXS intensity profiles for the same films after spin-coating (•) and after completion of crystallization (•). The lines are guides to the eye.

In order to obtain information of the buried mesoscopic structure, GISAXS measurements were performed both after spin-coating (Fig. 2.16a) and for films which had completely crystallized (Fig. 2.16b). Right after spin-coating, we observed diffuse Bragg reflections at the positions expected for the hexagonal morphology with the cylinders lying in the film plane. The repeat distance was found to be 10.0 ± 0.6 nm. In the GISAXS image for the completely crystallized sample (Fig. 2.16b), the diffuse Bragg reflections of the hexagonal structure were absent, which means that the hexagonal morphology had been destroyed by the crystallization. The GIWAXS experiment (Fig. 2.16c) show that, after spin-coating, there were no Bragg peaks from the crystalline structure of PEO. For the completely crystallized film, however, a Bragg peak at $q_{xy} = 1.35$ Å⁻¹ was present which corresponds to the 120 reflection of the monoclinic crystal lattice of PEO [4]. This means that the chain stems are perpendicular to the film/substrate interface.

In summary, we have observed break-away crystallization in thin films from a low molar mass, cylinder-forming PI-*b*-PEO diblock copolymer. The crystallization of PEO in cylinders immersed in a PI matrix results in the destruction of the already formed hexagonal arrangement of the cylinders. The resulting crystals have their *c*-axis of the unit cell parallel to the film normal. We attribute this behavior to the weak segregation of the diblock copolymer. This work was financially supported by DFG (Pa771/3) and by the Incentive Fund for Re-

search Collaborations between TU München and the Danish Technical University.

- D. J. Quiram, R. A. Register, G. R. Marchand, D. H. Adamson, Macromolecules **31**, 4891 (1998).
 G. Reiter, G. Castelein, P. Hoerner, G. Riess, A. Blumen, J. -U. Sommer, G. Floudas, Eur. Phys.
 J. E. **2**, 319 (2000). L. Zhu, S. Z. D. Cheng, P. Huang, Q. Ge, R. P. Quirk, E. L. Thomas, B. Lotz, B. S. Hsiao, F. Yeh, L. Liu, Advanced Materials **14**, 31 (2002).
- [2] A. J. Ryan, I. W. Hamley, W. Bras, F. S. Bates, Macromolecules 28, 3860 (1995).
- [3] S. V. Roth, R. Döhrmann, M. Dommach, M. Kuhlmann, I. Kröger, R. Gehrke, H. Walter, C. Schroer, B. Lengeler, P. Müller-Buschbaum, Rev. Sci. Instr. 77, 085106 (2006).
- [4] Y. Takahashi and H. Takadoro, Macromolecules 6, 672 (1978).

2.10 Structured organic solar cells

R. Meier, P. Müller-Buschbaum

Due to the limited processing possibilities and the high processing costs of silicon, polymers become more and more attractive for the development and production of organic solar cells. The basic phenomenon used for this device is the photo-induced electron transfer from donor-type semiconducting polymers onto acceptor-type polymers or molecules. Especially the low large-scale production costs, the mechanical properties of polymers (flexibility, solubility, etc.) and the steadily invention of novel polymer structures will lead to an increase of the already reported power conversion efficiencies of 5% [1].

The correlation between the morphology and the observed photophysical properties of organic solar cells is investigated by probing different surface structures resulting from selforganization and patterning.

For the investigation of the morphology scanning probe microscopy (e.g. AFM) and scattering techniques will be used. Grazing incidence small angle scattering (*GISAS*) provides structural information over a large sample area and allows to assign characteristic properties to the different components of the blend system. In addition, the recently installed ellipsometer with combined AFM (Nanofilm SPEM), which later will be introduced into a beamline at the synchrotron Hasylab, displays morphologies combined with thickness information.

Key control parameters for selforganized structures are the polymer solvents, the blend ratio and the interaction with the contact materials. The materials will be processed with a spin-on technique. Hence the spin parameters and the structure of the solar cell (e.g. adhesion forces between different layers) will have significant influence on the final performance of the device. Also postproduction treatments are important. Therefore different annealing procedures and storing methods in solvent vapor atmosphere have to be investigated.

Pattering allows creation of lateral structures in the range of $\approx 100nm$. These structures can be achieved by micro-contact printing (μ -CP), where a commercially available rubbery stamp (polydimetylsiloxan, PDMS) is soaked with the polymer solution and then pressed on the substrate. Such structures lead to well ordered conjugated polymer films. It doesn't provide any electron traps and has a large interface area where the excitons can be separated due to offset energy levels of the different materials. Such type of structure is known to be ideal for organic solar cells.

In order to optimize the absorption coefficient of polymer-based solar cells it is useful to sensitize them to the solar emission spectrum, which has a maximum photon flux at around

1.8eV. Nanoscale anorganic particles, e.g. Cadmium Telluride (CdTe) with an band gap energy $E_g \approx 1.6eV$, suit not only this goal, they also enhance the charge transport in the polymer, in which they are encapsulated.

Although the power conversion efficiencies of organic solar cells are still considerably low in comparison to the ones from silicon based cells (5% vs. 20%), the immense amount of effort spent in this research field makes it highly likely to reach the 10%-area in the near future [1].

[1] N. S. Sariciftci, Plastic photovoltaic devices, Materials Today, 9/2004, p.36-40

3 Polymer hybrid systems

3.1 Influence of maghemite nanoparticles on the microphase separated nanostructures in cylinder forming P(S-b-MMA) copolymer films

M. M. Abul Kashem, S. V. Roth¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

Nanocomposite material based on diblock copolymer and magnetic nanoparticles is a research area of growing interest. The core idea of such kind of nanocomposite material is to use the microphase-separated polymer nanostructures such as cylinders or lamellae as the template to arrange the inorganic particles. Another method to prepare ordered arrays of nanoparticles can be obtained from a blend of nanoparticles coated with polymeric hairs and diblock copolymer solution [1, 2]. After annealing of such a blend film, the nanoparticles go to a selective block and an ordered arrangement of particles is achieved. In the present investigation, we studied the effect of nanoparticles and annealing on the self-assembled nanostructures present in the thin nanocomposite film prepared from a diblock copolymer solution blended with magnetic nanoparticles.

The investigated composite films are prepared from polystyrene-block- polymethylmethacrylate, denoted as P(S-b-MMA), and maghemite nanoparticles. The molecular weight of the diblock copolymer is 77 kg/mol. The volume fraction of PMMA block is 0.29. Therefore, the polymer undergoes microphase separation in bulk and forms cylinders of PMMA in PS matrix. The maghemite nanoparticles are stabilized in toluene by attaching oleic acid and oleylamine. They have a diameter of 6.4 ± 0.6 nm measured from the SEM image of a monolayer of particles. The substrate used to prepare the thin film is silicon (100) wafer pieces which are exposed to 19% hydrofluoric acid bath for 2 minutes followed by the strong rinsing with deionized water and compressed nitrogen gas flow drying. The thin films having varying amount (0%, 0.25%, 0.5%, 1%, 2% and 4% by wt. with respect to amount of polymer) of nanoparticles are prepared by spin coating. Two sets of samples are prepared. One set of samples is annealed at 165^0 C in a vacuum oven for 72 hours followed by slow cooling and another set of samples is as prepared films without annealing. We used the surface sensitive grazing incidence small angle X-ray scattering (GISAXS) technique [3] to investigate both sets of nanocomposite films.

GISAXS measurements were carried out at the beamline BW4 of the DORIS III storage ring at HASYLAB (DESY, Hamburg). The selected wavelength was λ = 0.138 nm. The beam divergence in and out of the plane of reflection was set by two entrance cross-slits. The beam was focused to the size of 60 μ m × 30 μ m by using an assembly of refractive Beryllium compound lenses [4]. The sample was placed horizontally on a goniometer. A beam stop (a diode) was used to avoid direct beam to the detector. Besides, a moveable rod-like beam stop was also used to shield the specular peak and the high intensities at very low q_y on detector. An incident angle was selected α_i =0.31⁰, which is well above the critical angles of both polymers (PS and PMMA) and of the nanoparticles, so that the beam can penetrate the sample and the obtained data gives the information of not only the surface structure but also the structural information inside the film. The scattered intensities were recorded by a 2D detector (MARCCD; 2048×2048 pixel). To have an access to the lateral structural information, we made a horizontal cut from the two dimensional intensity distribution at a constant q_z , at the critical angle of polystyrene. Such kind of cut is called out-of-plane cut because it is perpendicular to the conventional scattering plane. A horizontal cut at constant q_z tells us about the geometry, size distribution, and spatial correlation of lateral structures present in the thin film [3]. In Fig. 3.1 the out-of-plane cuts of the scattering intensity distribution on the 2D detector of samples before and after annealing are plotted together to explain the effect of annealing and nanoparticles concentration on the microphase separated structure.



Figure 3.1:

Out-of-plane cuts of the GISAXS data showing the influence of annealing and nanoparticles concentration (left-before annealing; middle- after annealing). Two pronounced structure factor peaks 1 and 2 are visible. The increase of the lateral structure length due to annealing of the film and incorporation of the nanoparticles are shown in the right figure. The percentage numbers presented in the figure are the nanoparticle concentrations (wt%) in the polymer solution used to prepare the films. The dash line shows the limit to access the structure information due to presence of a rod-like beam stop.

In the left image (samples before annealing), we clearly see two structure factor peaks. The structure factor marked with "1" is located at $q_y = 1.67 \times 10^{-1}$ nm⁻¹ corresponding to a lateral distance of 37.6 nm and the structure factor marked with "2" is at 7.4×10^{-1} nm⁻¹ corresponding to a lateral distance of 8.5 nm. The structure factor peak 1 is assigned to the distance between two cylinders, which are oriented along the surface normal (perpendicular to the surface). The distance 8.5 nm corresponds to the distance between two neighbour particles. Both peak positions, structure factor 1 and 2, remain almost constant in case of un-annealed samples, independent of the amount of nanoparticles. In the annealed samples the position changes. After annealing the position of peak 1 changes towards lower q_y values, i.e., the distance between neighbouring cylinders of PMMA increases.

occurs two times: after annealing, and due to the incorporation of the nanoparticles. This shift is emphasized in the presentation shown in figure 1 (right image). The distance between two nearest cylinders increases to 55 nm in the sample without any nanoparticles after annealing. Thus this equilibrium structure is larger than the non-equilibrium structure which was installed in the films directly during spin-coating. The spin-coating structure is mainly driven by evaporation of the solvent, whereas the equilibrium structure is dominated by interactions and entropy. In case of composite samples, the nanoparticles go to the PS matrix and swell the PS phase, which lead the PMMA cylinders to arrange themselves at distance larger than that without nanoparticles. The increased distance is 65 ± 2 nm irrespective to the increase of nanoparticle concentration. A model fit of the data by using IsGISAXS software, which might interpret more details about the arrangement of the particles inside the microphase separated block copolymer nanostructures, is in progress.

- [1] V. Lauter-Pasyuk, H. J. Lauter, G. P. Gordeev, P. Müller-Buschbaum, B. P. Toperverg, M. Jernenkov, and W. Petry, Langmuir 19, 7783 (2003)
- [2] M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, W. Petry, P. Müller-Buschbaum; Macromolecules, 40, 5075 (2007).
- [3] P. Müller-Buschbaum, Anal. Bioanal. Chem. 376, 3 (2003)
- [4] S.V. Roth et al., Rev. Sci. Instr. 77, 085106 (2006)

3.2 Magnetic properties of magnetic nanoparticles in a copolymer matrix

L. Schulz¹, W. Schirmacher, S. Vallopilly², P. Böni³, W. Petry, P. Müller-Buschbaum

- ¹ Now at Dept. de Physique, Université de Fribourg, Switzerland
- ² LENS, Indiana University Cyclotron Facility, Bloomington, USA
- ³ Phys.-Dept. TUM. E21

Magnetic properties of nanoparticle systems have been and are until now of great interest due to a wealth of technological applications which vary from electronic data storage to medical applications. Samples involving magnetic nanoparticles can be powders, magnetic colloids or particles imbedded in a solid nonmagnetic matrix. If the particles are smaller than the typical radius of magnetic Bloch domains their atomic magnetic moments point all into the same direction (supermoment or superspin). If this direction can easily follow that of an applied field one speaks of superparamagnetism i.e. classical Landau-Lifshitz type magnetism with huge spins. The equation of states M(H) of classical spins is given by the Langevin function $M(H) = M_S [\coth(x) - 1/x]$ with $x = M_S V H/k_B T$ where M_S is the saturation magnetization and V the particle volume. If the material has an exchange anisotropy the reorientation of the moments can be blocked below a certain temperature or for particle volumes exceeding a certain limiting value. This is due to a reorientation barrier which leads to an activated reorientation rate of te form $\tau^{-1} = \nu_0 \exp\{-KV/k_B T\}$, where K is the exchange anisotropy per volume and ν_0 is an attempt frequency of the order of 10^{10} Hz.

In the present study magnetic properties of thin composite films, consisting of polystyrenecoated γ -Fe₂O₃ (maghemite) nanoparticles embedded into polystyrene-block-polyisoprene (P(S-b-I)) matrices, are investigated. Since the nanoparticles are coated with polystyrene, they show an affinity to the polystyrene lamellae [1].



Figure 3.2:

Left: "Superparamagnetic" magnetization curves of samples with different particle concentrations, fitted with the Langevin function, averaged over a Log-normal volume distribution of width $\sigma = 0.6$.

Right: Out-of phase AC susceptibility $\chi''(T)$ at $\nu = 10$ kHZ for FC and ZFC compared with the log-normal distribution of width $\sigma = 0.6$ and $\sigma = 0.8$.

Samples with nanoparticle weight concentrations of c = 0, 0.7, 2, 4, 8, 14, 16, 18, 20, 25 and 43 w% were prepared by the solution casting technique to allow for an equilibration of the morphology. Precleaned silicon wafers were used as substrates.

The magnetic properties of our samples were investigated with a Physical Property Measurement System (PPMS) from Quantum Design. The left part of Fig. 3.2 shows the magnetization curves observed at 300K. As the magnetic particles are polydisperse we fitted a Langevin function averaged over a log-normal volume distribution $P(V) \propto \exp\{-(\ln V/V_0)^2/2\sigma\}$ with width $\sigma = 0.6$



Figure 3.3: FC and ZFC magnetization (left) and in-phase AC susceptibility (right) vs. temperature

We found that the saturation magnetizations are proportional to the weight concentration of the magnetic additives, which indicates that interaction effects between the particles play a minor role.

Together with the magnetization we measured also the AC susceptibility $\chi(\nu, T) = \chi'(\nu, T) + i\chi''(\nu, T)$ at $\nu = 10$ kHZ, where χ' is the in-phase and χ'' the out-of-phase susceptibility. It is well known that the temperature dependence of χ'' follows precisely the volume distribution $P(V_T)$ with $V_T = k_B T \ln(\nu_0 t_m)/V$, because it is sharply peaked around V_T . In the right part of Fig. 3.2 we show χ'' vs. T for field-cooled (FC) conditions, (i.e. with decreasing temperature and an applied field of $H_0 = 500$ Oe) and for zero-field-cooled (ZFC) (i.e. the sample was cooled in zero field to T = 2 K, then an applied field of $H_0 = 500$ Oe was applied and the temperature was raised). We see that both types of data for different concentrations follow precisely the log-normal distribution with $\sigma = 0.8$. As the magnetization fits are not perfect, that indicated by the $\chi''(T)$ curve.



Figure 3.4:

Left: Magnetic-moment curves at 300K (full lines) and 2K (dashes) for the two highest concentrations (see Fig. 3.2).

Right: Hysteresis Curves at different temperatures calculated with a classical Néel-type switching model

As maghemite is known to have an appreciable exchange anisotropy it is not surprizing that the magnetization and in-phase susceptibility χ' differs below ~ 60 K, which is just near the maximum of χ'' . As - at a given temperature T - the super-magnetization of a nanoparticle with volume greater than V_T is essentially blocked, the curve in the right part of Fig. 3.2 represents the distribution of blocking temperatures. This is the reason for the discrepancy of the FC and ZFC curves in Fig. 3.3 below 60 K. Below this temperature also a finite hysteresis is to be expected. We measured the magnetization at T = 2K, which is depicted together with the 300 K magnetization in the left part of Fig. 3.4. It is astonishing that the slope of the curves is the same. Using the blocking model of Néel [2] we performed calculations of the hysteresis curve for different temperatures. It can be seen from the right part of Fig. 3.4 that for a temperature difference of more than 10 K an appreciable difference in slope is expected. However, our data at 2K and 300K have essentially the same slope.

So we found that the temperature dependence of our samples cannot be explained within the classical model. Néel's model of spin switching between different equilibrium angles has been generalized to include tunneling at low enough temperatures [3-5]. The result is that the relaxation rate becomes temperature independent below a certain crossover temperature $T_{\text{cross}} = \tilde{B}/Kk_B$, where \tilde{B} is the WKB tunneling exponent per volume, where it is equal to $\nu_0 \exp\{-KV/k_BT_{\text{cross}}\}$. We therefore claim to have evidence for quantum tunneling of the magnetization of the nanoparticles at low temperatures. Model calculations including this effect in order to explain our findings are under way. We see already from the right part of Fig. 3.4 that probably the 300 K data correspond to $T^* \sim 10$, whereas the 2K data correspond to $T^* \sim 1$, indicating that quantum tunneling starts below ~ 30 K.

- V. Lauter-Pasyuk, H. Lauter, G. Gordeev, P. Müller-Buschbaum, B. Toperverg, M. Jernenkov, W. Petry, Langmuir, 19, 7783 (2003).
- [2] L. Né el Ann. Geophys. 5, 99 (1949).
- [3] M. Enz and R. Schilling J. Phys. C: Solid State Physics 19 L711 and 1765 (1986).
- [4] J. L. van Hemmen, A. Sütö, Europhys. Lett., 1 (1986); Physica 141 B, 37 (1986).
- [5] E. M. Chudnovski, L. Gunther, Phys. Rev. Lett. 60, 661 (1988): J. Tejada, X. X. Zhang, E. M. Chudnovski, Phys. Rev. B 47, 14977 (1993).

3.3 In-situ observation of nanoparticle ordering at the air-water-substrate boundary in colloidal solutions using X-ray nanobeams

S.V. Roth¹, T. Autenrieth¹, G. Grübel¹, C. Riekel², M. Burghammer², R. Hengstler, L. Schulz, P. Müller-Buschbaum

- ¹ HASYLAB at DESY, Hamburg, Germany
- ² ESRF, Grenoble, France

Nanostructuring using solution casting is one method of choice to install large-area twodimensional (2D) thin films with specific morphology, offering the possibility to design 2D or three-dimensional (3D) photonic crystals. This method is especially important and applicable in the field of colloidal particles, as colloidal particles are often suspended in aqueous solutions.



Figure 3.5:

a) Quantitative analysis of the length scales in vertical direction as derived from the x-ray data. The time is calculated relative to t_b , hence t = 0 s corresponds to the arrival of the three-phase-boundary at the beam position. For 780 s = t = 2000 s, the layer thickness remains nearly constant. The subsequent increase stems from layer-by-layer deposition (one layer each 340 s). After the peak, compaction of the colloidal layer occurs, and the height stays constant. b) Most-prominent in plane length scale ξ . $\xi(t)$ follows a $t^{0.32\pm0.06}$ power-law. The lower symbols indicate the radius of the spherical gold nanoparticles for comparison. Clearly, the layer-by-layer deposition is retarded with respect to the lateral nanostructuring. Taken from [4].

However, nanostructuring is a very complex process involving several mechanisms. Solvent evaporates and increases the concentration of the colloidal particles. The increased evaporation near the contact line drives a convective flow within the drop that transports material towards the periphery. Additionally, an increased solute concentration and a decreased temperature near the three-phase contact line may trigger solutal and thermocapillary Marangoni flows. However, also the interaction with the substrate and transversal contact line instabilities have to be taken into account. Finally, capillary forces come into play as soon as the solution film has a comparable thickness as the colloidal particles' diameter.

Previous studies addressed the ordering of nanoparticles at the liquid-air interface [1]. However, for technical applications it is of great importance to transfer this order to a solid substrate [2]. The interaction with the substrate allows for tuning the arrangement of the nanoparticles and thus the layers' optical properties. Hence it is only natural to investigate in-situ the evolution of ordering at the three phase contact line liquid-air-substrate.

As samples, we chose commercial unconjugated colloidal gold solutions. Gold nanoparticles are inert and moreover have the advantage of strong scattering contrast to the solvent (water). A droplet of 25 μl volume was deposited on a blank, acidly cleaned Si-wafer surface using a high-precision, remotely controlled syringe pump available at ID13. The resulting droplet diameter on the surface was 3 mm.

For the first time a grazing incidence setup was operated with a nanometer sized x-ray beam, giving rise to an new class of experiments, namely nanobeam-grazing incidence small-angle x-ray scattering (nanobeam-GISAXS) experiments. We used the extremely brilliant 300 nm-size beam (FWHM) produced by Fresnel zone plates at a wavelength of 0.0976 nm. Due to the small beam diameter in the nanobeam small-angle x-ray scattering (nanoSAXS) geometry [3] and the incident angle of $\alpha_i < 0.543^\circ$, the footprint on the sample surface was only 0.3 μm x 32 μm . Hence the surface curvature of the droplet can be neglected and the droplet surface with respect to the beam can be considered as locally flat. The evaporation time was $t_b = 3250$ s.

The result is shown in Fig. 3.5. For times t < 2000 s, a constant height is found. This seems to correspond to a rapidly deposited, short-range order hexagonal close packing of an n=2 layer of colloidal spheres of 2 nm diameter. For t > 2260 s, which is much larger than the time where lateral growth sets in, a linear growth following 0.0049 nm/s $\times t$ in height H of the layers is found. At t = 3770 s the vertical growth is essentially finished and levels of into its final value H = 9.2 nm due to compaction. From the linear time-dependence 2080 s < t < 3770 s, one can estimate the establishment of a full layer with height increase of 2 nm $\times \sin 60^\circ = 1.7$ nm every 340 s, assuming close packing of the colloidal particles. This would correspond to a layer-by-layer growth every 340 s assuming close packing. As one can see the final ordering in this aqueous colloidal solution takes place with time scales on the order of some 10 s. More remarkably, the lateral growth is finished *before* vertical growth sets in. To our knowledge, this time delay between vertical and lateral growth has not been reported yet.

- [1] S. Narayanan et al., Phys. Rev. Lett. 93, 135503 (2004)
- [2] W. Cheng, et al., Nat. Mater. 5, 830 (2006)
- [3] P. Müller-Buschbaum et al., Europhys. Lett. 73, 35 (2006)
- [4] S.V. Roth et al., Appl.Phys.Lett. 91, 091915 (2007)

3.4 In situ GISAXS study of gold sputtering onto a polymer template

E. Metwalli, V. Körstgens, S. Couet¹, K. Schlage¹, R. Röhlsberger¹, S.V. Roth¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

Recent advances in the patterning of polymers have enabled the fabrication of integrated micro- and nanosystems with a high degree of complexity and functionality [1-3]. For example, block copolymers have attracted immense interest for nanotechnology applications because of easy processability and low-cost fabrications. The chemically distinct and immiscible polymer blocks in block copolymers microphase-separate and self-assemble into ordered patterns on the scale of nanometers. This soft nanostructured polymer film can further be used as a template for patterning of hard inorganic materials such as metal nanoparticles. Metal nanoclusters in a matrix of insulating polymer have unique physical properties and have been proposed for optical, electrical, and magnetic applications. The techniques used for the metal patterning along with the various mechanisms (adsorption, surface diffusion, nucleation, and agglomeration) involved in the dispersion process of the nanoparticles within the polymer film make it difficult to understand the dynamics of nanoparticle formation in polymer matrix. In the present study we used the sputtering technique to investigate the deposition of gold nanoparticles onto commercially important types of copolymers-the thermoplastic elastomers. A mixture of polystyrene-block-polyisoprene-block-polystyrene P(S-b-I-b-S) triblock and polystyrene-block-polyisoprene P(S-b-I) diblock copolymers is known for its use in pressure sensitive adhesive (PSA) applications [4]. Here, we report on using a detachable DC magnetron sputtering deposition system mounted at a beamline allowing for grazing incidence small-angle X-ray scattering (GISAXS) to investigate the in situ formation and growth of gold nanoparticles in the polymer film. The GISAXS measurements were carried out at beamline BW4 of DORIS III storage ring [5, 6] at HASYLAB (DESY, Hamburg). The sample inside the sputtering chamber was placed horizontally (xy plane) and at an incidence angle $\alpha_i = 0.4$ to the incidence x-ray beam by tilting the whole chamber using a goniometer. The incidence angle is well above the critical angle of both the polymer film and the substrate ($\alpha_{c(SIS/IS)} = 0.133$, $\alpha_{c(Si)} = 0.200$); therefore, the Yoneda peaks of both materials and specular peak are well separated on the 2D detector. At this angle of incidence both surface and bulk nanostructures of the polymer film are accessible. Structural information is obtained by horizontal (q_y) and vertical (q_z) cuts of the 2D intensity distribution. The resulting intensity profiles were fitted using a software IsGISAXS [7], which is based on the distorted-wave Born approximation and the DA (decoupling approximation) for particles encapsulated in a layer on a substrate. The interference function is fitted with a two parameter functions; the average distance, D and the disorder parameter, ω . The program was also used to model the full 2D intensity distribution. It allows us to determine the inter-particle distance, D, the particle shape, lateral size, and size distribution.

The GISAXS 2D images (Figure 3.6-a) of the thin blend copolymer film show two intensity maxima (marked with arrows), separated by the shadow of a rod-shaped beamstop, visible along q_y direction, that originate from the interference of the PS-domains. This interference effect arises because the PS domains are separated by a preferential nearest neighbors (center-to-center) distance, D. The detection of only one interdomain interference and the absence of additional secondary bcc peaks (at $q_2/q_1 = \sqrt{2}$ and $q_3/q_1 = \sqrt{3}$) indicate that no regular spatial arrangements of the PS-rich domains and a more liquid-like ordered structure best describe the morphology of the polymer film. The deposition of gold on this polymer template was performed for 6-second periods and the in situ GISAXS measurements were collected



Figure 3.6:

Composite images showing 2D scattering patterns of phase separated thin blend copolymer film, (a) 10 repetition of six-second corresponding to 0.43 Å deposition of gold per repetitions onto the polymer film (b-k), and after 10 h relaxation of the 4.3 Å gold covered copolymer film (l). The intensity is shown on a logarithmic scale. The gray rectangle in the middle of the images indicates the rod beam stop and the horizontal black line with pointlike end is the specular beam stop. Two white arrows indicate the two scattering intensity maxima along the q_y direction.

for 30 second immediately after the deposition step. The deposition steps (at a rate of 4.3 Å/min for six seconds) followed by the GISAXS measurements were both repeated for 10 times and the 2D intensity profiles are shown in Figure 3.6 b-k. As the amount of deposited gold increases, the prominent peak at $q_y = 0.015$ Å⁻¹ on both sides of the beam stop gradually grows in intensity along the q_z axis (Figure 3.6 b-k). The fitting of the out-of-plane cuts (q_y) of the 2D scattering intensity profile (at q_z position of 0.025 Å⁻¹) was performed for $q_y \ge 0.005$ Å⁻¹ and indicates no strong influence of the accumulated gold particles on the overall lateral structures of the polymer film. In addition, no additional characteristic scattering peak is observed for the gold particles on the q_y direction. On the other hand, the vertical cuts (q_z) obtained at the prominent peak (at q_y position 0.015 Å⁻¹; shown in Figure 3.6 as two vertical growing intensity) shows a gradually increase of the intensity with increasing of the amount of gold. The polymer film model was simulated using the high x-ray refractive index gold particles instead of the PS domains. The results of this simulation compared with the experimental one indicates that the gold diffuse inward, and aggregate inside the PS domains.

The polymer film sputtered with 4.3 Å gold was kept to relax for 10 h and then the GISAXS measurement was performed to investigate a possible structural reorganization of the gold nanoparticles inside the film (Figure 3.6-l). The GISAXS study indicates negligible changes in the film structure after 10 h relaxation time of the gold covered polymer film and reveals that the gold nanoparticles aggregate and form a stable morphology within the film.

As a conclusion, the in situ GISAXS investigation is critical for understanding how the arrangements of metal nanoparticles correlates with the structure of copolymer domains within the film and opens new possibilities for the investigation of metal-polymer interactions. Our results indicate that gold migrates to the central regions of the polymer film and decorates the spherical PS domains. The gold-gold interaction in PS regions dominates the gold-polymer interaction. Metal aggregation occurs at a rate faster than the diffusion of gold atoms in the polymer. Our study introduces the concept that, without thermal annealing of the gold attached polymer film, the gold assembly is not limited to the flat two dimensional but also included in the three dimensional structures.

- [1] Y. N. Xia, E. Kim, X. M. Zhao, et al., Science 273, 347 (1996)
- [2] S. R. Quake, A. Scherer, Science 290, 1536 (2000)
- [3] J. Schmitt, G. Decher, W. J. Dressick, et al., Adv. Mater. 9, 61 (1997)
- [4] A. Roos, C. Creton, Macromolecules 38, 7807 (2005)
- [5] S. V. Roth, R. Döhrmann, M. Dommach, et al., Rev. Sci. Instr. 77, 085106 (2006)
- [6] P. Müller-Buschbaum, Analytical and Bioanalytical Chem. 376, 3 (2003)
- [7] R. Lazzari, J. Appl. Cryst. 35, 406 (2002)

3.5 Structure of gold films as contact material in organic photovoltaic devices

G. Kaune, K. Schlage¹, S. Couet¹, R. Röhlsberger¹, S. V. Roth¹, P. Müller-Buschbaum

¹ HASYLAB at DESY, Hamburg, Germany

Photovoltaic energy conversion systems based on organic materials have attracted increasing interest within the last years. Due to easy available basic materials and simple processing methods organic solar cells are inexpensive in production and thus a promising alternative to inorganic solar cells for power supply of low-cost and mobile electrical devices. Common architectures for organic solar cells consist of two conductive polymers [1], an inorganic semiconductor and a polymer [2] or a blend of a polymer and a fullerene [3]. In order to pick off the generated voltage, two electrodes are required. Usually a transparent conducting oxide is used as front electrode and a thin metal film acts as back electrode. By its work function the metal electrode has a strong influence on the electrical performance of the solar cell, but additionally it can also change structural properties of the active layer. For this reason, it is necessary to understand the growth process and the interaction with the underlying components.

The model system used for this study consists of nanostructured titanium dioxide and poly-N-vinylcarbazole. On top of this, a thin gold layer was deposited by sputtering and structure evolution was monitored in-situ with grazing incidence small angle scattering (GISAXS). The experiment was carried out at HASYLAB beamline BW4, which was equipped with a DCmagnetron sputtering chamber. Sputtering power was set to 4 W, yielding a deposition rate of 0.43 nm/min. The sample-to-detector distance was set to 1.9 m and a wavelength of 0.138 nm was used. For the incident angle a value of 0.8° (above the critical angle of gold) was chosen. To achieve the required time resolution, the experiment was performed in cycles of one minute deposition and a subsequent measurement. In total, 49 cycles were carried out and a gold film of 21 nm thickness was deposited.



Figure 3.7:

2d GISAXS scattering images as probed during gold contact deposition: the upper left corner shows the image of initial state before deposition and the lower right corner the image of the final state after 49 deposition cycles.



Figure 3.8:

a) Vertical cuts and b) horizontal cuts taken from the 2d scattering images. Only the cuts of every third image are shown, deposition time increases from bottom to top. c) The time evolution of particle height and distance as determined from fitting the data.

Fig. 3.7 shows the 2d scattering images of all 49 cycles. It is clearly visible that within the first minutes of gold deposition the scattering image of the bare composite film is superimposed with the characteristic scattering image of gold. With ongoing deposition, the height growth of the gold film dominates the evolution of the scattering image by forming a modulation along the a_f -axis. With growth in film thickness, the wavelength of the modulation

decreases, while the number of modulations increases. This evolution is also visible in the vertical cuts taken at the centre position of the images shown in fig. 3.8a. Fig. 3.8b shows the corresponding horizontal cuts. The most prominent feature here is a weak side peak moving from the outer edge to the middle. For further analysis the cuts were fitted with IsGISAXS [4]. The best results were obtained by use of a model of cylindrically shaped particles arranged in an isotropic paracrystal distribution. With this model it was possible to determine particle height values from the vertical modulation and to assign the side peak to the distance of the gold particles (fig. 3.8c). Height growth is linear in time over the whole deposition time, with exception of the very first minutes, where no statement about particle height can be made from the scattering data. Due to lateral growth and coalescence of the gold clusters their average distance increases during deposition. The fastest increase is observed within the first minutes, after about 40 min deposition time lateral growth of the particles stops and the particle distance reaches a nearly constant value. At the chosen deposition conditions diffusion of the gold can be considered as low [5], what is confirmed by the observed linear height growth of the particles.

From this results it can be concluded that under the chosen conditions the gold top contact grows in an ordered and controlled manner, what is favourable for application in a photo-voltaic cell.

- A. J. Breeze, Z. Schlesinger, S. A. Carter, H. Tillmann, and H. H. Hörhold, Sol. Energy Mater. Sol. Cells 83, 263 (2004)
- [2] W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, Science 295, 2425 (2002)
- [3] W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, Adv. Funct. Mat. 15, 1617 (2005)
- [4] R. Lazzari, J. Appl. Crystallogr. 35, 406 (2002)
- [5] T. Strunskus, M. Kiene, R. Willecke, A. Thran, C. von Bechtolsheim, and F. Faupel, Mater. Corros. 49, 180 (1998)

3.6 Combinatorial investigation of nanostructures formed in a titanium dioxide based nanocomposite film on top of fluor-doped tin oxide layers

P. Müller-Buschbaum, J. Perlich, M.M. Abul Kashem, L. Schulz¹, S.V. Roth², Y.J. Cheng³, J.S. Gutmann³

- ¹ Université de Fribourg, Fribourg, Switzerland
- ² HASYLAB at DESY, Hamburg, Germany
- ³ MPI for Polymer Research, Mainz, Germany

In the past decade, there is a growing interest in the field of polymer-based photovoltaic (PV) technologies and conversion concepts. Typically, PV devices are built in a sandwich structure on indium tin oxide (ITO) or fluor-doped tin oxide (FTO) coated glass substrates. Both, ITO and FTO, are transparent metal oxides, and thus ideal as transparent electrodes. Because ITO/FTO has a variable workfunction, it is rarely used as the lone bottom electrode. Either PEDOT-PSS or TiO₂ is used for the transparent material deposited on top of the ITO/FTO substrate, resulting in opposite polarity devices due to differential workfunction steps. TiO₂ is a promising candidate as an electron acceptor and transport material, as confirmed by its use in dye-sensitized cells and hybrid polymer/TiO₂ cells . When light is incident on TiO₂, it becomes relatively conducting so that the quasi Fermi-level of the photodoped TiO₂ appears

to play an important role in determining the open circuit voltage. Both TiO₂ and PEDOT-PSS have been shown to improve device performance over bare ITO/FTO. The morphology of the TiO₂ layer greatly influences the efficiency of the devices and interface structure between ITO/FTO and the TiO₂ barrier layer is of special interest. One very promising way to fabricate nanostructured TiO₂ layers on top of ITO/FTO is a solution-based sol-gel process [1]. An amphiphilic block copolymer, poly(styrene)-block- poly(ethyleneoxide) denoted P(S-b-EO), is used as a template to obtain nanocomposite films, followed by calcination at 450° C for 4 hours to obtain crystalline TiO₂ nanostructures.



Figure 3.9:

a) Composite image comprising the 2d scattering patterns from 20 positions along the FTO-gradient (left to right and top to bottom). The top left scattering pattern was measured at the largest FTO thickness and the bottom right one at the bare glass substrate. Each 2d image shows an angular range of 1.05° in horizontal (out of plane) and 1.86° in vertical direction. The specular peak is blocked with a small beamstop. b) Sketch of the FTO gradient coated with a nanocomposite layer probed in the combinatorial approach. c) Detected characteristic lateral length of the FTO layer (solid symbols) and of the nanocomposite film (open symbols) plotted as a function of the position in gradient direction y. For comparison the relative change in the FTO signal I_{FTO}/I_o (solid line) is superimposed to show the gradient position. Taken from [4].

Within the present investigation we apply a combinatorial approach to focus on P(S-b-EO)titania nanocomposite structures on the FTO film. Thus we address the first important step in creating the anode of a PV device. Instead of a simple homogenous FTO layer on the glass substrate a thickness gradient between the homogeneous FTO layer and the bare glass surface is investigated. Part of the 654 nm thick FTO layer (Solaronix SA) on boroalumino silicate glass (TCO10-10) was removed by etching resulting in the wedge-shaped gradient between the intact FTO layer and the bare glass surface. The P(S-b-EO)-titania nanocomposite film results from spin-coating. The TiO₂ nanostructures have a nanowire-like shape due to the chosen conditions [2].

The structural investigation is based on a combination of the surface sensitive scattering technique, grazing incidence small angle X-ray scattering (GISAXS), and a moderate micro-focussed X-ray beam (size (H*V) 60*30 μ m²) [3]. The scattering experiment was performed at the beamline BW4 at HASYLAB (Hamburg) at wavelength of 0.138 nm. The FTO-gradient

was aligned perpendicular to the X-ray beam. Position sensitivity was achieved by scanning the FTO-gradient. A region of 1 mm was scanned in steps of 50 μ m. Thus the change in FTO thickness from 654 nm to the bare glass surface was probed completely. Fig. 3.9a shows the corresponding two dimensional (2d) GISAXS patterns [4]. Already the 2d GISAXS patterns show a clear change along the gradient due to the change in the morphology.

For analysis line cuts in out-of plane direction from the 2d GISAXS pattern [3] are performed. To emphasize on the structure of the FTO layer the cuts were performed at the critical angle of FTO and in addition to probe the structure of the nanocomposite film cuts were performed at the critical angle of PS. Characteristic lateral distances ξ of the FTO and the nanocomposite film were modelled with a structure factor. A Lorenzian-type distribution of was assumed to account for statistical deviations from this nearest neighbour distance. In the fit the experimentally determined resolution function was taken into account. Major result is the characteristic lateral length ξ for both layers. In Fig. 3.9c these information are plotted as a function of the position along the FTO-gradient.

The FTO film exhibits a dominant length of 18 nm, which is unchanged as a function of the position. The absence of FTO is correlated with the vanishing of this lateral length. The shape of the gradient is extracted from the intensity of the related structure factor peak normalized by the primary intensity I_{FTO}/I_o . As visible in Fig. 3.9c in the beginning the gradient is quite steep due to the applied etching [4]. Again the vanishing of this intensity marks the end of the part covered with FTO. FESEM is not suited to display the gradient properly, due to the angular parallax and atomic force microscopy fails due to its extremely localized sampling area.

The nanowire-shaped TiO₂ parts of the nanocomposite film give rise to a lateral length of 200 nm, corresponding to the distance between adjacent nanowires, on top of the thick FTO film. Along the gradient this structure changes. It decreases down to 90 nm on the pure glass surface. Between both limiting values the decrease is due to the FTO-gradient (see Fig. 3.9c). This dependence on the substrate surface shows that the applied sol-gel process is not only sensitive to parameters of the solution which define the position in the ternary phase diagram [2] and the applied preparation conditions in terms of humidity and temperature. The resulting structures of the nanocomposite film strongly depend on flow field installed during the spin coating and on the acting interface potential. The flow field on the rough FTO layer differs from the one on top of the smooth glass surface. FTO and glass as well as both blocks PS and PEO differ in polarity and surface energy. Consequently, different morphologies of the P(S-b-EO) matrix, which acts as a template during the sol-gel process, can be formed, depending on the FTO layer thickness [4].

- [1] D.H. Kim et al., Adv. Funct. Mater. 15, 1160 (2005)
- [2] Y.J. Cheng et al., J. Am. Chem. Soc. 128, 4658 (2006)
- [3] P. Müller-Buschbaum et al., Europhys.Lett. 61, 639 (2003)
- [4] P. Müller-Buschbaum et al., phys.stat.sol. (RRL) 1, 119 (2007)

3.7 Microbeam GISAXS investigation of the morphological modification of TiO₂ nanocomposite films

J. Perlich, M. Memesa¹, J. S. Gutmann^{1,2}, S. V. Roth³, P. Müller-Buschbaum

- ¹ Max-Planck Institute for Polymer Research, Mainz
- ² Institute for Physical Chemistry, Johannes Gutenberg University, Mainz
- ³ HASYLAB at DESY, Hamburg

The creation of nanostructured TiO_2 (titania) thin films is of great interest for many applications, due to their electrical performance. The performance is strongly dependent on the morphology of the nanocomposite films. For the preparation of the TiO₂ nanocomposite films we combine the amphilic diblock-copolymer P(S-b-EO), which acts as the templating agent, with an inorganic sol-gel chemistry [1]. First, the diblock copolymer is fully dissolved in 1,4-dioxane. 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) experiments were performed at the beamline BW4 [2,3]. For the experiments a moderate micro-focused beamsize of (H x V) 60 x 30 μ m² used. Synchrotron radiation with a wavelength of 1.38 Å was used for the measurements. A 2D-MarCCD detector (2048 x 2048 pixels) was used to record the scattered X-rays from the surface.

Recent experiments were performed on Si-wafer substrates covered μ GISAXS investigations of the TiO₂ nano-composite films in dependence of the basic sol-gel process parameters. However, the approach of modifying the morphology of the nanocomposite films by swelling the PS-block of the P(S-b-EO) expands the basic accessible components by a well-controllable parameter [4]. For this experiment, samples with identical sol-gel process parameters are prepared but different amounts of PS homopolymer are added. In Figure 3.10 2D scattering images of samples with different PS weight fractions are shown. The absence of a split Yoneda peak or side maxima at a constant exit angle corresponds to the fact that there are no highly ordered structures of a certain size in the film, which coincides with the existing structure of nanowires and nanowire aggregates verified by FESEM (see Figure 3.11a). From the recorded 2D intensities, it is recognized that the scattering intensity changes as a function of the PS weight fraction. For the presented 2D intensities with $w_{PS} = 0.03$ and 0.1, the main 2D features have a similar appearance, and only changes in a broader intensity distribution are recognized, hence representing merely a slight modification of the morphology as a function of w_{PS} . In contrast, for $w_{PS} = 0.5$ the Yoneda peak looks rather different and gives rise to the conclusion that the morphology changes to a larger extent. The corresponding horizontal cuts for TiO_2 are shown in Figure 3.11a for the samples after calcination. The plateau-like features of the cuts indicate the presence of structures that are not highly ordered. This necessarily coincides very well with our qualitative judgment of the 2D intensity distribution.

The dominant lateral lengths are determined by a model fit to the data, taking into account the form and structure factors as well as the resolution function. The obtained structures are



Ψ (deg)

Figure 3.10:

Composition of 2D scattering patterns of the sample series before (top row) and after (bottom row) calcination. In each row, the 2D scattering patterns correspond to PS homopolymer weight fractions of 0, 0.03, 0.1, and 0.5 (from left to right). For each 2D image, the horizontal (or out-of-plane) angle Ψ is plotted along the x axis, and the exit angle α_f is plotted along the y axis. The intensity is shown on a logarithmic scale. For color coding: blue/dark = low intensity and purple/white = high intensity. [4]



Figure 3.11:

(a) TiO₂ out-of-plane cuts (symbols) of the 2D intensity as a function of the q_y component of the scattering vector. The solid lines are the fits for determining the most prominent inplane length scale. From bottom to top, the PS homopolymer weight fraction increases as indicated for the samples after calcination. The dashed line indicates the resolution limit of the GISAXS experiment. The two structures are marked with I and II. The arrows roughly display the shift with changing PS weight fraction. The corresponding FESEM images of the samples after calcination are included in the figure. In (b) the most prominent inplane lengths Λ_I (triangles) and Λ_{II} (circles) of the structures related to features I and II, respectively, in (a). Data are plotted as a function of the PS weight fraction for the sample series before (open symbols) and after (filled symbols) calcination. For comparison, the Λ_I obtained from the PSD master curve for the sample series after calcination by AFM is included in the plot (stars). [4]

summarized in Figure 3.11b, where the most prominent in-plane length scales are plotted. For the sample series before calcination the larger structure Λ_I , identified as the distance between TiO₂ objects (i.e. nanowire aggregates), remains unchanged within the error bars. In

contrast, the Λ_{II} values, corresponding to the size of the nanowire aggregates, decrease with increasing w_{PS}.

In summary, fine tuning of the morphologies is achieved by using amphilic diblock copolymer P(S-b-EO) swelling as the structure-directing agent combined with so called good-poor solvent pair-induced phase separation coupled with sol-gel chemistry. Hybrid and calcined structures follow the desired behavior as in standard sol-gel structure formation [4].

- [1] Y.-J. Cheng, J. S. Gutmann, J. Am. Chem. Soc. 128, 4658 (2006)
- [2] P. Müller-Buschbaum, Anal.Bioanal.Chem. 376, 3 (2003)
- [3] S. V. Roth, R. Döhrmann, M. Dommach, M. Kuhlmann, I. Kröger, R. Gehrke, H. Walter, C. Schroer, B. Lengeler, P. Müller-Buschbaum, Rev. Sci. Instr. 77, 085106 (2006)
- [4] J. Perlich, L. Schulz, M. M. Abul Kashem, Y.-J. Cheng, M. Memesa, J. S. Gutmann, S. V. Roth, P. Müller-Buschbaum, Langmuir 23, 10299 (2007)

4 **Bio-polymers**

4.1 The influence of medium pressure on global and internal dynamics of human hemoglobin: observation by quasielastic neutron scattering.

M.-S. Appavou¹, S. Busch¹, W. Doster, A. Gaspar¹, T. Unruh¹

¹ FRM II, Garching

Pressure is a well spread physical parameter in life [1], which is increasingly used in sterilization and bio-conservation processes in food and pharmaceutical industries. Other applications in Life Sciences concern modulation of protein folding pathways or associationdissociation phenomena of macromolecular large scale structures [2]. Protein association has a major impact on the regulation of biochemical pathways. Pressure offers a reversible instrument to control the state of association of proteins and other biomolecular complexes. At pressures below 2 kbar mainly dissociation phenomena and pressure-induced structural changes occur. To unfold small proteins under stable conditions, requires pressures above 4 kbar. However cold-denaturation can occur below 2 kbar. Quasielastic neutron scattering allows to explore the effect of packing on fast internal motions of proteins [3,4]. Few neutron scattering studies on biomolecules were performed using this physical parameter up to date. The first unfolding study with inelastic neutron scattering was published by Doster et al [5,6] with myoglobin at pressures up to 7 kbar. Other studies were performed by Appavou et al for BPTI [7] and by Di Bari for Trypsin [8].



Figure 4.1:

dynamic susceptibility of hemoglobin in solution at 1 bar and 1 kbar, both protein diffusion and internal dynamics can be resolved by TOFTOF

As a first step the influence of pressure on biomolecular dynamics on a picoseconds time scale was investigated with neutron time-of-flight spectroscopy TOFTOF at the FRM2. Caseins form micelles, which transport the otherwise insoluble calcium phospate in neonates. It was suggested that the mobility of disordered proteins in the micelle contributes to its function. Also a tetrameric protein, hemoglobin, was studied. It is of interest, whether intermolecular

protein interactions due to association modify the chain dynamcis. For this purpose, a new flat pressure cell with high transmission, based on an aluminum alloy was designed for pressure ranges up to 2000 bar. The medium pressure cell is composed of 10 aligned channels with 1.6 mm diameter. The calculated transmission of the cell between the channels (5mm thickness) is about 91,2 %, whereas the transmission through the cell (3.4 mm thickness) is around 93,9%. These numbers were confirmed experimentally through TOFTOF experiments. With Antares it was demonstrated that all channels could be filled homogeneously without bubbles. A series of pressure experiments were performed with this setup on the time of flight spectrometer TOFTOF at FRM II (Garching, Germany). Changes in the state of association and internal dynamics versus pressure were detected for the tetrameric protein hemoglobin and the biomolecular complexes of β -casein. The diffusion of hemoglobin initially speeds up with pressure, suggesting dissociation, and then slows down slightly. The amplitude of internal motions decreases with pressure. Similar effects were observed with casein micelles. But in this case, the amplitude of internal motions increase with pressure or degree of dissociation, suggesting reduced intermolecular interactions.

[1] C. Balny, Bull. Soc. Fr. Biophys. 140 (2003) 10-13.

[2] C. Balny, P. Masson, K. Heremans, High pressure effects on biological macromolecules: from structural changes to alteration of cellular processes, Biochim. Biophys. Acta 1595 (2002) 1–402.

[3] J.A. McCammon, S.C. Harvey, Dynamics of Proteins and Nucleic Acids, Cambridge University Press, Cambridge, 1988, p. 29.

[4] M. Bée, Quasi-Elastic Neutron Scattering, Principles and Applications in Solid State Chemistry, Biology and Materials Science, Adam Hilger, Bristol, 1988.

[5] W. Doster and W. Gebhardt, High pressure – unfolding of myoglobin studied by dynamic neutron scattering, Chem. Phys. 292, 2003, 383-389.

[6] W. Doster, R. Gebhardt and A. Soper in: Advances in High Pressure Science and Biotechnology II p. 29, Springer 2003, Ed. R. Winter.

[7] M.-S. Appavou, G. Gibrat, M.-C. Bellissent-Funel, Influence of pressure on structure and dynamics of bovine pancreatic trypsin inhibitor (BPTI):

Small angle and quasi-elastic neutron scattering studies, Biochimica et Biophysica Acta 1764 (2006) 414–423.

[8] M. Di Bari, A. Deriu, A. Filabozzi, C. Andreani, A. Di Venere, N. Rosato, Dynamics of trypsin under pressure, Physica B 276–278 (2000) 510–511.

4.2 Separation of coherent and spin-incoherent neutron scattering from protein samples by polarization analysis

A. M. Gaspar¹, W. Doster, M.-S. Appavou, S. Busch, M. Diehl, W. Haeussler¹², R Georgii¹², S Masalovich¹

¹ FRM II, Garching

² Lehrstuhl E21, TU München

We explored the possibility to perform polarization analysis to experimentally separate coherent and spin-incoherent nuclear scattering processes, from a representative set of samples of interest for protein studies. Such a method [1,2] had so far limited application in the study of amorphous materials [3-5], despite of the relevance of the information that it provides. For instance, it allows for the experimental determination of the coherent structure factor $S_{coh}(Q)$ of materials containing a significant amount of hydrogen atoms, such as proteins, uncontaminated by the enormous incoherent background. Knowledge of the relative importance of the coherent and incoherent terms at different Q values is also a pre-requisite for the interpretation of dynamical neutron scattering experiments, performed at instruments in which the total dynamic structure factor is measured, as is generally the case of neutron time-of-flight and backscattering instruments.

The experiments performed rely on the principle that using a polarized incident neutron beam and counting separately neutrons scattered with and without spin-flip, a separation of the coherent from spin-incoherent nuclear scattering processes can be achieved. This is because only 1/3 of the spin-incoherent scattering events from a sample with random nuclear polarization are without spin flip (the other 2/3 being with spin flip), while all the coherent nuclear scattering events correspond to scattering without spin flip [6]. Hence from $I_{NSF} = I_{coh} + 1/3 I_{inc}$, $I_{SF} = 2/3 I_{inc}$ one directly obtains $I_{coh} = I_{NSF} - 1/2 I_{SF}$, $I_{inc} = 3/2 I_{SF}$. It should be noted however that in practice, the scattered intensities need to be corrected for a total finite flipping ratio, accumulating the effect of the imperfections in the spin analysis and manipulation components of the instrument (see e.g. [2]). Figure 6.4 illustrates how this separation was successfully achieved at the MIRA instrument at the FRM II, over the small-angle scattering region of a concentrated hemoglobin solution.



Figure 4.2:

Small-angle scattering intensities of neutrons scattered with and without spin flip from a concentrated solution of hemoglobin in D_2O . Results obtained at the MIRA instrument at the FRM II.

A more complete set of static scattering measurements was obtained on different samples of myoglobin (in dry powder, hydrated powder, and in deuterated solutions of different concentrations), combining data from the MIRA and RESEDA instruments at the FRM II with data from the D7 instrument at the ILL, thereby covering a wide Q range, from the small $(0.005 < Q < 0.05 \text{ Å}^{-1})$ to the wide angle region (up to $\sim 2.5 \text{ Å}^{-1}$). Results allowed obtaining quantitative information on the fractions of coherent and spin-incoherent scattering, which is displayed in figure 6.5 for the different myoglobin samples. From this figure it is possible to conclude that for the powder samples, for *Q* values above 0.3 Å^{-1} , the static incoherent term represents more that 80% of the signal and that, for $Q > 0.9 \text{ Å}^{-1}$, the coherent and incoherent terms converge to the coherent and incoherent fractions of the total cross section. This is not the case for the protein solutions. Only at high protein concentrations (say >100 mg/ml), and especially if the analysis can be restricted to $0.4 < Q < 1.2 \text{ Å}^{-1}$, we may also assume a dominating incoherent contribution of approximately 80% of the total scattering. Otherwise, as in the case of the more diluted solutions, the coherent and incoherent scattering contributions appear similarly important, even with interchangeable predominance.



Figure 4.3: Fractions of the total scattering corresponding to coherent and to spin-incoherent events, obtained for the different myoglobin samples investigated.

These results are particularly relevant to the interpretation of time-of-flight or backscattering results obtained on protein solutions, or on any other liquid or soft matter system, for which the structure factor changes significantly over the Q region generally investigated. Since the dynamical correlations at the origin of the coherent and incoherent parts of the spectra are not the same [7,8], interpretation of the spectra requires appropriate consideration of these two terms and of their relative importance.

A.M. Gaspar acknowledges the Portuguese Science and Technology Foundation (FCT) for support in

the form of a post-doc grant SFRH / BDP / 17571 / 2004

- [1] R. M. Moon, T. Riste, W. C. Koehler, Phys. Rev. 181, 920 (1969)
- [2] O. Schaerpf, Physica B 182, 376-388 (1982)
- [3] J. C. Dore, J. H. Clarke, J. T. Wenzel, Nucl. Instr. & Meth. 138 317-319 (1976)
- [4] B. J. Gabrys, Physica B 267-268 122-130 (1999)
- [5] B. J. Gabrys, W. Zajac, O. Schaerpf, Physica B 301 69-77 (2001)
- [6] T. J. Hicks, Adv. Phys. 45 243-248 (1996)
- [7] K. Skoeld, Phys. Rev. Lett. 19 1023-1025 (1967)
- [8] M. Bee: Quasielastic Neutron Scattering, Adam Hilger (1988)

4.3 Water vapour induced swelling of thin casein films

P. Müller-Buschbaum, E. Metwalli, J.-F. Moulin, R. Cubitt¹

¹ ILL, Grenoble (france)

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 [1-2]. In ancient Egypt casein-based glue was first used. Casein proteins in bovine milk include four main types: α_{1s} -casein (38 %), α_{2s} -casein (10 %), β -casein (36 %) and κ -casein (13%), which are involved in formation of hydrated casein micelles of size on the order of 150-300 nm [3].



Figure 4.4:

GISANS line-cuts of the 2d intensity measured for different D_2O swelling conditions (left). The dry sample is shown for comparison. Strong changes are visible in the q_y -range at $9*10^{-1}$ nm⁻¹. This increase in intensity is related to an increased size (e.g. swelling) of the casein micelles. Water uptake of the casein micelles as a function of swelling time (right).

Various models [4] 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 proposes the micelle as roughly spherically uniform sub-micelles which are linked together via a calcium phosphate ion clusters. The internal structure model specifies the mode





Figure 4.5:

AFM images (1 x 1 μ m²) for the casein films at 30 °C (left) and at 70 °C (right) in D₂O vapour. The surface topography changes, however no bulk information is accessible with AFM and GISANS is required to prove that this change is representative for the bulk.

of aggregation of different caseins. We have investigated thin casein films prepared using spin coating method [5]. The GISAXS measurements [5] of the casein thin films indicated a decrease of micelle size at the glass surface compared with the micelles in solution as probed by dynamic light scattering (DLS). The micelles are arranged on the surface in a compact structure due to the moderate force applied during spin coating process. The GISAXS investigation shows that for intermediate thickness of casein thin film, the size of the micelles shrink by more than a factor of 2. In the present study, we aimed to figure out the origin of this shrinkage by performing swelling experiments in a controlled (with respect to pressure and temperature) atmosphere of D_2O using a home-made vapour chamber. To the best of our knowledge this is the first in-situ GISANS study on the swelling of protein thin films.

Figure 4.4(left) shows clear structural variation upon D_2O uptake with the scattering being more significant with increasing the temperature of the swelling experiments. The experimental results were very impressive indicating the potential of this set up for the in-situ timedependent GISANS swelling experiments. Simply no alternative techniques would produce such lateral structural information on the protein structure as function of the water uptake. In the performed experiments, the micelle size can be probed as a function of the water uptake which would help to understand how water molecules affect the structure and hence which model structure best describes the casein micelle formation. From Figure 4.4(right)., the amount of incorporated water into the casein micelles linearly increases with time up to 3 min and reach an equilibrium state after 11 min. Figure 4.5 shows the AFM images for swelling experiments at low (30 °C) and high (70 °C) temperatures. From the images the contrast is low at the high temperature (70 °C) due to higher water content. Our main conclusion is that the relatively high water uptake into the casein micelles thin films would favorably support the sub-micelles structural model.

- [1] J.-L. Audic, B. Chaufer, G. Daufin, Lait 83, 417 (2003)
- [2] C. R. Southward, N. J. Walker, Dairy Sci. Technol. 15, 201 (1980)
- [3] J. E. Kinsella, CRC Crit. Rev. Food Sci. Nutr. 21, 197 (1984)
- [4] C. Phadungath, Songklanakarin J. Sci. Technol. 17, 201 (2005)
- [5] P. Müller-Buschbaum, R. Gebhardt, E. Maurer, E. Bauer, R. Gehrke, W. Doster, Biomacromolecules 7, 1773 (2006)

4.4 Micellar structure of casein investigated by µGISAXS

R. Gebhardt¹, M. Burghammer¹, C. Riekel¹, S.V. Roth², P. Müller-Buschbaum

- ¹ ESRF, Grenoble, France
- ² HASYLAB at DESY, Hamburg, Germany

The aim of our research is to investigate the micellar structure of caseins in dependence of the film microstructure. To achieve this, grazing incidence small angle x-ray scattering scans with high positional precision in combination with micrometer- sized beams are used. The sample for the casein film preparation [1] is obtained from the Chair for Food Process Engineering and Dairy Technology, TUM. Four different casein monomers and colloidal calcium phosphate built up the heterogeneous casein micelle. The casein monomers consist of blocks with a high amount of hydrophobic and hydrophilic amino acids. The colloidal calcium particles are linked to phosphoserin rich patches in the hydrophilic blocks. The hydrophobic regions of the caseins associate among themselves to stabilize the core of the micelle. An outer κ -casein layer, which can be regarded as a brush of polyelectrolyte molecules, prevents further unlimited growth of the micelle by shielding further hydrophobic contacts. Structural changes can be induced by destabilizing the layer structure, which was done in recent experiments by means of calcium and rennet gradients.



Figure 4.6:

Synchrotron radiation micro GISAXS setup: (A) incoming monochromated X-ray beam; (B) mirror chamber; (C) vertical microscope; (D) ionization chamber with micro aperture; (E) casein film prepared on a glass slide; (F) two-axis goniometer; (G) beamstop for direct beam; (H) MAR165 CCD detector position and beamstop for specular peak

The experiments were conducted on the ID13 microfocus beamline [2] of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The experimental setup is shown in Figure 4.6. The casein film sample (E), prepared on a pre-cleaned glass slide, is mounted on a two-axis goniometer (F) and x/y/z translation unit with 400 nm positional repeatability



Figure 4.7: Contour plot of calcium phosphate particle, casein mini-micelle and casein micelle size variation

ent, taken from [3]

along the calcium gradi-

for each axis. The monochromated beam from an in-vacuum undulator (A) is focussed by a Kirkpatrick-Baez (KB) mirror system (B). A micro-ionization chamber (D) with a 20 μ m guard aperture is used to monitor beam intensity and reduce stray radiation. The microstructure of the film surface is observed by a horizontal microscope (C). The direct beam is blocked by a motorized lead beamstop (G) of about 200 μ m diameter. The position of the MARCCD165 detector and a second beamstop, which shields the specular beam, is implied (H). In the following we present results obtained from a casein film with a superimposed calcium gradient [3]. Such films are prepared by solution casting which results in a film thickness of several micrometers. To find proper conditions for μ GISAXS on the film surface, height scans at a certain position in the calcium gradient are performed. So called out of plane cuts at the critical angle for casein are carried out to analyze the lateral structures within the casein film. The GISAXS cuts at varying positions along the calcium gradient are evaluated by a model, based on a set of three log-normal distributed particle sizes. The continuous variation of casein micelles, casein mini-micelles and colloidal calcium phosphate particles over the whole calcium gradient is shown as a contour plot in Figure 4.7. Increasing calcium concentration causes a decrease in the casein micelle sizes while the diameter of casein mini-micelles increases and the colloidal calcium phosphate particles remain unchanged. The results match in good approximation with those obtained in previous studies on casein films prepared by spin coating technique [4].

- [1] A. Tolkach, U. Kulozik, Journal of Food Engineering 67, 13, (2005)
- [2] C. Riekel, Rep. Prog. Phys. 63, 233, (2000)
- [3] R. Gebhardt, M. Burghammer, C. Riekel, S.V. Roth, P. Müller-Buschbaum, Macromol Biosci. mabi.200700203, (2007)
- [4] P. Müller-Buschbaum, R. Gebhardt, S. V. Roth, E. Metwalli, W. Doster, Biophys. J. 93, 960, (2007)

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

P. Müller-Buschbaum, R. Gebhardt¹, E. Metwalli, W. Doster

¹ ESRF, Grenoble, France

Caseins, a family of phosphoproteins, form the largest protein component in most milks. The major function of caseins in milk is to efficiently transport calcium, phosphate and protein from the mammary gland to the neonate. It has been suggested that casein micelles allow the total calcium and phosphate concentrations in most, if not all, milks to exceed the solubility of calcium phosphate, without causing uncontrolled precipitation of calcium phosphate in the mammary gland.



Figure 4.8:

Influence of added Ca on the size of the casein micelles in solution as probed by PCS revealing the hydrodynamic diameter $2R_H$ (open rhombohedra). For comparison, the distance between neighboring micelles in dry casein films as probed with GISAXS corresponding to the most prominent in-plane length Λ_p (filled triangles) is shown. Taken from [4].

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.

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 [2]. The non-adsorbing part of kappa-casein can be regarded as a salted polyelectrolyte brush. In the extended state the brush is about 7 nm long and provides the steric stabilization, while in the collapsed state the stabilization is absent and flocculation and gel formation become possible [19-21]. Calcium is essential for the micelle formation at all [22]. The casein proteins divide themselves into two groups, the calcium-sensitive and the non-calcium sensitive, which also in mixtures prevent or inhibit 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.

Whereas most investigations address solutions at different calcium concentrations, in the most prominent applications besides milk, films containing caseins are used. Recently, spincoating was shown to be an efficient technique to prepare well defined casein films of controllable thickness over a wide range of different pH values [3]. At high concentrations with spin-coating bulk like films are prepared, which structure matches well the micellar structure in solution. In contrast to the long times required for drying in the solution casting technique, spin-coating is very quick. After 30 seconds only, a well defined, homogeneous and dry film of very high quality is obtained. 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). 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. 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.

Figure 4.8 comprises the structural information resulting from PCS (open symbols) and GISAXS (filled symbols) [4]. Without added calcium, within the experimental error, both techniques yield a good agreement between the hydrodynamic radius, determined with PCS, and the distance between neighboring casein micelles, probed with GISAXS. Such agreement was observed in previous work as well [3] and translates into densely packed micelles (similar to hard spheres), which are unchanged by the spin-coating.

The colloidal properties of casein micelles change with the addition of calcium. After addition of calcium PCS detects a strong increase in the hydrodynamic radius (see figure 4.8). In contrast, GISAXS shows a slight decrease in the micelle distance together with an increase in the smaller structural feature. The increase in hydrodynamic radius agrees with previous investigations. By adding a small amount of calcium, first solvable caseins increase the micellar weight without increasing the size, as long as the casein micelle can incorporate calcium insensitive caseins (alpha(s1,2)- and beta-caseins). Upon further addition of calcium, the radius of the micelles increases up to a critical concentration. Above this critical concentration the addition of calcium causes gross aggregation and precipitation of the micelles. Within the presented work the critical concentration of precipitation was larger than 110 mM. Related to the thin casein films prepared by spin-coating this micelle aggregation does not translate in a similar increase in the characteristic distances.

In addition to these structures created by the commonly observed casein micelles, a further type with significantly smaller diameter is probed. These mini-micelles are observed in solution as well as in the thin films. AFM allows to visualize them on the casein film surface directly and GISAXS proves the statistical relevance of this type of micelle. Both micelle types, the mini-micelles (diameter 20 nm without added Ca) and the commonly observed micelles (diameter 260 nm without added Ca) exist in coexistence. In solution this might be a dynamical equilibrium, with an exchange of caseins between individual micelles. In contrast, in thin films a snap shot of this equilibrium is frozen-in and thus aggregates, micelles and mini-micelles are detected all.

- [1] Walstra, P., R. Jenness (1984) Dairy Chemistry and Physics, Wiley, New York.
- [2] C. Holt, D.S. Horne, Neth. Milk Dairy J. 50, 85 (1996)
- [3] P. Müller-Buschbaum et al., Biomacromolecules 7, 1773 (2006)
- [4] P. Müller-Buschbaum et al., Biophys. J. 93, 960 (2007)

4.6 Dynamics of phospholipids in stabilizing monolayers investigated by quasielastic neutron scattering

S. Busch, C. Smuda, T. Unruh

Many modern drugs are not water-soluble. To facilitate their intravenous applicability, a drug carrier has to be employed. Dispersions of lipid nanoparticles stabilized by dimyristoylphosphatidylcholine (DMPC) are promising candidates. It has been shown that not only the drug release rate but also the storage stability of these systems highly depends on the properties of the stabilizer [1,2,3]. These properties were investigated i. a. by SAXS [4], revealing that the structure of the monolayer is clearly distinct from what one would expect from the well-known structure of bilayers: its is thinner and the peaks in the electron density profile are less pronounced.

A series of experiments aiming to determine the dynamic characteristics of DMPCmonolayers is planned at TOFTOF. A major goal is to link the molecular dynamics with the before-mentioned properties like storage stability. First experiments were done comparing the picosecond-dynamics in a dispersion of vesicles, serving as model for phospholipid bilayers, which had a diameter of ≈ 40 nm (PCS *z*-average) with the one of a stabilizing phospholipid monolayer in an emulsion of deuterated hexadecane in D₂O (diameter ≈ 57 nm). The main difficulty in these measurements is the low content of phospholipid, being only 1.3 weight % of the sample in the beam.

The part of the sample spectra due to scattering from D_2O and possibly hexadecane molecules has to be subtracted. Then the quasielastic broadening caused by the dynamics of DMPC becomes visible which is depicted in figure 4.9 along with the instrumental resolution, determined by the measurement of a vanadium standard. The broadening caused by the dynamics of DMPC in a monolayer is clearly larger, indicating faster dynamics.



Figure 4.9:

Spectra of vanadium (innermost), vesicles, and emulsion (outermost) after background subtraction as described in the text plotted versus energy transfer at a momentum transfer of 1 Å^{-1} . It is visible that the quasielastic broadening of the central line is larger in the case of the emulsion (phospholipid monolayer).

To determine the type of dynamics, the spectra were fitted with a simple model consisting of a sum of two Lorentzians, which can roughly be assigned to diffusion of the DMPC molecules (narrow component) and internal motions of the DMPC (broad component). As both, water and hexadecane, are faster than the phospholipids, their dynamics does not influence the line width of the narrow component even if the subtraction was non-ideal but would only be visible in the broad component. The width of the narrow component shows a linearish dependence of Q^2 (confer to figure 4.10) which is a sign for non-local diffusive motions. The diffusion coefficient of DMPC is proportional to the slope and therefore in a monolayer about two times the one in a bilayer.



Figure 4.10:

The linewidth of the narrow component of a two-Lorentzian fit plotted versus the squared momentum transfer Q^2 . The one steming from the monolayer is about double the one of the bilayer.

The looser molecular arrangement of the phospholipid molecules in the monolayer [4] can intuitively be correlated with the increase of diffusional dynamics. This will be investigated more thoroughly. Currently, we try to find a more elaborated method to subtract the contributions of D_2O and hexadecane to the spectra so that the broad component can be evaluated more reliably. Furthermore, experiments investigating the influence of stabilizing coemulgators on the phospholipid dynamics are planned.

- [1] H. Bunjes, M. H. J. Koch, and K. Westesen. J. Pharm. Sci., 92:1509, 2003
- [2] H. Bunjes, F. Steiniger, and W. Richter. Langmuir, 23:4005, 2007
- [3] K. Westesen and B. Siekmann. Int. J. Pharm., 151:35, 1997
- [4] T. Unruh. J. Appl. Cryst., 40:1008, 2007.

4.7 Water-uptake in biocompatible hydrogel films: Neutron reflectivity study

E. Metwalli, J. Perlich, R. Georgii¹, P. Müller-Buschbaum

¹ FRM-II, TU München

Hydrogel films are used for immobilization of proteins for microarray applications [1-3]. The protein microarray is a crucial biomaterial for the rapid and high-throughput assay of many biological events where proteins are involved. The hydrated, porous nature of the hydrogel coatings can mimic the conditions found in vivo and can ideally ensure that the adsorbed proteins remains hydrated, functional and properly folded. Aldehyde or amino functional polyethylene glycol is currently used for this application. Since the hydration layer is very important, [4] the film is typically immersed in buffer solution prior to protein immobilization to ensure high water content. In the present investigation, the water-uptake of the hydrogel film is investigated as function of time. Silicon wafers were ultrasonically cleaned in dicholormethane, rinsed in DI water, and immersed in the cleaning bath containing a mixture of NH₃, H₂O₂ and H₂O for 2 h at 75 °C. The cleaned substrates are further rinsed in DI water and finally spin dried. Deuterated polyethylene glycol (dPEG) with a molecular weight Mn = 40 k was dissolved in D₂O and applied to the cleaned silicon wafer via spin coating method. As-prepared films were mounted in a home-made vapour chamber and were investigated with neutron reflectivity (NR) at MIRA instrument (FRM-II) with a wavelength of 9.83 Å.





Neutron reflectivity data of deuterated polyethylene glycol (dPEG) films on pre-cleaned silicon surfaces. (a) Dry versus hydrated films for different time periods; in situ-experiment, (b) swelling and deswelling effect on the hydrogel film, (c) temperature effect on the hydrogel film structure. The critical edge (q_c) shifts towards lower q values as the dPEG film swells in D₂O vapor. Hydrated films have weak fringes compared with the as-prepared and dry ones.

The q_z range from 0.004 Å⁻¹ to 0.12 Å⁻¹ was probed with high resolution (motor steps of = 0.01°). NR of the dry film was first measured and the swelling experiments were performed by inserting D_2O vapor in the chamber. The temperature of the chamber was kept constant at 30 °C using a water thermostat. A full NR curve was collected every 12 hrs in presence of D₂O vapor. A cycling swelling/deswelling experiment was also performed on hydrogel film by exposure to D_2O vapor at room temperature for 12 h followed by opening the chamber to air for 12 h. Additional samples were pre-heated at different temperatures viz. 20, 30 and 70 °C in vacuum oven and the NRs' were collected for these dry films. Figure 4.11 shows the neutron reflectivity data for the studied samples. The scattering length density of our dPEG film is 7.05 x 10^{-6} Å⁻², and the critical edge (q_c) is expected to shifts towards lower q_z values as D_2O (6.36 x 10^{-6} Å⁻²) is incorporated into the swollen film. In Figure 4.11a, the critical edge shifts to lower q values from dry to hydrated film after 12 hour of exposure to D_2O vapor. The hydrated gel film shows an equilibrium state as observed from unchanged NR with increasing swelling time to 24 and 36 h. From Figure 4.11b, the film shows a kinetic behavior as the critical edge responds to the film environment (D₂O vapor and air). The swelling/deswelling behavior indicates that the hydrogel films are very sensitive to humidity and the observed high inconsistencies in the microarray results [5] can be avoid if the humidity is well controlled during the microarray experiment. In the last set of experiments, the as-prepared films are dried using vacuum oven prior to the NR measurements in air Figure (4.11c). Preliminary data analyses were performed using Parratt32 as well as Motofit and indicate that the shrinkage of the film thickness from 112 nm (as-prepared film) to 71 nm (70 $^{\circ}$ C, 40 h) may reveal a possible collapse of the porous hydrated film upon heating. The results of additional measurements with complementary techniques such as x-ray reflectivity (thickness) and AFM (topography) are to be compared with the neutron results. In summary, the NR experiment was successful and useful for understanding the hydrogel film response to an external stimulus.

[1] D. V. Zubtsov, et al., J. Biotechnol. 122, 16 (2006)

- [2] P. T. Charles, et al., Biosensors and Bioelectronics 20, 753 (2004)
- [3] V. E. Barsky, et al., Molecular Biology 36, 437 (2002)
- [4] S. Kiyonaka, et al., Nat. Mater. 3, 58 (2004)
- [5] J. D. Hoheisel, M. Vingron, Res. Microbiol. 151, 113 (2000)

4.8 Conformational and structural changes of thin films from recombinant spider silk proteins upon post-treatment with methanol

E. Metwalli, U. Slotta¹, C. Darko, S. V. Roth², T. Scheibel, C. M. Papadakis

- ¹ Department Chemie, TU München
- ² HASYLAB at DESY, Hamburg

Nature provides the best example for processing polymers into materials. Orb-weaving spiders can utilize the optimal mechanical properties of biopolymer (protein) chains using far milder physical and chemical processing conditions than those used for high-strength manmade polymers [1]. Spider silk proteins consist of huge polypeptides that form sets of consensus repeats [2]. Generally, four types of consensus repeats are found: crystalline β -sheets, elastic β -spirals, α -helices, and spacers. These types of secondary structures contribute to the overall silk fiber structure and to the mechanical properties of spider silk, e.g. the β -sheet crystalline module of the silk forms parallel chains that interact via hydrophobic interactions providing the tensile strength [3]. This correlation between molecular sequence and mechanical properties of spider silk proteins is of interest for producing multi-purpose polymeric materials of controlled strength, extensibility, and stiffness.

Engineered recombinant spider silk proteins derived from the garden spider's two dragline silk proteins ADF-3 and ADF-4 can also be cast into films, e.g. [4]. By treatment with potassium phosphate or methanol, the helical structure is converted into a β -sheet structure, rendering the films water insoluble. Thus, by utilizing recombinant spider silk technologies and appropriate post-treatment, protein films with controlled physical properties can be achieved. We present here structural investigations on films of the recombinant protein C16, which is derived from the dragline spider silk ADF-4 from the garden spider. We have focused on the conformational transition of films prepared from hexafluoroisopropanol solution on Si wafers upon post-treatment with methanol [4]. The initial film thickness was $\sim 2.6 \ \mu$ m.



Figure 4.12:

The amide I spectra of the protein film (a) before and (b) after methanol treatment. Seven bands (lines) were used to fit the FTIR experimental results (•).

The conformational transition of the protein was verified using FT-IR reflection spectroscopy. The usual three main bands, amide A, amide I, and amide II, were observed. Structural information like the fractions of α -helix, β -sheet, β -turn, and random coil motifs of the proteins can be derived from the positions and areas of the deconvoluted peaks in the amide I band.
It reveals seven peaks (fig. 4.12). Assigning their areas to the fractions of various secondary structure elements, it was found that the fractions of the β -turns and of the β -sheets increase from 24 to 31% and from 20 to 28%, respectively, whereas the one of the α -helices decreases from 37 to 23% and the one of the random coils is unchanged (18-19%). Methanol treatment of the films thus leads to severe conformational changes of the spider silk protein.



Figure 4.13: (•) In-plane GIXRD intensity profiles before (a) and after (b) methanol treatment. Lines: Fits of Gaussian functions to the Bragg reflections (120), the water peak and two broad peaks forming the halo.

Grazing-incidence X-ray diffraction (GIXRD) was employed in order to obtain direct information on the changes of the crystalline structure upon methanol treatment. Experiments were carried out at beamline BW 2 at HASYLAB, DESY. Figure 4.13 shows the in-plane GIXRD intensity profiles before and after methanol treatment. While before treatment, the film reveals two broad peaks, methanol treatment results in the appearance of strong Bragg reflections from β (L-polyalanine) crystals at 1.20 and 1.40 Å⁻¹. Furthermore, a peak due to structured water and a broad halo, presumably due to amorphous material, are present in the intensity profiles. In the untreated film, the (200) reflection is not present, but there is an additional broad peak at lower $q_{||}$ -value (0.92 Å⁻¹), which we assign to the amorphous matrix of the film. From the positions of the Bragg reflections, the lattice constants *a* (i.e. the interchain repeat) and *b* (i.e. the intersheet distance) are found to be 10.46 and 9.35 Å, respectively. The size of the crystalline domains is 75 Å, as calculated from the width of the strong (120) reflection of the treated protein film.



Figure 4.14: GISAXS images before (a) and after (b) methanol treatment. The gray rectangles in the center of the images indicate the beam stop.

The shape, size, and size distribution of the crystalline domains formed by the β -sheets was characterized using grazing-incidence small-angle X-ray scattering (GISAXS). Experiments were carried out at beamline BW 4 at HASYLAB, DESY. The 2D GISAXS images before and after methanol treatment (fig. 4.14) indicate a clear structural variation on the mesoscopic lenthscale, with the scattering being much more significant after the treatment. This change can be modelled by the appearance of (crystalline) parallelepipedal domains having an average lateral size of 80 Å, which is in good agreement with the value from GIXRD. The size is widely distributed, sizes range from 20 to 400 Å. This reflects the presence of crystallites from folded protein conformations, but also from fully stretched C16 proteins.

We conclude that methanol treatment of thin films of recombinant C16 spider silk proteins leads to an increase of the fraction of β sheets, which form β (L-polyalanine) crystallites with a wide distribution of sizes. The film geometry allowed us to correlate the conformational to the structural changes.

This project was funded by SFB 563 'Bioorganic functional systems on solids (TP A10)'.

- [1] J.M. Gosline, P.A. Guerette, C.S. Ortlepp, K.N. Savage, J. Exp. Biol. 202, 3295 (1999)
- [2] C.Y. Hayashi, N.H. Shipley, R.V.Lewis, Int. J. Biol. Macromol. 24, 271 (1999)
- [3] E. Oroudjev, J. Soares, S. Arcidiacono, J.B. Thompson, S.A. Fossey, H.G. Hansma, PNAS 99, 6460 (2007)
- [4] E. Metwalli, U. Slotta, C. Darko, S.V. Roth, T. Scheibel, C.M. Papadakis, Appl. Phys. A 89, 655 (2007), invited paper
- [5] D. Huemmerich, U. Slotta, T. Scheibel, Appl. Phys. A 82, 219 (2006)

5 Solid state dynamics

5.1 Mode-coupling description of the dynamics of simple liquids

W. Schirmacher, H. Sinn¹

¹ Hasylab, DESY, Hamburg

Mode-coupling theory (MCT) [1] has been extremely sucessful in explaining the occurrence of the liquid-to-glass transitions and the nontrivial dynamic scaling phenomena in the vicinity of the transition. This triggered numerous experimental investigations by inelastic Neutron-, X-ray and light scattering, as well as dielectric spectroscopy studies to verify these phenomena and discuss them in terms of the MCT terminology.

Later it became clear in light scattering experiments on non-glass-forming liquids in our lab [2] that the spectra can also be perfectly explained by a schematic version of MCT. Therefore we posed the question, whether MCT away from the glass transition is able to describe the dynamics of simple hard-sphere-like liquids (like liquid metals [3-5]) as described by the dynamical structure factor $S(q, \omega)$. We found that this, indeed, is the case.



Figure 5.1:

Left: Static structure factors of several liquid metals. Thin black line: Hard-Sphere PY structure factor, thick black line: Smoothed hard-sphere structure factor, used as input into the MCT calculations, both calculated with packing fraction $\eta = 0.45$. References for the experimental data can be found in [3].

Right: dispersion of the maxima of $\omega^2 S(q, \omega)$ of several liquid metals [3-5] together with the MCT results for $\eta = 0.40$ (dashes) and $\eta = 0.45$ (full line).

As the only input into the MCT equations is the static structure factor S(q) we first compared the structure factors of several liquid metals in the vicinity of their melting points with each other (left part of Fig. 5.1) as well as with the smoothed structure factor of hard spheres, calculated in Percus-Yevick (PY) approximation. If scaled with the appropriate hard-sphere diameter σ all curves collapse onto each other, indicating (as is, in fact well known) that only the repulsive forces are important for the liquid structure as represented by S(q). Now, as stated above, S(q) is the only input into the MCT equations. If MCT describes the liquid dynamics also away from the glass transition the dynamics therefore must also be dominated by the hard-sphere-like structure and also the dynamics should exhibit the scaling behavior of S(q). The scaling frequency corresponding to the hard-sphere liquid is the isothermal sound velocity divided by the hard-sphere diameter σ :

$$\omega_0 = \frac{1}{\sigma} \sqrt{\frac{k_B T}{m S(q=0)}}$$



Figure 5.2:

Left: spersion and half widths at half maximum of $\omega^2 S(q, \omega)$ for $\eta = 0.40$ (dots), 0.45 (straight line), 0.49 (short dashes), 0.52 (long dashes), 0.55 (dash-dots). Right: Normalized Memory functions for (from bottom to top) $\eta = 0.40$, $\eta = 0.45$, $\eta = 0.49$, $\eta = 0.52$, $\eta = 0.55$, $\eta = 0.60$ and for wavenumbers $q\sigma = 1$ (dots), 3 (short dashes), 5 (long dashes) 7 (lines), 9 (dash-dots). The maximum of S(q) is at $q\sigma = 7$.

The characteristic excitation frequencies of the collective excitations of a liquid ("liquid dispersion") $\Omega(q)$ is obtained from the spectrum $S(q, \omega)$ by the ω -maximum of the function $\omega^2 S(q, \omega)$. In the right part of Fig. 5.1 we have plotted the experimentally determined dispersion with that predicted by MCT with the thick solid line of the left figure as input. We conclude that MCT correctly predicts the position of the collective excitations of simple liquids.

In the left part of Fig. 5.2 we have plotted both the dispersion and the width of the peak of $\omega^2 S(q, \omega)$ calculated by MCT for different values of the packing fraction $\eta = (\pi/6)\rho\sigma^3$, where ρ is the number density of the atoms. We see that both quantities are predicted not to depend strongly on density. To verify this prediction is a challenge for future experiments.

Another important quantity, which essentially at high density controls the glassy arrest, is the generalized frequency dependent damping constant $M(q, \omega)$ or its Fourier transform M(q, t), which is called memory function. This function enters into the equation of motion of the intermediate scattering function S(q, t), which is the Fourier transform of $S(q, \omega)$:

$$\ddot{S}(q,t) + \int_0^t \mathrm{d}\tau M(q,t-\tau) \dot{S}(q,\tau) + \Omega_0^2(q) S(q,t) = 0.$$

with the "unrenormalized" sound dispersion $\Omega_0^2(q) = v_{th}^2 q^2 / S(q)$

This function has in the past [3] been fitted with a sum of two exponentials, which gave rather good fits to experimental data and results of computer simulations on simple liquids. One of the decay rates in these fits was on the microscopic scale and did not depend on the

density, whereas the other was much slower and strongly density dependent. Exactly such a behavior is obtained in MCT. The interpretation is that the second relaxation rate, which strongly increases with density is produced by the so-called cage effect. This effect describes the high-density phenomenon that the adjacent particles cannot move away immediately to let a particle pass, i.e. the form a temporary cage around a given particle. This cage becomes permanent in the glassy state.

- U. Bengtzelius, W. Götze, A. Sjölander, J. Phys. C 17, 5915 (1984); W. Götze, in *Liquids, Freezing and the Glass Transition*, J.-P. Hansen, D. Levesque, J. Zinn-Justin, Eds., North-Holland, Amsterdam 1991.
- [2] S. Wiebel, J. Wuttke, New J. Phys. 4, 56.1 (2002).
- [3] T. Scopigno, G. Ruocco, F. Sette, Rev. Mod. Phys. 77, 881 (2005).
- [4] A. H. Said, H. Sinn, A. Alatas, C. A. Burns, D. L. Price, M. L. Saboungi, and W. Schirmacher, Phys. Rev. B 74, 172202 (2006).
- [5] H. Reichert, F. Bencivenga, B. Wehinger, M. Krisch, F. Sette, H. Dosch, Phys. Rev. Lett. 98, 096104 (2007).
- [6] W. Schirmacher, H. Sinn, J. Condensed Matter, in print

5.2 Vibrational excitations in systems with correlated disorder

W. Schirmacher, B. Schmid¹, C. Tomaras, G. Viliani², G. Baldi³ G. Ruocco⁴, T. Scopigno⁴

- ¹ Now at Fachbereich Physik, Universität Mainz
- ² Dipt. di Fisica, Universitá di Trento, Italy
- ³ INFM-CNR CRS-SOFT OGG, c/o E.S.R.F., Beamline ID16, Grenoble, France
- ⁴ Dipt. di Fisica, Universitá di Roma, Italy and CRS SOFT-INFM-CNR c/o Universitá di Roma, Italy

The vibrational properties of disordered solids differ very much from those of crystals. The vibrational density of states (DOS) $g(\omega)$ ($\omega = 2\pi$ times the frequency ν) shows a low-frequency enhancement over Debye's ω^2 law, which appears as a peak in the reduced DOS $g(\omega)/\omega^2$ ("boson peak") at a certain frequency $\omega_{\rm BP} \ll \omega_D$, where ω_D is the Debye frequency. The reduced specific heat $C(T)/T^3$ shows a peak at $T_{\rm BP} = \hbar \omega_{\rm BP}/k$ (k is Boltzmann's constant), and the thermal conductivity shows a characteristic dip or shoulder near $T_{\rm BP}$. All three anomalies can be explained and shown to be related to each other using a model of fluctuating elastic constants [1]. The same model has been used to establish a relationship between the excess DOS and the acoustic attenuation in the THz regime [2] as well as the anomalous Raman scattering [3]. In these model calculations the fluctuations of the elastic constant were assumed to be zero-range correlated. This is a simplifying assumption which cannot be justified a priory. We therefore have investigated a d-dimensional model (d = 2,3) for sound waves in a disordered environment, in which the local fluctuations of the elastic modulus are spatially correlated with a certain correlation length. The model is solved analytically [4] by means of a field-theoretical effective-medium theory (self-consistent Born approximation [1-3]) and numerically [4] on a square lattice. As in the uncorrelated case the theory predicts an enhancement of the density of states over Debye's ω^{d-1} law ("boson peak") as a result of disorder. This anomay becomes reinforced for increasing correlation length ξ , as can be seen from the left part of Fig. 5.3.

The theory predicts that ξ times the width of the Brillouin line should be a universal function of ξ times the wavenumber. Such a scaling is found in the 2*d* simulation data, so that they can be represented in a universal plot. We see from the right part of Fig. 5.3 that in the low-wavenumber regime (where the lattice structure is irrelevant) the scaling is obeyed and we



Figure 5.3:

Left part:

Reduced DOS $g(\omega)/\omega^2$ for $\xi = 1/k_D$ (dashed lines) and $\xi = 5/k_D$ (full lines) and for three disorder parameters (from left to right) $\gamma = 0.49$, 0.47 and 0.45. Right part:

Symbols: Linewidths Γ of the simulated Brillouin spectra, multiplied with the correlation length ξ and divided by the sound velocity v. $\circ: \xi = 2.79a$, $\Delta: \xi = 5.42a$, $\nabla: \xi = 10.56a$, $+: \xi = 20.55a$, $\mathbf{x}: \xi = 40.0a$, Straight line: theory.

- [1] W. Schirmacher, Europhys. Lett. 73, 892 (2006).
- [2] W. Schirmacher, G. Ruocco, T. Scopigno, Phys. Rev. Lett. 98, 025501 (2007).
- [3] B. Schmid and W. Schirmacher, submitted to Phys. Rev. Lett. and subsequent annual report contribution.
- [4] W. Schirmacher, B. Schmid, C. Tomaras, G. Viliani, G. Baldi, G. Ruocco, T. Scopigno, phys. stat. sol (c) in press

5.3 Theory of low-frequency Raman scattering in disordered solids

- B. Schmid¹, W. Schirmacher
- ¹ Now at Fachbereich Physik, Universität Mainz

We have worked out a theory of low-frequency Raman scattering in glasses, based on the concept that light couples to the elastic strains via spatially fluctuating elasto-optic (Pockels) constants. We show that the Raman intensity is not proportional to the vibrational density of states (as was widely believed), but to a convolution of Pockels constant correlation functions with the dynamic strain susceptibilities of the glass. Using the dynamic susceptibilities of a system with fluctuating elastic constants we are able for the first time to describe the Raman intensity and the anomalous vibrational spectrum of a glass on the same footing.

Raman scattering data in disordered solids show a continuous band of excitations at low frequencies ($\sim 100 \text{ cm}^{-1}$) which is absent in crystalline materials. It had been conjectured by Shuker and Gammon [1] that this band can be described by the formula

$$I_{\text{Shuker}} = C \cdot [n(\omega) + 1] \frac{g(\omega)}{\omega} \qquad (*$$

)

where $\omega = 2\pi\nu$, ν is the frequency and $g(\omega)$ is the vibrational density of states (DOS) of the material and $n(\omega) = [\exp{\{\hbar\omega/kT\}} - 1]^{-1}$ is the thermal boson occupation factor. However,



Figure 5.4:

Left part:

a) Measured reduced DOS [4] and reduced specific heat [5] of glassy As₂S₃ compared with our theory (calculated with a transverse velocity of sound $v_T = 1.4$ km/s, longitudinal velocity of sound $v_L = 1.8v_T$, Debye wavenumber $k_D = 1.32 \cdot 10^{10}$ m⁻¹, correlation length $\xi = 2/k_D$, and the strength of the disorder of the shear modulus $\gamma = 0.352v_T^4$). The dashed lines correspond to the Debye model ($\gamma = 0$). Right part:

a) Measured reduced intensity $I_{VH}(\omega)/\omega[n(\omega)+1]$ of glassy As₂S₃ \triangle : [6], \circ : [4] compared with our theory (full line) using the same parameters as in Fig. 1 and $\xi = 2/k_D$. The dashed and dash-dotted lines are the Martin-Brenig theory (i.e. $\gamma = 0$) with $\xi = 2/k_D$ (dashed line) and $\xi = 4/k_D$ (dash-dotted line); b) same data divided by ω^2 ; c) Measured depolarization ratio [6] compared with theoretical curves (calculated with a ratio between the fluctuations of the two Pockels constants of 0.65).

determinations of the DOS by other means (e.g. inelastic neutron scattering or resonant Xray scattering from nuclei) have revealed that the spectra can *not* be described by (*). So one introduced a *frequency dependent* prefactor $C(\omega)$ and called it the light-vibration coupling factor, to be determined by comparing Raman spectra with other data. Our new theory can be summarized by the formula

$$I(\omega) \propto [n(\omega) + 1]\chi''(\omega)$$

where $\chi''(\omega)$ is a weighted sum over **q** (wavevector) integrals over the dynamical susceptibilities $\chi''_{L,T}(\mathbf{q}, \omega)$ times **q**-dependent form factors $f_{L,T}(\mathbf{q})$, which are proportional to the Fourier transform of correlation functions of fluctuating elasto-optic (Pockels) constants.

Using our existing theory for $\chi''_{L,T}(\mathbf{q},\omega)$ [2,3] we are now able to reconcile measured Raman spectra with data on $g(\omega)$ or the coherent neutron scattering law $S(\mathbf{q},\omega) \propto [n(\omega)+1]\chi''_{L}(\mathbf{q},\omega)$. The theory is based on a model of fluctuating elastic constants and has been quite successful for explaining the deviation of $g(\omega)$ from Debye's $g(\omega) \propto \omega^2$ law, which appears as a peak in the reduced DOS $g(\omega)/\omega^2$ ("boson peak"). Within the same theory it is also possible to explain the corresponding deviation of the temperature dependent specific heat C(T) from Debye's T^3 law and the characeristic dip or shoulder in the temperature dependence of the thermal conductivity [2]. Moreover within this theory it was possible to derive a relation between the boson peak and the sound attenuation constant in the regime accessible by inelastic X-ray and neutron scattering [3].

We demonstrate how our theory works at the example of glassy As₂S₃. In the left part of Fig. 5.4 we have compared the reduced density of states $g(\omega)/\omega^2$ as obtained from neutron scattering data [4] as well as the reduced specific heat $C(T)/T^3$ [5] with the prediction of our theory. The dashed curves correspond to the Debye theory. In the right part of Fig. 5.4 we compare the measured Raman spectra at different temperatures with our theory using the same parameters as in the calculations of the left figure. The dashed curves are obtained if for the dynamic susceptibilities those of free Debye-like acoustic waves are inserted. This procedure corresponds to an early theory of Martin and Brenig [7].

It is easily seen from comparing the figures that the peak in the Raman spectrum does *not* correspond to the peak in $g(\omega)/\omega^2$ as conjectured by Shuker and Gammon. However if the data are divided by ω^2 the peak appears at the same frequency as the one of $g(\omega)/\omega^2$. This corresponds to a peak in $\chi''(\omega)/\omega^3$, namely a deviation of this quantity from the Rayleigh ω^3 law, which should hold for $\omega \to 0$ in the absence of anharmonic interactions.

In the third part of the right figure we compare the depolarization ratio $\rho := I_{VH}/I_{VV}$ predicted by our theory with the one found experimentally, again, using the same parameters as in the other calculations.

We are convinced that it does not make sense any more to extract something like $C(\omega)$ from Raman data. However one can define such a quantity by dividing the correct theory by the wrong theory:

$$C(\omega) \propto \chi''(\omega)\omega/g(\omega)$$

If one calculates this quantity one arrives at curves which start with a constant and then increase linearly, as found in many investigations.

- [1] R. Shuker, R. Gammon, Phys. Rev. Lett. 25, 222 (1970).
- [2] W. Schirmacher, Europhys. Lett. 73, 892 (2006).
- [3] W. Schirmacher, G. Ruocco, T. Scopigno, Phys. Rev. Lett. 98, 025501 (2007).
- [4] V. K. Malinovsky et al., Europhys. Lett. 11, 43 (1990).
- [5] N. Ahmad, K. W. Hutt, W. A. Phillips, J. Phys. C: Solid St. Phys. 19, 3765 (1986).

- [6] R. J. Nemanich, Phys. Rev. B 16, 1655 (1977).
- [7] A. J. Martin, W. Brenig, phys. stat. sol. (b) 64, 164 (1974).

5.4 Low-frequency vibrational excitations in niobium-phosphate glasses for Raman gain application

A. Schulte¹, W. Schirmacher, T. Unruh², T. Cardinal³

- ¹ Department of Physics and College of Optics & Photonics-CREOL, University of Central Florida, USA
- ² FRM II, TU München
- ³ CMCB, CNRS, University of Bordeaux, France

Raman gain for all-optical amplification depends significantly on the cross section for spontaneous Raman scattering [1]. The spectra of these glasses show a low-frequency enhancement of the vibrational density of states ("boson peak") suggesting a significant gain profile for application in Raman amplifiers as well as providing an additional mechanism for Raman gain [2]. In order to explore the vibration spectrum with another spectroscopic technique we



Figure 5.5:

Intensity of Raman scattering (Stokes side) in 40 Nb₂O₅ - 60 NaPO₃ glass in three different representations: Raman intensity (top), Raman susceptibility (middle), and reduced Raman intensity (bottom).

carried out an inelastic neutron scattering investigation of 40 Nb₂O₅ - 60 NaPO₃ using the time-of-flight spectrometer (TOF-TOF) at the FRM 2 neutron source in Munich. The boson peak appears between 40 and 70 cm⁻¹ as an increase of the reduced density of states over the flat Debye expectation. In Fig. 5.5 relevant representations of the low-frequency Raman spectrum of the 40 Nb₂O₅ O₅ - 60 NaPO₃ glass on the Stokes side are shown. These are the measured *vv* polarized intensity $I(\nu)$, the Raman susceptibility $\chi''(\nu) = I(\nu)/n(\nu) + 1$] and the reduced intensity $I_r(\nu) = I(\nu)/\nu n(\nu) + 1$]. Here $n(\nu, T) = \exp[(h\nu/kT) - 1]^{-1}$ is the boson occupation factor. The susceptibility is proportional to the Raman gain curves relevant for



Figure 5.6:

Left figure: Reduced Raman intensity (top) $\chi''(\nu)\nu$ and reduced neutron intensity (averaged over the measured wavenumber range [3,4,5]) $g(\nu)/\nu^2$ against frequency. Right figure: The function $C(\omega) = \chi''(\omega)\omega/g(\omega)$ as determined by the experiment and by the theory of Schmid and Schirmacher (previous contribution)

optical amplifyers [2]. It is seen that the low-frequency peak in $I(\nu)$ and $I_r(\nu)$ near 65 cm⁻¹ appreciably enhances the amplification power near this frequency. This is the main reason for the low-frequency performance of our Raman amplifiers.

In the left part of Fig. 5.6 we compare the reduced Raman intensity $I_r(\nu)$ with the reduced q-averaged neutron intensity $\langle S(q,\nu) \rangle_q \nu/[n(\nu) + 1]$, which is believed [3,4,5] to be proportional to an effective, reduced DOS $g(\nu)/\nu^2$. It is clearly seen that the positions of the maxima of the spectra do not coincide. Until recently it was believed that the Raman susceptibility would be equal to a "modified DOS" $C(\omega)g(\omega)$ ($\omega=2\pi\nu$), divided by the frequency, where $C(\omega)$ would be a frequency-dependent light-vibration coupling function. However, this function was never theoretically calculated for a disordered solid. As we have now a theory for $\chi''(\omega)$ (see previous annual report contribution) we can calculate the quantity $C(\omega) = \chi''(\omega)\omega/g(\omega)$ and compare it to the corresponding experimental quantity (right part of Fig. 5.6). We see that the theory reproduces the almost linear increase of $C(\omega)$ in the boson peak range. Such an increase of the "Raman-divided-by-neutron" function has been observed in many other glassy materials. Of course it is more reasonable to compare the experimental data directly with theory as done in the previous contribution. This will be done shortly.

- R. Stegeman, L. Jankovic, H. Kim, C. Rivero, G. Stegeman, K. Richardson P. Delfyett, Y. Guo, A. Schulte, T. Cardinal, Optics Letters 28 (2003) 1126.
- [2] Y. Guo, S. Nonnenmann, A. Schulte, C. Rivero, K. Richardson, R. Stegeman, G. Stegeman, T. Cardinal, Conference on Lasers and Electro-Optics Technical Digest (OSA) (2004) CThP2.
- [3] J.M. Carpenter, and C.A. Pelizzari, Phys. Rev. B 12 (1975) 2391.
- [4] U. Buchenau, Z. Phys. B 58 (1985) 181.
- [5] A. Fontana, F. Rossi, G. Viliani, S. Caponi, E. Fabiani, G. Baldi, G. Ruocco, R. Dal Maschio, J. Phys.: Condens. Matter 19 (2007) 205145
- [6] A. Schulte, Y. Guo, W. Schirmacher, T. Unruh, T. Cardinal, Vibr. Spectrsoc. (2008) in press

5.5 Rotational dynamics of methyl groups in pentafluorotoluene and pentafluoroanisole

C. Smuda, G. Gemmecker¹, J. Wuttke², T. Unruh

- ¹ Technische Universität München, Bayerisches NMR-Zentrum, Garching
- ² Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH, Aussenstelle am FRM II, Garching, Germany

Almost the half of the hydrogen atoms in the oligoisoprene derivative coenzyme Q_{10} are bound to methyl groups. For a detailed evaluation of QENS spectra obtained from TOFTOF measurements of liquid Q_{10} , it is essential to know the contribution of these methyl group hydrogen atoms to the quasielastic intensity [1]. Up to now the rotation of methyl groups in liquids of organic molecules is scarcely investigated. Therefore it is of special and general interest to characterize methyl group rotation in the solid as well as in the liquid state. The aim of the investigations is to find a preferably universally applicable model for the description of the QENS of methyl groups in liquids of small organic molecules.

Pentafluoroanisole and pentafluorotoluene were investigated as model compounds. QENS spectra of solid pentafluoroanisole were fitted with a scattering function $S(Q, \omega)$ which comprises one Lorentzian function, whereas the dynamics of methyl groups in solid pentafluoro-toluene could only be described using two Lorentzian functions indicating a non-equivalence of the methyl groups in the investigated polycrystalline phase. The obtained linewidths for the compounds in the solid state are displayed in Fig. 5.7 [2].



Figure 5.7:

Arrhenius plot of half widths at half maximum (HWHM) Γ obtained from best fits for the two nonequivalent methyl group in polycrystalline pentafluorotoluene (PFT) and pentafluoroanisole (PFA), respectively. The solid lines represent best fits to the Arrhenius equation yielding activation energies of 6.4 kJ/mol for PFA and 2.74 kJ/mol and 0.96 kJ/mol for the two different types of methyl groups in the lattice of PFT, respectively.

As the methyl group dynamics is a thermal activated process, it shows an Arrhenius behaviour in the solid state for both compounds, whereas in the liquid state it was found that the frequency of the methyl group rotation is independent of temperature. The used model for data analysis includes not only the methyl group rotation but also long-range diffusion and isotropic rotational diffusion of the molecule

$$S(Q,\omega) = S_{\text{Methyl}}(Q,\omega) \otimes S_{\text{Trans}}(Q,\omega) \otimes S_{\text{IRD}}(Q,\omega)$$
(5.1)

and describes the experimental data perfectly (cf. Fig. 5.8). Evaluation of the QENS spectra without consideration of the methyl group rotation results in worse fits.

The long-range diffusion of the molecules in the liquid phase could for all investigated temperatures clearly be separated from the internal motions. Diffusion constants extracted from the model are comparable to PFG-NMR diffusion coefficients. The temperature dependence



Figure 5.8:

QENS spectra of pentafluorotoluene at 268 K and 293 K, respectively. Best fits obtained with model Eq. (5.1) are displayed as solid lines.

of the obtained Q independent rotational diffusion constants can be described with the Arrhenius equation. The Q independent HWHM for the methyl group rotation was determined to be about 1 meV for pentafluorotoluene as well as pentafluoroanisole.

Interestingly at very low temperatures inelastic lines were detected which were assigned to rotational tunneling transitions of the methyl group. The position of the tunneling lines at 5 K is about 215 μ eV (cf. Fig. 5.9).



Figure 5.9:

Tunneling spectra of pentafluorotoluene for different temperatures obtained at TOFTOF with an energy resolution of 40 μ eV. The curves are shifted on the y-scale for better visualization. Between 66 K and 76 K a phase transition takes place involving an increase in methyl group dynamics.

A small shift of the tunneling lines with increasing temperature can be extracted from the spectra which is typical for such tunneling lines. Notice that the intensity of the tunneling lines is only about 1% of the intensity of the elastic line. Usually the intensity ratios $I_{\rm inel}/I_{\rm el}$ are higher, as e. g. in the range of 0.04 to 0.25 for xylenes and fluorotoluenes [3]. Furthermore between 66 K and 76 K a structural phase transition can be observed which is accompanied by a significant increase in the quasi-elastic broadening of the elastic line. The investigated methyl group dynamics by QENS in the solid state characterizes only the "high-temperature phase".

From backscattering measurements of different monofluorotoluenes tunnel splitting energies $\hbar \omega_t^0$ are known [3]. We estimate from the results of 2-fluorotoluene that additional tunnel-

ing lines for pentafluorotoluene will be in the range of about 5 μ eV at 5 K, which could be confirmed by backscattering measurements at SPHERES at FRM II (cf. Fig. 5.10).



Figure 5.10: Methyl tunneling in pentafluorotoluene at 3 K at an energy resolution of about 0.65 μ eV performed at the backscattering spectrometer SPHERES at FRM II ($Q = 1.65 \text{ Å}^{-1}$).

The position of the tunneling lines at 3 K is about 4 μ eV. From these complementary measurements performed at TOFTOF and SPHERES two types of methyl groups could be identified in the low-temperature phase of pentafluorotoluene.

- [1] T. Unruh, C. Smuda, G. Gemmecker, H. Bunjes, MRS QENS 2006 Conf. Proc. 137 (2007)
- [2] C. Smuda, G. Gemmecker, T. Unruh, J. Phys. Chem., (submitted)
- [3] M. Prager, R. Hempelmann, H. Langen, W. Müller-Warmuth, J. Phys.: Condens. Matter 2, 8625 (1990)

5.6 Self-diffusion measurements of medium-chain molecules at TOFTOF

C. Smuda, T. Unruh

It could be demonstrated in [1] that QENS is best suited for investigations on molecular selfdiffusion inside nanosized droplets dispersed in another liquid. However, by measurements of the self-diffusion coefficients of the oligoisoprene derivative coenzyme Q_{10} in nanosized droplets and in the bulk, respectively, at the time-of-flight spectrometer TOFTOF discrepancies to the PFG-NMR diffusion constants of more than one order of magnitude have been found [2]. In order to study this effect more systematically, QENS measurements on a series of different medium-chain *n*-alkanes were performed with the aim to understand the influence of the chain length of the molecules to their diffusivities.

Eleven *n*-alkanes covering chain lengths from C_8 to C_{54} were studied. The alkanes were measured in a temperature range between 10–150°C with respect to their melting and boiling points.

For data evaluation, different models for the dynamic structure factor $S(Q, \omega)$ were used to extract diffusion constants: (i) sum of two Lorentzian functions, (ii) convolution of long-range diffusion and isotropic rotational motion, and (iii) convolution of long-range diffusion and diffusion inside a sphere [3]. Additionally, an evaluation in the time domain via the intermediate scattering function I(Q, t) was performed using a sum of two exponential functions as scattering law.

The experimental data could be satisfactorily described with any of the four models, and it turned out that the determined diffusion constants are independent of the applied model. The



Figure 5.11:

Arrhenius plots of diffusion constants of selected investigated *n*-alkanes obtained from QENS spectra compared to results from PFG-NMR measurements [4]. Diamonds (\diamond) represent NMR diffusion constants and circles (\diamond) QENS values. Corresponding values for the higher *n*-alkane in the same plot are indicated by filled symbols.

derived diffusion constants were compared with values obtained by PFG-NMR [4]. Arrhenius plots of diffusion constants are shown in Fig. 5.11.

One main result is that with increasing chain length the ratio of the QENS diffusion coefficient to the PFG-NMR diffusion coefficient increases [5].

The increase of this ratio is better visible when plotting an isotherm of the diffusion constants of different *n*-alkanes on a double logarithmic scale as it is demonstrated for 110°C in Fig. 5.12.





Diffusion constants of *n*-alkanes determined by QENS at 110°C as a function of the molecular weight in comparison with PFG-NMR values [4].

This discrepancies of the diffusion constants determined by the two different methods are related to their different timescales and not caused by contributions of internal motions. Further efforts with respect to data evaluation have to be made in order to find the true reason the observed discrepancies of the QENS and NMR results. Some more experimental information will be obtained by neutron spin-echo measurements, which are in progress to determine the *Q* dependence of the diffusion constants at low *Q*-values. In addition, the study is intended to be extended on other medium-chain molecules like oligomers of polyoxyethylene, fatty acids, alky alcohols or silicon oils.

[1] T. Unruh, C. Smuda, G. Gemmecker, H. Bunjes, MRS QENS 2006 Conf. Proc. 2006, 137 (2007)

- [2] C. Smuda, G. Gemmecker, H. Bunjes, T. Unruh, FRM II annual report 2006, 84 (2006)
- [3] M. Bée, Quasielastic Neutron Scattering, Adam Hilger, Bristol, PA, (1988)
- [4] E. von Meerwall, S. Beckman, J. Jang, W. L. Mattice, J. Chem. Phys. 108, 4299 (1998)
- [5] C. Smuda, G. Gemmecker, T. Unruh, Langmuir, (in preparation)

5.7 Water diffusion in hydrous silicate melts as seen by QENS

- F. Yang, A. Meyer¹, T. Unruh, J. Kaplonski
- ¹ Institut f
 ür Materialphysik im Weltraum, Deutsches Zentrum f
 ür Luft- und Raumfahrt (DLR), K
 öln

Dissolved water has significant influence on the macroscopic properties of silicate melts and is thus of great importance for understanding many geological processes. By adding just a few weight percent of water to a silicate melt, the viscosity of the melt can be decreased by 5-10 orders of magnitude. It is very important for geoscience to obtain the knowledge of water and water species diffusion in silicate melts and therefore to predict the properties of the melts and to understand the processes relevant to active volcanisms. For reviews on this topic see [1,2].

Although there were varies investigations of water diffusion in silicate melts based on the in-situ diffusion couple method, the chemical diffusion coefficient of water in silicates shows strong dependence of the dry silicate composition. The basic underlying transport mechanism of the water species is still not understood.

We apply quasielastic neutron scattering method to study water diffusion in silicate melts. The water relaxation in the melt above the glass transition temperature of these systems is on the ps to ns time scales, which can be accessed by quasielastic neutron scattering. High pressure in the range of several kbars is necessary simultaneously to suppress water evaporation. The intrinsic q resolution of quasielastic neutron scattering allows to study the diffusion mechanism in great detail.



Figure 5.13: Measured I (2θ , ToF) at TOFTOF, FRM II of the empty pressure cell and a NS3+10mol% H₂O sample at 1250 K under 1800 bar.

In order to measure at high temperature relevant for volcanic processes as well as under high pressure, samples will be placed in a Nb1%Zr pressure cell. The pressure cell is heated up internally using Pt wire around the sample and using He gas as pressure medium. Here we report our very first results on hydrous sodium trisilicate melts investigated by quasielastic neutron scattering using the time-of-flight spectrometer TOFTOF at FRM II.

Sodium trisilicate samples with 10 mol% H₂O have been measured. A D₂O substituted sample was measured as well but it turned out that for this experiment a H/D exchange reaction happened during sample preparation, so a contrast variation was not possible. A dry sodium trisilicate sample was measure therefore for reference. The sample environment built for high temperature and high pressure neutron scattering has been working properly. Spectra were recorded using an incoming neutron wavelength of 5.1 Å, chopper speed at 12,000 rpm and chopper ratio 3, which gives an energy resolution of about 90 μ eV.

Fig. 5.13 shows the measured intensity as function of neutron time-of-flight for the empty pressure cell and a hydrous sodium trisilicate sample at 1250 K under 1800 bar. It can be clearly seen that the quasielastic broadening of the signal arises only in the spectrum the sample. So the He gas used as pressure medium did not contribute significantly to the quasielastic signal. Therefore a good resolution of the quasielastic signal from the sample was obtained. The spectrum of the water bearing sample measured at 1250 K shows a signal to background ratio of about 10:1 with respect to the empty cell within the elastic and quasielastic region. In the inelastic region, the spectra of the sample and empty cell are rather close. This makes the separation between the sample and the background signals in this region quite difficult.



Figure 5.14:

(a) $S(q,\omega)$ of the measured water bearing sodium trisilicate sample at 1250 K and the corresponding dry sample at the same temperature; (b) Temperature dependence of the diffusion coefficient of the H atoms, fitted with Arrhenius equation.

Using the pressure cell the hydrous sodium trisilicate sample has been measured at 5 different temperatures from 850 K up to 1250 K under a pressure of 200 MPa. Due to the presence of the sodium atoms, which also has a relaxation time scale within the instrument accessible range [3], the measured dynamic structure factor $S(q, \omega)$ contains both contribution from the hydrogen and the sodium atoms (Fig. 5.14 (a)). Therefore a separation between these two dynamics was done by subtracting the intensity of the dry sample from the corresponding water bearing sample. The resulting signal, which arises dominantly from the incoherent scattering of the H atoms, is used to extract the diffusion coefficient (Fig. 5.14 (b)). For the measured temperature range the deduced diffusion coefficient varies from $0.31 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ to $1.47 \cdot 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, respectively. The temperature dependence of the diffusion coefficient obeys an Arrhenius law. The diffusion mechanism still needs to be addressed.

It should be still appointed out that a differential signal refers to a dry sample does not com-

pletely exclude the contribution of the sodium. Since the hydrous sample and the dry sample has slightly different density and therefore the number density of the scatterers is different. Further measurement on a D_2O substituted sample will give more accurate results, since it is identical to the protonated sample except in scattering cross-sections.

- [1] J.S. Gilbert, R.S.J. Sparks (Ed.): *The Physics of Explosive Volcanic Eruptions*, The Geological Society, London (1998)
- J.F. Stebbins, P.F. McMillan, D.B. Dingwell (Ed.): Structure, Dynamics and Properties of Silicate Melts Rev. Mineralogy 32 (1995)
- [3] A. Meyer, H. Schober, D. B. Dingwell, Europhys. Lett. 59, 708 (2002).

5.8 Structure and dynamics in Ni₃₆Zr₆₄

S. Stüber, F. Yang, A. Meyer¹, D. Holland-Moritz¹, C. Tomaras, W. Schirmacher

¹ Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR)

Diffusion and viscosity are important material parameters to characterize multicomponent metallic alloys. In five-component ZrNi-based melts Ni-dominated diffusion was found to be significantly faster than predicted from viscosity; it was also found that the Ni-dominated incoherent scattering function from which the diffusivity is extracted, depends little on the melt composition [1]. From these observations, binary ZrNi systems emerge as the simplest metallic melts where Ni diffusion can be measured in the viscous regime, serving as a proxy for understanding the dynamics in more complicated bulk metallic glass formers.

The technique of electromagnetic levitation (see last year's report for details) was combined with quasielastic neutron scattering at the time-of-flight spectrometer TOFTOF of the FRM II to study the Ni self diffusion in the binary alloy $Ni_{36}Zr_{64}$. As Zr is very reactive, containerless processing is needed to enable stable and long measurements with good statistics. Furthermore as there are reduced cristallization seeds, undercooling for several hours is possible, testing dynamics in the metastable state of an undercooled metallic melt.

From the measured scattering function $S(q, \omega)$, the diffusion constant is derived using the half width at half maximum $\Gamma_{1/2}$, which is proportional to q^2 in the range of small momentum transfer q:

$$D = \frac{\Gamma_{1/2}}{\hbar q^2} \tag{5.2}$$

This was done in a temperature range from 70 K below to nearly 400 K above the liquidus of $Ni_{36}Zr_{64}$ of 1283 K, compare fig. 5.15.

In semilogarithmic representation, the measured diffusivities lie on a straight line. So in the available temperature range, the Ni self diffusion follows Arrhenius' law

$$D(T) = D_0 \exp(-E_A/k_B T),$$
(5.3)

with E_A as activation energy of the diffusion process, and the prefactor D_0 containing the temperature-independent contributions of change of entropy, coordination number etc. For Ni₃₆Zr₆₄, we find $E_A = 0.64$ eV per atom and $D_0 = 0.19 \cdot 10^{-6} \text{ m}^2 \text{s}^{-1}$.

To study the complete dynamics – also of Zr, and the interdiffusion –, and a possible interplay between microscopic dynamics and structure, we measured the partial structure factors of $Ni_{36}Zr_{64}$.



Figure 5.15: Ni self diffusion in Ni₃₆Zr₆₄ as function of inverse temperature. D(T) follows an Arrhenius law with an activation energy of 0.64 eV/atom.

This was achieved via isotopic substitution, measuring the static structure factor of three $Ni_{36}Zr_{64}$ samples in a similar levitation set-up as for the measurement of the Ni self diffusion, but at the neutron diffractometer D20 of the ILL. One sample was pepared with Ni in natural isotopic composition, one was enriched with ⁵⁸Ni, and one with ⁶⁰Ni. The respective measured structure factors relate to the partial structure factors via a matrix containing the scattering lengths and the stoichiometric concentrations of Zr and the Ni isotopes. Matrix inversion produces the partial structure factors of the left hand side of fig. 5.16.





The structure is dominated by the Zr, whose structure factor looks similar to a simple hard sphere structure factor. The NiNi partial structure factor has a minimum for the q value of the ZrZr maximum and a double peak, also for the higher maximums, Ni atoms chiefly occupy places left free by Zr. A chemical ordering is not clearly visible yet. For this, it is better to study the correlation functions of the density fluctuations $\delta \rho$ and the concentration fluctuations δc , compare right hand side of fig. 5.16. The number-number (or density-density) correlation is

again hard-sphere like, but we find a contribution from S_{cc} at the q value of the first ZrZr structure factor maximum.

These partial structure factors are vital as input for mode-coupling theory (MCT). MCT in the context of alloys with chemical short-range order can be used to calculate self-diffusion and interdiffusion coefficients. In the case of the Ni-Zr system this has already been done [2], predicting that the self diffusion of both constituents proceeds with almost equal rates, due to the strong coupling between Ni and Zr.

- [1] A. Meyer, W. Petry, M. Koza, and M.-P. Macht, Appl. Phys. Lett. 83, 3894 (2003).
- [2] Th. Voigtmann, A. Meyer, D. Holland-Moritz, S. Stüber, T. Hansen, T. Unruh, submitted

5.9 Change of microstructure and shape of solid materials by external magnetic fields

T. Mehaddene, J. Neuhaus¹, W. Petry¹, K. Hradil¹

¹ Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II), Garching, Germany

Studies of the lattice dynamics provide a link between experiments and theoretical descriptions, based on the underlying potentials for the microscopic origin of various transformations. Magnetic shape memory alloys undergo a martensitic transition within their ferromagnetic phase. They are able to recover induced strains up 11% in moderate magnetic fields. In our group, we investigate their dynamical behaviour using inelastic neutron scattering.

Normal modes of vibration along the high-symmetry directions in a Ni₄₉Mn₃₂Ga₁₉ single crystal have been measured by inelastic neutron scattering. The phonon dispersion curves along [$\xi\xi$ 0] are depicted in Fig. 6.4 [1]. The striking feature of the dispersions is the wiggle in the TA₂[$\xi\xi$ 0] branch within the ξ -range of 0.15–0.5 r.l.u. The wiggle softens anomalously with decreasing temperature but remains finite even at vicinity of the martensitic transition (M_s=353K). Based on density functional theory, Entel et. al. have calculated the phonon spectra of a stoichiometric Ni₂MnGa alloy along [$\xi\xi$ 0] [2]. The calculations, performed at T=0K, predict a complete softening of the TA₂[$\xi\xi$ 0] branch in the ξ -range 0.2-0.45 r.l.u. Despite of the difference in the chemical composition of the measured sample and the assumed stoichiometry in the calculations, the overall behaviour of the phonon spectra and the extension in q-space of the phonon anomaly are in good agreement. The degree of softening is enhanced at 373K when the system is in the ferromagnetic state (T_c=390K). This is a signature of the coupling of the magnetism to the lattice vibrations which is unique to NiMnGa. For instance, no enhancement in the softening is observed in NiMnSn below its Curie temperature (not shown here).

We have extendend the lattice dynamics investigation to the martensitic phase of NiMnGa. The lattice dynamics of two single variant samples, with different martensitic structures have been measured. The 5M (7M) structure has a tetragonal (orthorhombic) cell with a periodic stacking sequence of 5 (7) (110) atomic layers along [110]. The crystals have been measured with their c-axis and a-axis perpendicular to the scattering plane, giving access to the phonon dispersions along the [$\xi\xi 0$] and [$0\xi\xi$] directions, respectively.

The acoustic phonon spectra of the 5M and 7M structures show fundamental differences. In the 7M structure, neither the dispersion of the TA₂[$\xi\xi$ 0] nor of TA₂[$0\xi\xi$] shows an anomalous behaviour. The two phonon branches show a normal sinus-curve like dispersion. The same phonon branches have been measured in the 5M-sample. Fig.6.6 shows an iso-intensity map





Measured (symbols) and calculated (lines) phonon dispersion [2] along [$\xi\xi$ 0] in NiMnGa. The measurements have been performed on a Ni₄₉Mn₃₂Ga₁₉ single crystal [1] at 373K.

of the scattered intensity. We clearly see the dispersion of the $TA_2[\xi\xi 0]$ branch with an extra inelastic scattered intensity from a low-energy excitation arising from the elastic peaks of the modulated structure. The low-energy excitation is dispersive and levels off at higher qvectors. The iso-intensity map suggests that this branch interacts with the $TA_2[\xi\xi 0]$ phonons around $\xi = 0.3$ r.l.u where the latter shows a wiggle in the dispersion. The intensity of the low-energy excitation decreases very fast at higher energies and becomes weaker at higher q-vectors.



Figure 5.18:

Iso-intensity map of the scattered intensity along [$\xi\xi$ 0] with a < 1–10 > polarisation measured in a 5M-Ni₄₉Mn₃₂Ga₁₉ crystal at room temperature.

The appearance of the low-energy excitation in the martensitic 5M structure of NiMnGa is very striking. A similar feature has been recently observed in 5-layered structure of a sto-ichiometric martensitic Ni_2MnGa crystal in which the single variant has been achieved by

applying a magnetic field of 1.5T while cooling down the sample through the martensitic transformation [3]. Contrary to the observations of Shapiro et al. [3], the intensity of the excitation is more pronounced in our sample in which the dispersion could be followed up to the zone boundary. Moreover, we have observed elastic peaks of the modulated structure centred on 0.4 r.l.u which is definitely different from to the incommensurate value 0.423 r.l.u reported by Shapiro et al. Shapiro and his co-workers assigned their observations to a Charge Density Wave (CDW) of which the origin is unclear. The fact that this low-energy excitation does not show up (so clearly) in the 7-layered structure makes its interpretation as a CDW quite ambiguous. This point has to be addressed with extended investigations.

This research project is part of the SPP 1239. We kindly ackknowledge funding by SPP 1239.

- [1] The crystals have been made by R. Schneider, M. Mecklenburg, K. Rolfs, HMI
- [2] P. Entel, V. D. Buchelnikov, V. Khovailo, A. T. Zayak, W. A. Adeagbo, M. E. Gruner, H. C. Herper, and E. F. Wassermann, J. Phys. D: Appl. Phys. 39, 865 (2006).
- [3] S.M. Shapiro, P. Vorderwisch, K. Habicht, K. Hradil and H. Schneider, Eur. Phys. Lett. 77, 56004 (2007).

Mößbauer spectroscopy and nuclear inelastic scattering studies on a polynu-5.10 clear oxo-bridged iron catalyst - first results

T. Asthalter¹, S. Rajagopalan¹, U. van Bürck, F.E. Wagner, V. Rabe², S. Laschat²

- Institut für Physikalische Chemie, Universität Stuttgart Institut für Organische Chemie, Universität Stuttgart
- $\mathbf{2}$

Selective catalytic oxidation using molecular oxygen is highly promising for the synthesis of complex natural products and pharmaceutically active agents. Recent developments in catalysis aim at the optimization of yield, turnover frequency and selectivity, as well of the sustainability of the entire processes. Thus, it is desirable to replace expensive heavy metal catalysts by materials containing economic, non-toxic iron within their active centre.



Figure 5.19: Structure of the catalyst precursor

In this paper we report first results obtained from Mößbauer spectroscopy (MS) and Nuclear Inelastic Scattering (NIS) of synchrotron radiation on such a selective oxidation using molecular O_2 and a novel polynuclear iron catalyst. A first X-ray crystallographic study on a water

adduct indicates that the precursor is a tetranuclear iron complex as shown in Fig. 5.19. The geometry of the cluster may be described as a 'butterfly' of type II, based on two edge-sharing Fe₃(μ_3 -O) triangular units [1,2].



GIF-CONDITION : Fe Catalyst/Zn/O2 in Pyridine/acetic acid

Figure 5.20: Scheme of the reaction

The precursor is prepared from Fe(NO₃)₃·9 H₂O using appropriate ligands. The active catalyst was prepared by adding 61 mg of precursor to 131 mg of Zn powder, 230 μ l of acetic acid and 2.8 ml of pyridine. The reaction was then started by adding 10.5 ml of the substrate, cyclohexene. The reaction scheme is shown in Fig. 5.20. All reactions were performed under inert gas (N₂). One sample was also prepared without substrate and in the presence of O₂. For the NIS experiments, Fe(NO₃)₃·9 H₂O, which is the starting material for the precursor and all other samples, was prepared from 95.38 % enriched ⁵⁷Fe powder.

The Mößbauer spectra were measured in a bath cryostat at 4.2 K by using a gas proportional detector in transmission geometry and a ⁵⁷Co source (Rh-matrix). The isomer shifts were calibrated with respect to Fe at 4.2 K. In order to study the reaction kinetics, measurements were also done at different times after starting the reaction. The samples were freeze-quenched [3] by taking approximately 120 μ l of the oxidation reaction mixture in a syringe, then immediately injecting it into the sample holder and immersing the sample holder in liquid nitrogen. In order to study the influence of different reactants in detail, measurements were also done on different combinations (with or without substrate in inert gas and in O₂).

The NIS experiments were performed at 70 K at the beamline ID18 of the ESRF, with an energy bandwidth (FWHM) of 1.2 meV. The collection times were roughly 10 h per spectrum.

Details of the Mößbauer results can be found in [4]. The Mößbauer parameters (isomer shift, IS and quadrupole splitting, QS) are tabulated in Table 5.10. In summary, the data are consistent with the assumption that the precursor is a high-spin Fe(III) complex, which converts into a high-spin Fe(III) active catalyst. During reaction, also a Fe(III) side product is observed.

Compound	$IS [mm s^{-1}]$	$QS [mm s^{-1}]$
Precursor	0.290	0.652
Active catalyst under N ₂	0.949	3.392
Active catalyst + cyclohexene under N_2	0.950	3.372
Active catalyst under O ₂	0.947	3.287
	0.305	1.040
Reaction after 1 min	0.973	3.217
Reaction after 2 min	0.952	3.091
	0.289	1.008
Reaction after 30 min	0.962	3.203
	0.304	1.052

Table 1: Mößbauer parameters of precursor, catalyst and reaction mixtures at 4.2 K



Figure 5.21: VDOS of the catalyst precursor

Turning now to the NIS experiments, Fig. 5.21 shows the partial Fe vibrational density of states of the solid precursor. From the VDOS, the mode composition factor (e_{ac}^2) , which is the fraction of kinetic energy associated with the resonant atom in the respective mode, can be easily computed. The mode composition factor of pure acoustic lattice modes is given by [5,6]



Figure 5.22: Reduced VDOS of the catalyst precursor

$$e_{ac}^2 = \frac{n \cdot m_R}{M} , \quad (1)$$

where *n* (4 in our case) is the number of the Mößbauer nuclei present in the molecule, m_R is the mass of the Mößbauer nuclei and *M* (1198.93 *u*) is the total mass of the molecule. According to Eq. 1, the mode composition factor for acoustic modes should be 19%, and the integrated VDOS reaches this value at 14.5 meV. From Fig. 5.21 it is obvious that the upper limit of the acoustic modes extends into a molecular mode. Using the Debye approximation, the correct upper limit of the acoustic modes can be determined directly from the experimental data as described in [6]. According to the Debye approximation, the upper limit of the acoustic modes, E_{up} , is given by

$$E_{\rm up} = \left(\frac{\pi}{2\beta}\right)^{1/3} , \quad (2)$$

- 10

where the proportionality coefficient β can be computed from the reduced VDOS $g(E)/E^2$ as shown in Fig. 5.22. Using Eq. (2), the correct upper limit is found to be 9.5 meV, which is in good agreement with the lower limit of the acoustic region/peak in Fig. 5.21. These differences in the limit of lattice modes are due to the fact that inter- and intramolecular vibrations overlap. The limits predicted by the Debye approximation and by Eq. (1) are indicated by arrows in Fig. 5.21. The NIS spectrum of the active catalyst (not shown) differs strongly from the one of the precursor. Quantum chemical calculations and normal mode analysis are currently be used to analyse the molecular modes. NIS spectra of frozen solutions will be discussed in a forthcoming paper.

- [1] W. H. Armstrong, M. E. Roth, S. J. Lippard, J. Am. Chem. Soc. 109, 6318–6326 (1987).
- [2] J. Overgaard, D. E. Hibbs, E. Rentschler, G. A. Timco, F. K. Larsen, Inorg. Chem. 42, 7593–7601 (2003).
- [3] A. Vértes, D. L. Nagy (eds.): Mössbauer Spectroscopy of Frozen Solutions, Akadémiai Kiadó, Budapest (1990).
- [4] S. Rajagopalan, T. Asthalter, V. Rabe, U. van Bürck, F. E. Wagner, S. Laschat, accepted by Hyperfine Interactions.
- [5] J. T. Sage, C. Paxson, G. R. A. Wyllie, W. Sturhahn, S. M: Durbin, P. M. Champion, E. E. Alp, W. R. Scheidt, J. Phys.: Cond. Matter 13, 7707–7722 (2001).
- [6] A. I. Chumakov, R. Rüffer, O. Leupold, I. Sergueev, Struct. Chem. 14, 109–119 (2003).

6 Instrumental and methodical developments

6.1 Status of the instrumentation at the Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II)

W. Petry

Diffractometers		
materials diffractometer StressSpec	HMI / GKSS	routine operation
powder diffractometer SPODI	TU Darmstadt/LMU M.	routine operation
therm. single crystal diffract. RESI	Uni Augsburg/LMU M.	routine operation
hot single crystal diffractometer HEIDI	RWTH Aachen	routine operation
beam for neutron optics MIRA	TUM physics	routine operation
reflectometer liquid samples RefSANS	GKSS/LMU Munich	routine operation
reflectometer for hard matter n-REX+	MPI-Stuttgart	routine operation
high intensity reflectometer MARIA	JCNS	2009
small angle scattering KWS 1	JCNS	2008
small angle scattering KWS 2	JCNS	routine operation
small angle scattering KWS 3	JCNS	routine operation
small angle scattering SANS-1	TUM physics/GKSS	2009
bio diffractometer	TUM physics/JCNS	2011
high intensity diffractometer POWTEX	RWTH/Uni Göttingen	2012
Spectrometers		
classical spin echo NSE	JCNS	routine operation
resonance spin echo RESEDA	TUM physics	2008
back scattering SPHERES	JCNS	routine operation
time-of-flight ToF-ToF	TUM physics	routine operation
diffuse & inelastic DNS	JCNS	2008
thermal time-of-flight TOPAS	JCNS	2011
spin echo three axes TRISP	MPI-Stuttgart	routine operation
cold three axes PANDA	TU Dresden	routine operation
thermal three axes PUMA	Uni Göttingen	routine operation
polarised three axes KOMPASS	Uni Cologne/TUM ph.	2012
Fundamental Physics		
cold beam nuclear physics MEPHISTO	TUM physics	routine operation
prompt gamma analysis PGAA	Uni Cologne/TUM ch.	routine operation
ultra cold neutrons UCN	TUM physics	> 2012
Radio- & Tomography		
with cold neutrons ANTARES	TUM physics	routine operation
with fast neutrons NECTAR	TUM chemistry	routine operation
Positrons		
NEPOMUC	TUM ph/ Uni BW	routine operation
Clinical Tumor Therapy		
with fast neutrons MEDAPP	TUM FRM II	routine operation

Table 2: Status of beam hole instrumentation at FRM II

In 2007 — the 3rd year of routine operation – the Forschungsneutronenquelle Heinz Maier Leibnitz (FRM II) operated for 233 full power (20 MWatt) days. In early spring 2007 the east building with its large second neutron guide hall has been finished and the Jülich Centre for Neutron Sciences (JCNS) moved into its offices and labs on top of the guide hall. All this was celebrated in an inauguration event on 9th of May 2007. Step by step the first instruments of the JCNS became operational (see table 1) and typical gains in performance by factors 10 to 100 were achieved, when compared to their performance at DIDO, FZ-Juelich. Here gain in performance is defined by increase in flux at the detector times increase in resolution. This gain is the result of both, higher flux of the neutron guides at FRM II and a sophisticated upgrade of each of the instruments. A first proposal round for the JCNS instruments took place in March 2007.

With July 2007 the Federal Ministry for Education and Science (BMBF) renewed its engagement in funding instruments at FRM II. PUMA, SPODI, polarized HEIDI and biological sample environment at RefSANS continue under the patronage of BMBF. Further funds for three more instruments or upgrades have also be allocated, POWTEX, KOMPASS and automatic sample set-up at StressSpec. The universities in charge of the BMBF instruments are Uni Göttingen, TU-Darmstadt, RWTH Aachen, LMU Munich and the TU-Clausthal. Some of them engage at several instruments.

For the first time laboratory courses for the advanced semesters of the study of physics at the Physics Department took place at selected instruments of the FRM II in 2007. Each course meant hands-on-training on a particular instrument for 24 our with subsequent evaluation of the results.

Similar training happened within the annually organized neutron school of the FZ-Juelich. Here about 40 PhD students from all over Europe learn the essentials of neutron scattering in a one week crash course at FZ-Juelich and complement this by a one week training on site at the instruments installed at FRM II.

Early 2007 the Bavarian Ministry for Environment, Consumer Protection and Health granted to FRM II the permission to treat tumors by fast neutron irradiation. This was immediately followed by the first patients, coming from TUM's own clinic.

6.2 Upgrade of the tandem Fabry-Perot interferometer

J. Wiedersich, A. Meier-Koll, P. Müller-Buschbaum, W. Petry

The light scattering laboratory at E13 underwent a major instrumental upgrade of the set-up of the Sandercock tandem Fabry-Perot interferometer. The instrument was in successful operation for more than a decade [1], but both mechanical wear and technical progress over that time pointed towards a fundamental refurbishment. From the beginning of the year, the Ar ion laser showed signs of the end of the tube's lifetime, which fortunately could be delayed up to the end of November. Both soft- and hardware of instrument control and data acquisition were running on a more than ten year old computer, and neither could be technically ported to modern hardware or to a current operating system (OS). Some mechanical parts were failing, suggesting a testing and maintainance or replacement of all electronic or mechanical parts. Furthermore, it turned out that the proper operation of the interference filters could not be verified any more with the lack of a dispersive prism within the interferometer [2], see report 6.3.

All this pointed towards a fundamental upgrade of the experiment, that eventually turned all parts of the instrument towards a 'brand new' state. The main changes of the tandem's experimental set-up are the following:

- The Ar ion laser is being replaced by a solid state Nd:Vanadate laser, operating at a wavelength of 532.3 nm instead of 514.5 nm. The laser is in the process of being delivered at the time of writing. One disadvantage of the new laser is the reduction of output power by a factor of 10 compared with the Ar laser. At present, E14 has very kindly lent us a more powerful Nd:Vanadate laser and we hope that we can keep that for a bit longer.
- The change in wavelength requires a new set of interference filters in order to suppress higher transmission orders (cf. report 6.3).
- The optical system of the interferometer and the housing have been replaced by a more compact design. Most day-to-day adjustment and the operation of the photo detector can now be achieved without opening the housing of the interferometer, avoiding thermal and other disturbance of the delicate instrument (interferometer mirrors have to be kept parallel over hours within less than $\approx 10^{-8}$ rad while two of them are constantly scanned).
- A dispersive prism was reinserted into the optical system. Together with the interference filter, the prism allows a flexible and controlled adjustment of the required bandpass of the interferometer, avoiding contributions of higher transmission orders of the tandem. Without an additional bandpass the Sandercock configuration of two Fabry-Perot interferometers suppresses the next transmission orders, but every 20th order will transmit again [2]. In order to faciliate measurements over a broad frequency range, flexible and verifiable control over the instrument's bandpass is required.
- The numerical aperture, ie. the foci of the lenses within the interferometer, were changed in order to better match the available pinholes.
- Additional apertures were placed within the optical path of the interferometer in order to reduce interferometer ghosts and to increase the practicable contrast.
- An new microscope allows direct viewing of the light entering the instrument through the entrance pinhole. This faciliates alignment, especially for weak scattering signals.
- New hard- and software for data acquisition. Unfortunately the old home developed software of Joachim Wuttke could not be ported to new hardware or a modern OS. Therefore the software was replaced by proprietary software. Since there is a personal contact between our lab and both developers and the vendor of the software it is hoped that the inherent disadvantage of proprietary software will be small.
- In the course of refurbishment, every single part of the experimental set-up was taken apart, each precision engineered mechanical part was disassembled and serviced, and all optics were cleaned.

Figure 6.1 shows the very first spectrum measured after the upgrade, employing E14's Nd:Vanadate laser. The spectrum of scattered light from the polymer p-(methyl-methacrylate) (PMMA) covers about four orders of magnitude and shows a background at high frequencies that still is one order of magnitude above the dark count level of the detector.



Figure 6.1:

Brillouin spectrum of PMMA obtained in back scattering geometry. From 0 GHz outwards the following features are observed: elastic peak (reference signal), longitudinal Brillouin line, ghosts of the reference signal (two peaks close to each other), ghosts of the Brillouin line (two peaks on either side). Note that the fit by the instrumental function is practically indistinguishable from the reference signal.

Note that the signal is larger by about an order of magnitude or more for frequencies below the Brillouin line than at frequencies higher than the Brillouin line. Therefore, taking the logarithmic intensity scale, the Brillouin spectrum cannot be described by a conventional Lorentz function.

There are still a few open points. The narrowest interference filter and the new laser are expected to be delivered within a few weeks and it is being worked on improving the temperature stability of the lab.

In conclusion, it is hoped that the present refurbishment leads to a better performance of the tandem interferometer – especially for the study of weaker signals – due to the more flexible adaption of the bandpass and due to the expected improvement of the experimentally usable contrast.

- [1] J. Wuttke, M. Seidl, G. Hinze, A. Tölle, W. Petry, G. Coddens; Eur. Phys. J. B 1, 169 (1998)
- [2] J. R. Sandercock, Tandem Fabry-Perot interferometer TFP-1, Operator Manual

6.3 Characterisation of the upgraded Fabry-Perot interferometer

A. Meier-Koll, J. Wiedersich, P. Müller-Buschbaum, W. Petry

We are interested in the dynamical behaviour of fast relaxations and vibrations. Excitations in the corresponding frequency range of GHz to THz are conveniently studied with Fabry-Perot

interferometers (FPIs). The most prominent excitations in this domain are longitudinal and transverse sound waves which lead to a frequency shift of the scattered light. In disordered solids like polymers, relaxation processes lead to a contribution to the signal which is serval orders of magnitude smaller than peaks originating from scattering at sound waves. In order to reveal these relaxation processes and the underlying mechanisms, it is neccessary to obtain spectra with intensity and frequency variying over several orders of magnitude. Therefore, it is essential to operate the Fabry-Perot interferometer with a very high signal-to-background ratio.

In the light scattering laboratory at E13, we use a six-pass Tandem Fabry-Perot interferometer manufactured by Sandercock. In the tandem setup, two Fabry-Perot interferometers with a fixed relation of the mirror distances are coupled. With this fixed relation the tandem transmits every 20th order of the free spectral range. With this arrangement, the higher transmission orders of a FPI are suppressed. However, due to the high resolution and the broad range of light scattered by disordered systems, it is not sufficient to suppress the next couple of higher transmission orders, but a sufficient suppression of *all* further transmission orders is required. (At a typical free spectral range of 20 GHz the visible optical range contains more than 10^4 transmission orders of a FPI.) The tandem FPI alone, however fully transmits every 20th higher order, ie. it suppresses about 95% of those orders. To further enhance the spectrometer, higher orders of transmittance have to be suppressed with a suitable optical bandpass. Over the past years, our interferometer was equipped with a set of interference filters for this purpose. In order to be more flexible and to ensure the elimination of higher orders of transmittance also at large frequency scales, a pinhole-prism combination as an additional bandpass was added to the setup. The whole optical system is now in a state that is equivalent to currently delivered systems, including a diffractive prism and pinhole combination. As light source we changed from an Ar-ion laser (514.5 nm) to a Nd:Vanadate laser (532.3 nm). Therefore, we also had to order new interference filters, transmitting at the different wavelength (for details see section 6.2)



Figure 6.2:

Characterisation of a 2 nm bandfilter with the new setup: raw data. Upper curve: raw data spectra measured with a free spectral range of 3000 GHz. Middle curve: raw data spectra measured with a free spectral range of 1500 GHz. Lower curve: dark count-rate of the detector

As a first technical test, we verified that the upgraded tandem setup suppresses higher than the 20th order of transmittance effectively and determined the transmission function of the new interference bandpass filter. The entrance of the tandem setup is illuminated with white light from a bulb. Since the lamp's emission spectrum is much broader and more intense than the spectrum of any scattered light from a sample, it can be considered as a 'worst case senario' one has to deal with.

In figure 6.2 raw data spectra of a bandpass filter (central line 532.3 nm, FWHM=2 nm)

recorded with the new setup are plotted. The middle curve is measured with a free spectral range of 1500 GHz. In the logarithmic representation it is clearly visible that the intensity drops from the maximum at the central line to a value which is about the same level as the dark counts of the detector (1.5 cts/sec). The curve measured at a free spectral range of 3000 GHz looks similar. The additional peaks are ghost signals of the filter transmission and the central line. Again the signal returns to the detector background level at high frequencies. This clearly demonstrates that the pinhole-prism combination sufficiently suppresses transmittance contributions from all higher orders of the free spectral range.



Figure 6.3:

Transmission of a 2 nm bandfilter with the new setup. Upper curve: meassured with free spectral range 3000 GHz. Middle curve: meassured with free spectral range 1500 GHz.

From the raw data (figure 6.2) and additional measurements of the white light spectra without the interference filter, the transmission function is derived (figure 6.3). With exception of the priviously mentioned ghosts of the central line the derived transmission function from both free spectral ranges are the same and go down to the dark count level at high frequencies. This again confirms that the overall bandpass of tandem FPI, interference filter and prism sufficiently suppresses all the light from the light bulb except for the desired very narrow wavelength range. For the displayed spectra, the sum of all residual transmission outside the interval $\lambda_0 \pm 0.03$ nm is less than 10^4 times the accepted signal.

6.4 Implementation and testing of a GISAXS fluidic cell

J.-F. Moulin, P. Müller-Buschbaum, S. V. Roth¹

¹ HASYLAB at DESY, Hamburg, Germany

Flow of a liquid upon a solid surface is controlled by interactions on different length scales: the interactions between the constituents of the liquid and the solid substrate on the atomic scale as well as the substrate morphology in terms of corrugation, roughness and topography at large length scales give rise to a rich, system-specific behavior. These problems can in theory be conveniently studied via scattering techniques, but up to now, no GISAXS setup has been described allowing to investigate the fluid/substrate interface under flow conditions. We have thus designed and realized a new fluidic chamber optimized to perform GISAXS scattering at beamlines offering a microfocus option[1].

As seen from figure 6.4 this setup is basically a Y shaped plastic channel which is clamped over a substrate (glass or silicon), this geometry making it possible to study mixing or liquid separation. The geometry of the channel has been optimized to minimize absorption and



Figure 6.4: GISAXS Fluidic cell and the scattering geometry



Figure 6.5:

2D Scattering Patterns obtained for (a)Bare glass substrate, (b) Empty fluidic cell, (c) 20nm gold nanoparticles suspension flowing in the cell

parasitic scattering and the material used (TOPAS) has been selected owing to its good optical properties. Optical characterization of the flow profile as a function of flow rate has been performed using a coloured solution and quantitative image analysis showed that laminar flow conditions are maintained at all used flow rates.



Figure 6.6:

Out of plane cut of the 2D scattering patterns at the Yoneda peak position of gold. The continuous line for the gold nanoparticles data shows the results of a fit of the intensity for 20nm particles.

In order to test the setup from the point of view of scattering applications, we performed injection of gold nanoparticles acqueous suspensions and compared the scattering to that observed for an empty cell and for the bare substrate (see figure 6.5).

One notices immediately the strongly enhanced scattering due to gold nanoparticles. This is better seen in an out of plane cut of the 2D scattering pattern at the position of the Yoneda peak of gold.

Figure 6.6 shows these cuts as well as a model fit of the intensity in the case of the gold suspension data. This fit shows that particles of 20 nm can be detected at the interface between the solid and the fluid in motion. To the best of our knowledge this is the first time such an experiment is reported. We believe that this setup and its use for characterization of systems such as natural or synthetic colloids as well as polymer interfaces under flow will open new perspectives to the field of fluidics.

[1] J.-F. Moulin, S.V. Roth, P. Müller-üschbaum, Rev. Sci. Instr. (2007) Accepted for publication

6.5 Time-of flight grazing incidence small angle neutron scattering

P. Müller-Buschbaum, J.-F. Moulin, V. Kudryashov¹, M. Haese-Seiller¹, R. Kampmann¹

¹ GKSS-Forschungszentrum, Geesthacht, Germany

Polymers with controlled nanoscale morphologies continue to be of considerable interest for a wide range of applications in electronics, optoelectronics, photonics, sensors, and drug delivery. In particular, nanostructured polymer films allow for new properties, which are mainly based on surface effects and a size reduction down to a regime in which a characteristic length scale of a physical phenomenon becomes comparable with the typical length scale of the nanostructure. In many applications polymers are favoured because many of them are transparent, compliant, and biocompatible and/or biodegradable. Moreover, polymer devices are inexpensive and disposable, which is highly desirable for cost-effective applications.



Figure 6.7:

Selection of twelve 2d intensities measured simultaneously in the TOF-GISANS experiment. The corresponding mean wavelengths are a) 0.50, b) 0.55, c) 0.61, d) 0.68, e) 0.75, f) 0.82, g) 0.91, h) 1.00, i) 1.11, j) 1.22, k) 1.35 and l) 1.48 nm. The intensity is shown on a logarithmic scale represented by colours following the EOS2 palette (white= low and black= high intensity). Taken from [4].

In addition to a real space image of surface structures, a meaningful statistical analysis is advantageously performed with scattering techniques. Synchrotron radiation based grazing incidence small angle X-ray scattering (GISAXS) turned out to be a powerful advanced scattering technique to probe nanostructured polymer films. Similar to AFM a large interval of length scales between molecular and mesoscopic ones is detectable with this surface sensitive scattering method. While with AFM only surface topographies are accessible, with GISAXS in addition the buried structure is probed. Due to the larger area probed by GISAXS, this technique provides data having a much higher statistical quality than AFM. However, contrast between different components building-up nanostructures might be small and consequently, the possibility of tuning contrasts, which is possible by (partial) deuteration in case of neutron scattering, can be extremely advantageous. Thus neutron surface scattering as analytical techniques is a very successful technique. Using neutrons instead of x-rays in combination with the grazing incidence small angle scattering geometry results in grazing incidence small angle neutron scattering (GISANS). As compared to GISAXS measurements based on synchrotron radiation, experiments using neutrons are still very rare. So far all GISANS experiments were performed with a monochromatic neutron beam. These single wavelength experiments are typically very time consuming in case several different incident angles are probed. Within this article we report on a new approach, combining GISANS with the time-of flight mode (TOF). TOF mode allows for a specular and off-specular scattering experiment, in which neutrons with a broad range of wavelengths are used simultaneously and recorded as a function of their respective times of flight. Such white beam experiments are impossible with x-ray beams due to the immediate radiation damage to the sensitive (bio-) polymer structure. Due to the different interaction, neutron scattering experiments overcome all problems related to radiation damage and are thus a unique probe to detect radiation sensitive surface structures. So far TOF-mode based surface sensitive neutron scattering experiments were restricted to neutron reflectivity and standard off-specular scattering.

To demonstrate the possibilities of the new analytical technique TOF-GISANS we focus on a simple polymer nanostructure. The model system consists of an arrangement of small droplets, called nano-dots, containing a deuterated homopolymer which are prepared on top of a solid support [1]. Historically, a comparable polymer nano-dot sample was used as model system for the first GISANS experiments as well [2]. Thus the nanostructure is accessible with AFM and single wavelength GISANS measurements exist, which allows for a detailed evaluation of a TOF-GISANS experiment.

The presented experiments were carried out at the REFSANS beamline at the neutron reactor Heinz Maier-Leibnitz (FRM II). The total intensity, integrated over all TOF channels, and hence over all wavelengths is strongly dominated by the channels with highest intensity. However, the wavelength integration is equivalent to a strong smearing, because at individual wavelengths the detector pixels cover different q_yq_z -areas. Thus for a quantitative analysis only the 2d intensities related to individual TOF channels are suited. In figure 6.7 the 2d intensity distributions at 12 TOF channels is shown for a fixed number of effective pixels. Due to the different wavelengths each 2d intensity in figure 2 corresponds to a different (q_y , q_z)-range. Thus each 2d image in figure 6.7 is equivalent to the GISANS signal obtainable in a standard GISANS set-up [3] for the wavelength of the TOF channel.

Figure 6.7 shows the anisotropy of all observed scattering patterns. Different main features are already determined right from the two-dimensional images: The intense specular reflected peak, the Yoneda peak (which position depends on the related wavelength) and the splitting of the diffuse scattering into two strong Bragg-rods. The Yoneda peak is located at the position of the critical angle α_c . [4]

- [1] P. Müller-Buschbaum et al., J. Phys. Condens. Matter 17, S363 (2005)
- [2] P. Müller-Buschbaum et al., Phys Chem Chem Phys 1, 3857 (1999)
- [3] P. Müller-Buschbaum et al., Physica B 283, 53 (2000)
- [4] P. Müller-Buschbaum et al., submitted

6.6 Spectral fluence rates of the fast neutron beam MEDAPP at FRM II

H. Breitkreutz

This report is a summary of [1], which gives detailed information about the calculations and experiments carried out for my diploma thesis. The work was supervised by Franz Wagner in custody of Winfried Petry. All experiments were located at the MEDAPP facility at FRM

II. Thermal neutrons from the reactor core induce fission in two converter plates containing 498 g U-235. Some of the fast neutrons created here enter a beam tube and can be used for experiments. For this, the spectrum of the beam, its geometrical shape and the total flux have to be known.

The neutron spectrum of the MEDAPP fission beam at FRM II has been simulated by a Monte Carlo calculation using MCNP 4C2. This has already been done earlier [2], but with huge errors in the important (fast) part of the spectrum. The simulation was improved using some uncommon variance reduction methods and a special approach on the interface between two parts of the simulation: In a first step [3], the reactor core and the converter plates were simulated. Particles entering the beam tube were saved to a special file. This file was then analysed and modified, so that more particles were heading towards the point of interest, the so called patients position at the end of the beam tube (in fact, angels between the particles flight direction and the beam tube axis were halfed). The simulation was then continued for the beam tube using this file as start file. This reduced the error by a factor of 2. The resulting spectrum has then been compared with a transmission calculation and an analytical fit that was obtained from a typical reactor spectrum that passed a 1/v-filter. This approach was reasonable since MedApp has a near-pencil-beam geometry. All three approaches agreed well.

The simulated spectrum was then verified using multiple foil activation. For this, effective cross sections based on point data from ENDF and the simulated spectrum were calculated:

$$\bar{\sigma}_i = \frac{\int_0^\infty \sigma_i(E)\phi_{\text{trial}}(E)\mathrm{d}E}{\int_0^\infty \phi_{\text{trial}}(E)\mathrm{d}E}.$$
(6.1)

These cross section were then used to calculate a flux for every foil based on the measured decay rate of the activated materials. Materials included Ti, Fe, Al, Mg, Ni, Rh, In, Au and some others. In this experiment, the main focus was set on threshold reactions like (n,p)- and (n, α)-reactions, but also (n, γ)-reactions were included.

$$\phi_i = \frac{Z_i}{C_i \cdot \bar{\sigma}_i}.\tag{6.2}$$

The constant C_i incorporates all material constants, times and detector efficiencies. If the trial spectrum is right, fluxes ϕ_i are equal for every foil and reaction. As results were quite good, in a next step, an equalisation calculation as required by DIN 1319-4 was performed using the program MSITER from the NMF90 package with updated cross sections from IRDF 2002. It must be mentioned that MSITER does not fully meet the requirements of DIN 1319-4 as no adjustment of the cross sections is performed.

The adjusted results are show in fig. 6.8. The measured data confirmed the simulated spectrum in most parts, only minor adjustments were made.

The mean energy was determined to be 1.9(1) MeV, Kerma weighted 2,7(2) MeV. The median energy is 1.5(1) MeV.

Furthermore, the total flux was measured. This was done using a modified gold-water-bath technique: A bath filled with water was equipped with gold foils. Fast neutrons enter the bath through a short tunnel and are moderated in the water. The gold foils are activated by thermal and epithermal neutrons. The measurement is then repeated with Cd-covered gold foils that are only activated by epithermal neutrons in resonance capture. The difference between both measurements can be used to calculate the thermal flux at a given point. This way, a total flux of $3.2(2) \cdot 10^8 \,\mathrm{cm}^{-2} \mathrm{s}^{-1}$ was measured. This value agrees with other measurements (neutron



Figure 6.8: Adjusted spectrum of MEDAPP with standard filters (1 cm B₄C epoxy and 3.5 cm lead).



Figure 6.9:

Measured and calculated profile of the MEDAPP neutron beam. Note that flux values are slightly larger than $3.2 \cdot 10^8 \text{ cm}^{-2} \text{s}^{-1}$, as indium was used, which tended to give higher flux values than other materials. The hatching indicates the different regions (from left to right: full flux, inner penumbra, outer penumbra, shadow).

dose, multiple foil activation). It is slightly lower than expected from simulations, as MCNP did not take the burnup of the converter and the poisoning of the converter plates with Xe-135, Sm-149 and other fission products into account.

The geometrical beam profile was measured using small indium wires that were placed on a thin PMMA plate, as only the fast neutrons were of interested. A very simple geometrical model of MedApp was used for an analytical approach to determine the width of the penumbras. Measurement and theory showed a very good agreement (see fig. 6.9).

- [1] H. Breitkreutz, Diplomarbeit, FRM II, 2007
- [2] S. Kampfer, Diplomarbeit, FRM II, 2005
- [3] A. Röhrmoser, Neutrons designed for usage at FRM II, Annual Report 2006 Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II)
6.7 Heavy ion bombardment of UMo/Al dispersionn fuel

R. Jungwirth, W. Schmid, W. Petry, L. Beck¹, A. Bergmaier²

- ¹ Maier-Leibnitz-Laboratorium (MLL), München, Germany
- ² Universität der Bundeswehr München, Neubiberg, Germany

It was shown, that heavy ion bombardment of U-Mo/Al dispersion fuel allows to simulate the effects of radiation damage during in-pile irradiation [1]. Heavy ion bombardment avoids activation of the specimens. They may therefore be readily examined in simple laboratory experiments.

The examined specimen was irradiated with I^{127} at 80MeV. The angle between the incident ion beam and the sample surface was 60 degree. The temperature of the sample was below 370K during bombardment with heavy ions (compare fig. 6.10).

In contrast to irradiation experiments with heavy ions, which were conducted under tem-



Figure 6.10: Sketch of the irradiation setup [2]. The specimens are irradiated with I¹²⁷ at 80MeV.

peratures of \approx 470K before [3], the sample broke apart. SEM pictures show a large, asymetric interdiffusion layer (IDL) around every UMo particle. The asymetry of the interdiffusion layer is due to the direction of the incident ion beam (compare figure [6.11]).

An EDX analysis was carried out on different positions on the UMo grain surface (positions

Position	U[at%]	Mo[at%]	Al[at%]
1	20,9	2,8	76,3
2	88,3	11,7	
3	24,3	3	72,7
4	20,5	0,8	78,8

Table 3: Data of EDX analysis carried out on positions 1-4 on figure [6.11]

1-4, fig [6.11]). It was found, that the composition of the IDL differs significantly on positions 3 and 4. However, position 1 and 4 show the same composition. EDX analysis on position 2 revealed the original composition of the UMo grain. It did not change during irradiation (compare table [3]). The distribution of elements inside the IDL corresponds to UAL₄. X-ray



Figure 6.11:

SEM picture of an specimen after bombardment with heavy ions at 370K. A UMo grain embeded in an AL-matrix is visible. A great part of the grain was consumed during irradiation and changed into an assymetric interdiffusion layer (IDL) around a UMo core The assymetry is due to the direction of the incident ion beam. Smaller grains were completly consumed during irradiation. EDX analysis shows that the IDL consists of U, Al and Mo (compare table[3]).

diffraction measurements are planed for end of january 2008 to confirm or reject this assumption. However, post irradiation examination of the samples irradiated at \approx 470K found that the interdiffusion layer mainly consists of UAl₂ and UAl₃.

- D.G. Walker, P.A. Morel, X-ray diffraction studies of ion bombarded U₃Si, Journal of Nuclear materials 39, p. 49-58, 1971
- [2] W. Schmid, private communication, 2005
- [3] N. Wieschalla: Heavy ion irradiation of UMo/Al dispersion fuel, Dissertation at TUM, 2006

6.8 Influence of microstructural parameters on macro residual stress analysis

J. Repper, M. Hofmann¹, C. Krempaszky²

- ¹ ZWE FRM II, TU München
- ² CDL, WKM, TU München

Mechanical and thermal treatments during the manufacturing process inevitably cause the accumulation of residual stresses in parts consisting of materials with complex microstructure (e.g. high performance multiphase Ni- or Ti-alloys). It is well known that residual stresses affect the service life time of industrial used parts. Neutron diffraction is particularly well suited to determine residual stress distributions within the bulk of the component. The analysis of residual stresses from diffraction data can be strongly influenced by inhomogeneities of microstructural parameters (texture, grain size, distribution of precipitates, phase composition). We were able to show this influence by means of a simple sample geometry (flat disc shaped IN718 specimen, diameter = 100 mm) where process relevant boundary conditions allow us to predict the stress distribution in one principle - here axial - direction [1]. The residual





Variation of the calculated reference values $2\theta_0$ with the measuring depth x across the thickness of a forged IN718 pancake. The variation results from differences in the chemical composition across the thickness of the pancake.



Figure 6.13:

Residual stress distribution in the three principal axes hoop, radial and axial plotted against measuring depth x across the thickness of an IN718 disc (dashed lines indicate the position of the surfaces of the disc). The black line shows the stress distribution in the radial and hoop direction predicted by a simple semi-analytical model [1,3].

stress determination with neutrons were carried out at the Materials Science Diffractometer STRESS-SPEC [2], hosted by the FRM II.

For the determination of the residual stress distribution in the IN718 forged pancake it was not possible to cut a reference sample from the specimen itself as the pancake will be used for further experiments. In this case a reference value was calculated on the basis of mechanical equilibrium assuming the axial stresses to vanish. This assumption is valid in case of thin plate-like components of constant thickness with a thermo-mechanical treatment which is symmetrical to the mid-plane of the disc and homogenous and isotropic with respect to the in-plane coordinates [3]. Mechanical equilibrium then yields that the stress in thickness direction is zero. Taking this into account it could be shown that the calculated reference value varies across the thickness of the pancake as shown in figure 6.12 [1]. This stems from inhomogeneities in the microstructure caused by the manufacturing process (forging and quenching). The temperature of regions near the surface decreases faster than the interior of the pancake during the quenching. This leads in addition to strain gradients to changes in the chemical composition of the matrix over the thickness of the pancake. Therefore, each measuring point necessitates its own reference value to obtain the true macroscopic stress. Figure 6.13 shows the resulting stress distribution through the thickness of the pancake. The residual stresses derived from the experiment show good quantitative agreement with the predictions of a simple semi-analytical thermo-mechanical model based on the work of Landau et al. [4] elucidating the transient thermal stresses during quenching. For a detailed understanding of the relations between stresses (macroscopic and microscopic stresses as well) and microstructural parameters further experiments (e.g. tensile tests, relaxation tests) are planned within a DFG founded project (PE-580/7-1).

- J. Repper and M. Hofmann and C. Krempaszky and W. Petry and E. Werner. Mat. Sci. Forum, (accepted 2007).
- [2] M. Hofmann and J. Rebelo Kornmeier and U. Garbe and R.C. Wimpory and J. Repper and G.A. Seidl and H.G. Brokmeier and R. Schneider. Neutron News **18** (4), 27-30 (2007).
- [3] C. Krempaszky and E. Werner and M. Stockinger. Proceedings of the Sixth International Special Emphasis Symposium on Superalloys 718, 625, 706 and Derivatives, 527 (2005).
- [4] H.G. Landau and J.H. Weiner and E.E. Zwicky. J. Appl. Mech., 27, 297-302 (1960).

6.9 Manufacturing of monolithic U-Mo test fuel plates by cathode erosion

W. Schmid, Ch. Bogenberger, R. Hengstler, R. Jungwirth, W. Petry, P. Boeni¹, L. Beck², A. Breitner², H. Welzenbach²

¹ Physik Department E21

² Maier-Leibnitz-Laboratorium (MLL)

Over the next years many research reactors worldwide which currently use Highly Enriched Uranium (HEU) are supposed to be converted to Low Enriched Uranium (LEU). Monolithic LEU U-Mo fuel has become the most promising fuel material to convert several of these research reactors [1]. Unfortunately it was not possible so far to produce full size fuel plates from monolithic U-Mo, because the materials' difficult mechanical properties let all common processing techniques fail[2].

A new approach to this problem is the use of the cathode erosion or sputtering technique. Sputtering is a commonly used process to grow metal layers of micrometer or sub-micrometer thickness on different substrates, whereat the deposited layers provide excellent substrate adhesion and high density [3]. We want to use this technique in a first step to grow a massive full size meat layer of U-Mo. In a second step sputtering is used to surround this meat layer with several ten micrometers of Al as pre-cladding. The resulting U-Mo Al sandwich structure could then be further processed by common and less extensive welding, rolling or pressing techniques to finalize the Al cladding and thus to produce a full size fuel plate.

For this purpose a DC magnetron sputtering setup was built up (see fig. 6.14). The dimensions of the apparatus were chosen to enable production of structures with 700 x 65 mm in size, which corresponds to the size requirements of the currently used FRM 2 fuel plates. A 15 kW self-adjusting plasma power supply provides up to 800 V and 30 A to feed the glow discharge. The magnetron racetrack consists of more than 300 magnets with a surface



Figure 6.14: Scheme of the used DC magnetron sputtering setup

magnetic field of 1.43 T. The basic pressure in the setup is 5e-6 mbar, the argon working pressure during the sputtering process can be regulated by a flow controller to typical 5e-3 to 1e-1 mbar.

Substrate carrier and sputtering target are water cooled and temperature monitored. The whole process volume is further surrounded by an aluminum shield to prevent a coating of the vacuum vessel.

In preliminary tests the deposition of different metals (Cu, Al, Zn) and alloys (brass, stainless steel) for process pressures between 1e-3 and 1 mbar was studied. Achieveable plasma current and deposition rate was determined for each material in the given pressure range. The temperature evolution of target, substrate, shield, magnets and cooling water was monitored. In the result we gained an operational range for each of the parameters, which is now our guidline for further deposition experiments.

Based on this effort the second step was the deposition of very thick mono- and multilayers of size 700 x 65 mm to examine the general feasibility of depositing metal foils and blank sheets. We were able to produce Cu monolayers (blank sheets) of 1300 micrometers thickness and multilayer structures of 200 micrometer thick Cu (foils) surrounded by 20 micrometers of Al(6.15). The Cu layers were stable and comparable to standard industrial foils and blank sheets. The Al cladding showed a good adhesion to the Cu layer.

The third step will be the fabrication of multilayer structures from U-Mo and AlFeNi.



Figure 6.15:

(a) Sputtered blank sheet from Cu, 1300μ m thick, size 700 x 65 mm.(b) Microscopy image of a cross section of the mulilayer structure from figure c. The inner Cu layer has a thickness of 200μ m, the Al cladding has on one side 15μ m thickness, on the other side 25μ m.(c)Sputtered multilayer foil from Cu with Al cladding, size 700 x 65 mm.

Targets of each of these materials were obtained in the fourth quarter of 2007. The sputtering setup was installed inside a glovebox and is right now prepared for the use of U-Mo. We expect the first U-Mo deposition tests to begin in April 2008.

- [1] A. Travelli, Status and Progress of the RERTR Program in the year 2004, RERTR Vienna (2004)
- [2] C. R. Clark, Monolithic fuel plate development, RERTR Chicago (2003)
- [3] H. Frey, G. Kienel, Duennschichttechnologie, VDI Verlag (1987)

7 Outreach

7.1 Electronic repository of student's problems

J. Wiedersich

E13 has a large archive of physics problems for students: previous tutorial sheets (Übungen) and exams. That archive is in the form of paper folders and therefore cumbersome to use in the age of the computer. As a result, the archive contains many problems from the 1980s, fewer from the 1990s and almost none from the present millennium. The author could not even find last year's problems in the archive, although copies of the sheets and the solutions (Musterlösung) were available from last year's staff privately. On reusing a problem from last year, however, it turned out that the digital source of the figures is no longer available. Since problem sheets are nowadays no longer produced on a photo copying machine, but are distributed as pdf files, in practice this means that the digital format of the figures has to be recreated from scratch. To avoid these kinds of burdensome extra work, a state of the art digital archive of student's problems has been implemented.

The use of this collection of student's problems is straightforward and involves practically no extra work as compared the creation of student's problem sheets without the use of the central repository of problems. On the other hand, the effort is dramatically reduced for anyone who would like to reuse or modify an existing tutorial including its solution.

In a similar manner to E13's annual report, each problem consists of a single LATEX file with a few handy custom commands to facilliate the creation, changing and reuse of physics problems. It is best to give a short demonstration of how a problem looks both in full code and printed:

```
\begin{aufgabe}{Frauenkirche}
Wir lassen einen Stein von einem der Türme der Frauenkirche fallen.
Nach \lambda_{1}, \lambda_{1}, \lambda_{1}, \lambda_{2}, \lambda_{2}, \lambda_{3}
Berechnen Sie die Endgeschwindigkeit $v_{\mathrm{end}}$,
die mittlere Geschwindigkeit $v_{\mathrm{mit}}$ und die Fallhöhe $h$.
\lsg{%
x(t) = x_0 + v_0 \quad t + \int a(1){2} \quad a(t^2)
\qquad v(t) = \frac{x(t)}{ud x(t)} = v 0 + a, t;
\qquad d(t) = \frac{v(t)}{v(t)} 
x_0 = 0 \in \mathbb{H}\{m\}; \quad qquad v_0 = 0 \in \mathbb{H}\{m/s\}; \quad qquad a=g
   ($x$-Achse zum Boden!)
\ = x(t=\tau) = \frac{1}{2}\, a \tau^2
   = 0,5\cdot 9,81\EH{m/s^2} \cdot (4,3\EH{s})^2 = 91\EH{m}$$
\$v \ end = v(t \ tau) = a \ tau
   = 9,81\EH{m/s^2} \cdot 4,3\EH{s}= 42\EH{m/s}$$
Vorlesung:
st_x(t_2) - x(t_1) \{t_2 - t_2\}
= \frac{x(\lambda u) - x(0 EH\{s\})}{\lambda u - 0 EH\{s\}}
= \frac{91}{EH\{m\}} \{4, 3 \in \{s\}\} = 21 \in \{m/s\}
\end{aufgabe}
```

The code is standard LAT_EX code with the additional environment aufgabe, that begins and names a problem and the additional command \lag that adds the solution to the

Physikdepartment E13

WS 2007/08

Übungen zu Experimentalphysik 1 für MW

Prof. Dr. Peter Müller-Buschbaum, Dr. Johannes Wiedersich, Alexander Diethert, Oliver Meisenberg, Jan Perlich, Andreas Meier-Koll *Vorlesung 26.10.2007, Übungswoche 29.10.–02.11.2007*

Blatt 2

1. Frauenkirche

Wir lassen einen Stein von einem der Türme der Frauenkirche fallen. Nach $\tau = 4,3 \,\text{s}$ schlägt er unten auf. Berechnen Sie die Endgeschwindigkeit v_{end} , die mittlere Geschwindigkeit v_{mit} und die Fallhöhe h.

 $\begin{aligned} x(t) &= x_0 + v_0 \cdot t + \frac{1}{2} a t^2; \qquad v(t) = \frac{dx(t)}{dt} = v_0 + a t; \qquad a(t) = \frac{dv(t)}{dt} = a = \text{const} \\ x_0 &= 0 \text{ m}; \qquad v_0 = 0 \text{ m/s}; \qquad a = g \text{ (x-Achse zum Boden!)} \\ h &= x(t = \tau) = \frac{1}{2} a \tau^2 = 0.5 \cdot 9.81 \text{ m/s}^2 \cdot (4.3 \text{ s})^2 = 91 \text{ m} \\ v_{\text{end}} &= v(t = \tau) = a \cdot \tau = 9.81 \text{ m/s}^2 \cdot 4.3 \text{ s} = 42 \text{ m/s} \end{aligned}$ Vorlesung: $v_{\text{mit}} = \frac{x(t_2) - x(t_1)}{t_2 - t_2} = \frac{x(\tau) - x(0 \text{ s})}{\tau - 0 \text{ s}} = \frac{91 \text{ m}}{4.3 \text{ s}} = 21 \text{ m/s} \end{aligned}$

Figure 7.1:

Short example of a problem sheet for students with one simple problem. The solution is typset indented with italics and is of course not part of the published problem sheet given to students.

"Musterlösung", but of course not to the student's problem sheet. The code for the solution at first glance looks a bit involved, but it is the nature of a physics problem, that the solution contains a lot of mathematical formulas. It is also possible to include the solution in form of a scanned hand written sheet.

Only a single letter of the document has to be changed in order to either give the problems without solutions, give the problems with full solution or to only include a short solution. There are a few additional commands to 'automagically' include figures and to structure problems into parts (Unteraufgaben a, b, etc.). Problems are sorted in subfolders like 'Mechanik', 'Elektrodynamik', 'Thermodynamik', 'Optik', etc. to facilliate later access. Of course the repository is also searchable and contains an index with all titles of problems. The archive is fully version controlled, i. e. all changes to existing problems (for example modifications for exams) are tracked and can be easily visualised or reverted.

The full archive of currently 880 problems together with the complete documentation is available on pluto: /plutodaten/Aufgabenpool

7.2 Report of the women's representative of the Physics Department

C. M. Papadakis

In 2007, it was again time for drawing the balance of the equal opportunities situation at the Physics Department. A committee including the women's representatives of the Physics Department together with female and male profesors, scientists and students took a close look at the situation at the student, the scientist and the professor level and suggested measures to increase the fraction of women at all levels.

It was found that the fraction of female students has stayed constant at 13 % over the last years. This number is significantly lower than at other German physics faculties, also including other technical universities. The reasons are not known and are difficult to investigate. The challenge is thus to attract more female high-school students to study at the Physics Department. In addition to many existing acitivities for girls at TU München (Girls' Day, Herbst-universität, Mädchen machen Technik, mentorING Programm, Science Career Program), the committee suggests to offer an annual day for girls interested in studying physics, and to make sure that female students and scientists will be more visible during public activities of the Physics Department.

Among the Ph.D. candidates, the percentage of women has significantly increased and is now 19-20 %. No women has taken a habilitation in the last two years, however, at the moment, three women are working on their habilitation or have group leader positions in the Physics Department. This is a very positive development!

The committee also found that still, only very few women at the Phyiscs Department have a permanent position. The change of generations should be used in order to increase the fraction of women at this level. The Department has already created and filled a position for a young female scientist who wishes to build up a research group. Moreover, in 2008, young female scientists may apply for a similar position which was created in the framework of the Gender Issue Incentive Fund of TU München. Other activities are planned, such as a survey among female Ph.D. students about their career plans and close collaboration with the new family service of TU München.

At the professor level, a female associate professor has just been appointed, i.e. there are now three female associate professors at the Physics Department. However, there is no female chair holder. The committee suggests to include more women as referees for finding committees.

To conclude, the situation at the Physics Department has improved over the last years, e.g. at the level of Ph.D. students. However, especially at the student and the professor level, the percentages of women should be increased. Women at the Department should be made more visible and should participate at all levels.

[1] C.M. Papadakis, M. Göger-Neff, C. Scharnagl, K. Krischer, C. Pfleiderer, M. Ratz, T.M. Undagoitia, B. Englert, S. Kossler, 4. Gleichstellungsplan des Physikdepartments, Sept. 2007

8 Teaching and conferences

8.1 Lectures, seminars and lab courses

Spring semester 2007

Prof. Dr. Peter Müller-Buschbaum, Angewandte Physik: Polymerphysik 2
Prof. Dr. Peter Müller-Buschbaum, Experimentalphysik 2 für Maschinenwesen
Prof. Dr. Peter Müller-Buschbaum, Seminar über Struktur und Dynamik kondensierter Materie
Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine Papadakis, Seminar über spezielle
Probleme der weichen Materie
Prof. Dr. Christine Papadakis, Angewandte Physik: Experimentalphysik 2 für LB (EI/BT/MT)
PD Dr. Wolfgang Doster, Experimentalphysik 2 für LB
Prof. Dr. Walter Schirmacher, Theory of liquids and polymers II

Fall semester 2007/2008

Prof. Dr. Peter Müller-Buschbaum, Angewandte Physik: Polymerphysik 1
Prof. Dr. Peter Müller-Buschbaum, Experimentalphysik 1 für Maschinenwesen
Prof. Dr. Peter Müller-Buschbaum, Seminar über Struktur und Dynamik kondensierter Materie
Prof. Dr. Peter Müller-Buschbaum, Prof. Dr. Christine Papadakis, Seminar über spezielle
Probleme der weichen Materie
Prof. Dr. Christine Papadakis, Experimentalphysik 1 für LB (EI/BT/MT)
PD Dr. Wolfgang Doster, Experimentalphysik 1 für LB
Prof. Dr. Walter Schirmacher, Field-theoretical methods in the theory of disordered solids

Lab courses 2007

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

8.2 Conferences

RLFB-Tagungsprogramm

31. Edgar-Lüscher-Physikseminar am Gymnasium Zwiesel

Thema: Geophysik und Katastrophen

Freitag, 23. März bis Sonntag, 25. März 2007

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

Wissenschaftliche Leitung: Prof. Dr. Walter Schirmacher, TU München, Prof. Dr. Donald Dingwell, Dr. Kai-Uwe Hess, Universität München

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

Freitag, 23. März 2007

15.30 – 16.00	Begrüßung, Organisatorisches	MB Drauschke, OStD Kratzer, OStR Haller
16.00 – 17.15	Einführung: Plattentektonik ,Vulkanis-	Dr. Birger Lühr,
	mus und Erdbeben	Geoforschungszentrum Potsdam
17.15 – 17.45	Diskussion und Kaffeepause	
17.45 – 19.00	Explosiver Vulkanismus	Prof. Dr. Donald Dingwell, Dr. Kai-Uwe Hess
		Universität München
19.00 – 19.15	Diskussion	

Samstag, 24. März 2007

9.00 - 10.15	Naturgefahr Tsunami	Dr. Birger Lühr,
		Geoforschungszentrum Potsdam
10.15 – 11.00	Diskussion und Kaffeepause	
11.00 – 12.15	Seismologische Überwachung	Dr. Joachim Wassermann
	aktiver Vulkane	Universität München
12.15 – 12.30	Diskussion	
15.00 – 16.15	Risiken durch Katastrophen	DiplGeophys. Ernst Rauch
		Münchner Rück
16.15 – 17.00	Diskussion und Kaffeepause	
17.00 – 18.15	Bergstürze in den Alpen	Prof. Dr. Ludwig Masch,
		Universität München
18.15 – 18.30	Diskussion	

Sonntag, 25. März 2007

9.00 - 10.15	Extremes Wetter	Dr. Gregor Leckebusch, FU Berlin
10.15 – 11.00	Diskussion und Kaffeepause	
11.00 – 12.15	Satellitenbeobachtung von Wald-	Dr. Eckehard Lorenz, DLR Berlin
	bränden	
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

EDGAR–LÜSCHER–LECTURES DILLINGEN/DONAU 2007 Thema: Biophysik

Datum: Mittwoch, 10. Oktober bis Freitag, 12. Oktober 2007 Tagungsort: Akademie für Lehrerfortbildung Dillingen Veranstalter: Akademie für Lehrerfortbildung Dillingen und TU München wissenschaftliche Leitung: Prof. Dr. W. Schirmacher und Prof. Dr. M. Rief, Technische Universität München.

PROGRAMM

Mittwoch, 10. 10. 2007	
15:30 - 17.00	Prof. Dr. M. Rief, TU München
	Einführung; Molekulare Maschinen
18.30 - 20.00	Dr. B. Nickel, Univ. München
	Die Physik der Zelle
Donnerstag, 11. 10. 2007	
8.30 - 10.00	Prof. A. Bausch, TU München
	Die Physik des Zytoskeletts
10.15 - 11.45	Dr. Peter Gilch, Univ. München
	Optische Femtosekundenpulse in der Biophysik
15.30 - 17.00	Prof. F. Parak. TU München
	Proteinstruktur und -dynamik
18:30 - 20.00	Prof. M. Stutzmann, TU München
	Bio-Elektronik
Freitag, 12. 10. 2007	
8.30 - 10.00	Dr. Thomas Franosch, Univ. München
	Molekularer Strassenverkehr
10.15 - 11.45	Dr. F. Simmel, Univ. München
	Nanotechnologie mit DNS

DPG Jahrestagung und DPG Frühjahrstagung des AKF

Regensburg, 26. - 30. März 2007

Symposium Bioinspired Materials (SYBM) Organisation: Prof. Dr. Eduard Arzt, MPI für Metallforschung Stuttgart, Prof. Dr. Peter Fratzl, MPI Potsdam, Prof. Dr. Peter Müller-Buschbaum, Technische Universität München,

Special Symposium "Bio-inspired Materials" in Regensburg / Germany at the 29th March 2007 in the framework of the spring meeting of the Division Condensed Matter of the Deutsche Physikalische Gesellschaft (DPG). The symposium is jointly held by the section Biological Physics (AKB) and by the divisions Chemical and Polymer Physics (CPP), Thin Films (DS), Dynamics and Statistical Physics (DY), Metal- and Material Physics (MM) and Surface Physics (O).

Nature provides a wide source of inspiration for chemists, physicists and engineers to create highly sophisticated functional materials. Many natural materials with complex, often hierarchical structure provide an unequalled level of adaptivity, multifunctionality, and mechanical performance. Biomimetic materials research provides a unique opportunity for physicists in a rapidly expanding field between the worlds of biology, physics and materials science. It starts by elucidating the physical origins of the outstanding functionality of biological materials, and aims at designing improved or even radically new materials based on the knowledge of natural systems. Bio-inspired materials will have an impact on various fields, from engineering to functional materials, as well as regenerative medicine. This symposium addresses students, experienced researchers and senior scientists working in the field of and exploiting the potentials of bio-inspired materials. Aim of the symposium is to present the state of the art in this class of materials, to highlight new experimental and theoretical developments and to allow for discussions among experts about latest trends and ideas. Invited talks will provide an overview of dedicated topics of bio-inspired materials. In special contributed lectures each topic will be deepened and illustrated by additional examples. A large poster session concludes the symposium.

The symposium language is English.

Invited speakers (confirmed):

A. P. Tomsia (Lawrence Berkeley National Laboratory, USA) Boaz Pokroy (Technion Israel Institute of Technology, Haifa, Israel) Ulrich Wiesner (Cornell University, Ithaca, USA) Ullrich Steiner (University of Cambridge, GB) Bharat Bhushan (Ohio State University, USA

Dates: 29th March 2007 Location: University Regensburg (Germany)

Additional info: http://regensburg07.dpg-tagungen.de/index.html?lang=en&

Symposium Bioinspired Materials (SYBM)

Overview

Symposium Bioinspired Materials (SYBM)

jointly organized by Section Metal and Materials Physics (MM), Section Biological Physics (BP), Section Chemical and Polymer Physics (CPP), Section Thin Layers (DS), and Section Dynamics and Statistical Physics (DY)

Eduard Arzt Max-Planck-Institut für Metallforschung Heisenbergstr. 3 70569 Stuttgart arzt@mf.mpg.de Peter Müller-Buschbaum Technische Universität München Physik Department E13 85747 Garching muellerb@ph.tum.de Peter Fratzl Department für Biomaterialien MPI für Kolloid und Grenzflächenforschung Am Mühlenberg 14476 Potsdam peter.fratzl@mpikg-golm.mpg.de

Nature provides a wide source of inspiration for chemists, physicists and engineers to create highly sophisticated functional materials. Many natural materials with complex, often hierarchical structure provide an unequalled level of adaptivity, multifunctionality, and mechanical performance. Biomimetic materials research provides a unique opportunity for physicists in a rapidly expanding field between the worlds of biology, physics and materials science. It starts by elucidating the physical origins of the outstanding functionality of biological materials, and aims at designing improved or even radically new materials based on the knowledge of natural systems. Bioinspired materials will have an impact on various fields, from engineering to functional materials, as well as regenerative medicine.

Overview of Invited Talks and Sessions

(lecture room H1)

Invited Talks

SYBM 1.1	Thu	9:30 - 10:00	H1	Using Ice to Mimic Nacre: From Structural Materials to Artificial Bone
				$-\bullet$ A. P. Tomsia, S. Deville, E. Saiz
SYBM 1.2	Thu	10:00-10:30	H1	On the structure of biogenic $CaCO_3 - \bullet B$. POKROY
SYBM 1.3	Thu	10:30-11:00	H1	Bio-Inspired Hybrid Materials from Block Copolymer Assemblies and
				Nanoparticle Co-assemblies — \bullet U. WIESNER
SYBM 1.4	Thu	11:15-11:45	H1	Bio-Inspired Organic-inorganic Hybrid Materials — •U. STEINER
SYBM 1.5	Thu	11:45 - 12:15	H1	Structural, Nanomechanical, and Nanotribological Characterization of
				Human Hair Using Atomic Force Microscopy and Nanoindentation $-$
				•Bharat Bhushan

Sessions

SYBM 1.1–1.5 Thu 9:30–12:15 H1 Symposium Bioinspired Materials

Continuation with contributed tallks in FV MM, session MM35, lecture hall H16 on Thursday 14:45-19:00. Poster session from 19:00 in front of lecture hall H16.

Symposium Bioinspired Materials (SYBM)

SYBM 1: Symposium Bioinspired Materials

Time: Thursday 9:30-12:15

Invited Talk

SYBM 1.1 Thu 9:30 H1 Using Ice to Mimic Nacre: From Structural Materials to Artificial Bone — • A. P. TOMSIA, S. DEVILLE, and E. SAIZ -- Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Despite extensive efforts in the development of fabrication methods to prepare porous ceramic scaffolds for osseous tissue regeneration, all porous materials have a fundamental limitation - the inherent lack of strength associated with porosity. Shells (nacre), tooth and bone are frequently used as examples for how nature achieves strong and tough materials made out of weak components. So, the unresolved engineering dilemma is how to create a scaffold that is both porous and strong. The objective of this study was to mimic the architecture of natural materials in order to create a new generation of strong hydroxyapatitebased porous scaffolds. The porous inorganic scaffolds were fabricated by the controlled freezing of water-based hydroxyapatite (HA) slurries. The scaffolds obtained by this process have an ordered and homogeneous lamellar architecture that exhibits striking similarities with the meso- and micro- structure of the inorganic component of nacre. Compressive strengths of 20 to 60 MPa were measured for lamellar scaffolds with densities of 32 to 45%, significantly better than for the HA with random porosity. In addition, the lamellar materials exhibit gradual fracture unlike conventional porous HA scaffolds. These biomimetic scaffolds could be the basis for a new generation of porous and composite biomaterials.

Support is provided by the National Institute of Health under grant number NIH/NIDCR 1R01 DE11289 and 1 R01 DE015633-01

Invited Talk SYBM 1.2 Thu 10:00 H1 On the structure of biogenic $CaCO_3 - \bullet B$. POKROY — Department of Materials Engineering, Technion Israel Institute of Technology, Technion City, Haifa 32000 (Israel)

Organisms produce a large number of minerals in the course of biomineralization. These biogenic minerals have been extensively studied because of their fascinating mechanical, optical and magnetic characteristics and their capability to effectively control the polymorph selection and crystal morphology. Calcium carbonate, $\mathrm{CaCO}_3,$ is by far the most abundant biogenic mineral and it exists in different structural forms (listed in the order of descending thermodynamic stability at normal conditions): calcite, aragonite, vaterite and amorphous calcium carbonate.

By performing accurate structural measurements by high-resolution x-ray powder diffraction on a synchrotron beam line the unit cell parameters of biogenic $CaCO_3$ crystals were found to be slightly distorted as compared to that of their geological counterparts. Moreover, neutron diffraction revealed that the atomic bonds of these biogenic crystals are also distorted.

I will show that these structural distinctions are caused by intracrystalline organic molecules.

Theses results imply that organisms can control biogenic crystals on the nm scale.

SYBM 1.3 Thu 10:30 H1 Invited Talk Bio-Inspired Hybrid Materials from Block Copolymer Assemblies and Nanoparticle Co-assemblies — •U. WIESNER Department of Materials Science & Engineering, Cornell University, Ithaca, NY 14853-1501, USA

The study of bio-inspired block copolymer based self-assembly (bottom-up) approaches to multifunctional polymer-inorganic hybrid materials is an exciting emerging research area interfacing solid state and soft materials and offering enormous scientific and technological promise. By choice of the appropriate synthetic polymer blocks as well as nanoparticles unprecedented morphology control down to the nanoscale is obtained. Tailoring of the polymer-inorganic interface is of key importance. The structures generated on the nanoscale are a result of a fine balance of competing interactions, a typical feature of complex biological systems. The potential for new multifunctional materials lies in the versatility of the polymer chemistry as well as that of the inorganic chemistry that can be exploited in the materials synthesis. In the present contribution the synthesis and characterization of nanostructued hybrid materials will be presented with potential applications ranging from microelectronics to nanobiotechnology. In all cases cooperative self-assembly of organic and inorganic species is induced by amphiphilic macromolecules, either block copolymers or extended amphiphilic dendrons, which are blocked species with one block being highly branched. Besides amorphous and crystalline oxide materials novel systems toward high temperature SiCN and SiC structures are introduced.

15 min break

SYBM 1.4 Thu 11:15 H1 Invited Talk Bio-Inspired Organic-inorganic Hybrid Materials University of Cambridge, Department of Physics, STEINER Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE (UK) Pattern formation in physics and chemistry is a consequence of nonlinear processes, which are of fundamental interest. Recently, pattern formation by self-assembly or by instabilities in liquids were also employed in soft-lithographic methods. Patterns occurring in living organisms, on the other hand are formed under stick biological control and serve a specific purpose for the organism. Since the relationship between the pattern and its function was optimised by evolution, patterns occurring in nature are an interesting repository for physical effects that can be achieved by controlling physico-chemical pattern formation processes

My presentation will discuss three examples of this biomimetic approach: (i) optical effects in structured films (anti-reflection and structural colours), (ii) structured super-hydrophobic surfaces, and (iii) structured bio-mimetic minerals.

SYBM 1.5 Thu 11:45 H1 Invited Talk Structural, Nanomechanical, and Nanotribological Characterization of Human Hair Using Atomic Force Microscopy and Nanoindentation - •BHARAT BHUSHAN - The Ohio State University, Columbus, Ohio 43210 USA

Maintaining the health, feel, shine, color, softness, and overall aesthet-ics of the hair is highly desired. Hair care products such as shampoos and conditioners, along with damaging processes such as chemical dyeing and permanent wave treatments, affect the maintenance and grooming process and are important to study because they alter many hair properties. Nanoscale characterization of the cellular structure, mechanical properties, and morphological, frictional, and adhesive properties of hair are essential to evaluate and develop better cosmetic products, and to advance the understanding of biological and cosmetic science. Another property of interest is surface charge of hair which has a significant effect on manageability, feel, and appearance. Controlling charge buildup to improve these factors is an important issue in the commercial hair care industry. The atomic/friction force microscope (AFM/FFM) and nanoindenter have recently become important tools for studying the micro/nanoscale properties of human hair. In this talk, we present a comprehensive review of structural, mechanical, and tribological properties of various hair and skin as a function of ethnicity, damage, conditioning treatment, and various environments.

Thursday

Location: H1

MM 35: SYBM Bioinspired Materials

Time: Thursday 14:45-20:45

Location: H16

MM 35.1 Thu 14:45 H16

Reflection of water jets on biological and bio-inspired artificial surfaces — \bullet Michael Scharnberg¹, VLADIMIR ZAPOROJTCHENKO¹, RAINER ADELUNG¹, SRDAN MILENKOVIC², and ACHIM WALTER HASSEL² — ¹Chair for Multicomponent Materials, Technical Faculty, University of Kiel, Germany — ²Electrochemistry and Corrosion, Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Water jets impinging on a nasturtium leaf, a biological ultrahydrophobic surface (lotus effect), were observed to flow across the surface for a distance in the order of several jet diameters before it is reflected off the surface as a coherent jet under an angle that is close to or smaller than the angle of incidence. Design and technical applications of ultrahydrophobic surface require understanding of the physical processes involved, however biological surfaces often have defects and irregularities like leaf veins that impede experiments. A ds-NiAl-W alloy, microstructured by etching and coated with a sputtered polytetrafluoroethylene (PTFE) thin film is also ultrahydrophobic (contact angle $> 160^{\circ}$). Due to the regular microstructure of its surface that can also be easily varied by controlling the needle length, this ultrahydrophobic material system is well suited for investigation of the water jet reflection phenomenon. In this presentation the influence of the microstructure, the water pressure and the angle of incidence will be discussed.

MM 35.2 Thu 15:00 H16

Enhancement of capillary forces by multiple liquid bridges — •EMERSON JOSE DE SOUZA¹, CAMILLA MOHRDIECK², MARTIN BRINKMANN³, and EDUARD ARZT⁴ — ¹Max Planck Institute for Metals Research, Heisenbergstr, 3, Stuttgart, Germany — ²Institute of Physical Metallurgy, Universitä Stuttgart, Stuttgart, Germany — ³Max Planck Institute for Dynamics and Self-Organisation, Göttingen, Germany — ⁴Max Planck Institute for Metals Research, Heisenbergstr, 3, Stuttgart, Germany

Capillary forces can significantly increase the adhesion of micro-scale objects in biology and technology. We calculate numerically the force exerted by a liquid meniscus between two homogeneous flat plates for different contact angles. The resulting force distance curves show good quantitative agreement with previous investigations. On this basis, we set an initial separation and split the volume of one bridge into n smaller ones. The results for the total force as a function of n show a novel and unexpected maximum force for moderately hydrophilic surfaces (i.e. contact angles around 70 degrees). Further, we calculate the minimum area for multiple bridges, the stress (i.e. force per area) and the work required to separate the plates. The results are presented in two dimensional maps, which may be very useful in the understanding and design of biological and artificial contact systems.

MM 35.3 Thu 15:15 H16

Bacterial S-layers used as bio-templates for the regular arrangement of nanoparticles — •UTE QUEITSCH¹, ELIAS MOHN¹, FRANZISKA SCHÄFFEL¹, LUDWIG SCHULTZ¹, BERND RELLINGHAUS¹, ANJA BLÜHER², and MICHAEL MERTIG² — ¹IFW Dresden, P.O. Box 270116, D-01171 Dresden, Germany — ²Max Bergmann Center for Materials Research, TU Dresden, D-01069 Dresden, Germany

Owing to the statistical nature of the deposition process nanoparticles from the gas phase are usually randomly distributed on the substrate. For many applications however, a regular arrangement of the particles is mandatory. We have therefore investigated to which degree the use of so-called S-layers – regular protein crystals with different 2-dimensional lattice symmetries – allows to compensate for this disadvantage. S-layers of bacillus sphaericus NCTC 9602 with p4 symmetry and a square lattice of pores with a lattice constant of 12.5 nm are used as bio-templates for the deposition of gas-phase prepared FePt nanoparticles. Sheets of these S-layers were deposited onto amorphous carbon films, which were then exposed to a beam of FePt nanoparticles under high vacuum conditions. Structural characterization of likewise prepared particle films is carried out by transmission electron microscopy (TEM). We find that the structure of the S-layers remains unaltered upon particle deposition. Furthermore, a symmetry transfer from the bio-template to the arrangement of the deposited particles is clearly observed. Statistical analysis of the TEM micrographs reveals that the majority of the particles are located within or in the close vicinity of the pores of the bio-template.

 $\begin{array}{ccc} MM \ 35.4 & Thu \ 15:30 & H16 \\ \hline \\ \mbox{Inversion of micro-patterned polymer surfaces based on bi$ $component polyelectrolyte layers — <math>\bullet$ ALLA SYNYTSKA¹, MAN-FRED STAMM¹, STEFAN DIEZ², and LEONID IONOV² — ¹Leibniz Institute of Polymer Research Dresden, 01009 Dresden, Hohe Strasse 6, Germany — ²Max-Planck-Institute of Molecular Cell Biology and Genetics, Pfotenhauerstrasse 108, 01307 Dresden, Germany

Micropatterned surfaces are of considerable importance for microelectronics, printing technology, microfluidic and microanalitical devices, information storage, biosensors, etc. However, once a pattern is generated it cannot be easily changed on the fly. Therefore, it is desirable to develop methods for fabrication of structured surfaces with switchable and rewritable patterns.

In the present study, we report on the fabrication of micropatterned surfaces which allow the switching of topography, wettability, and charge in an inverse manner. The concept of these stimuli-responsive surfaces, which are made by a combination of photolithography, liftoff and grafting to techniques, is based on the site-selective grafting of two oppositely charged polyelectrolytes. Depending on the pH of the surrounding one kind of the polymer chains is swollen (charged and hydrophilic) while the other is collapsed (uncharged and hydrophobic). The main advantage of such surfaces is their capability of inverse switching, for example hydrophilic patterns can be reversibly converted into hydrophobic ones and vice versa, via external stimuli.

15 min break

MM 35.5 Thu 16:00 H16

Structure and dynamics of biological materials — •MARTIN MÜLLER — Institut für Experimentelle und Angewandte Physik, Christian–Albrechts–Universität zu Kiel

Almost all biological materials are hierarchically structured on many different length scales. On a mesoscopic level, usually a composite morphology with nanocrystalline regions embedded in a softer, disordered matrix is found. The matrix is accessible to water, and the water content is of major influence on the mechanical properties of biomaterials.

We investigate structural changes of biomaterials (cellulose fibres, wood and particularly silkworm silk) under mechanical load in *in situ* X–ray scattering experiments with microbeam synchrotron radiation. A novel sample environment allows us to systematically vary the water content of the samples. The soft, water–accessible matrix plays an important role in the microscopic model we obtain for deformation mechanisms in dry and wet biomaterials [1].

The combination of the X-ray results with those from the complementary technique of inelastic neutron scattering allowed us to develop a deeper understanding of the interplay of crystalline and disordered regions in silkworm silk [2].

[1] I. Grotkopp, PhD thesis, Kiel, 2006.

[2] T. Seydel, K. Kölln, I. Krasnov, I. Diddens, N. Hauptmann, G. Helms, M. Ogurreck, S.-G. Kang, M. M. Koza, M. Müller, Macro-molecules, in press.

MM 35.6 Thu 16:15 H16

The actuation of organ movement by the generation of tensile and compressive stresses in wood cell walls — •INGO BURGERT, MICHAELA EDER, NOTBURGA GIERLINGER, and PETER FRATZL — Max Planck Institute of Colloids and Interfaces, Department of Biomaterials, 14424 Potsdam, Germany

Active movement is usually associated with animals rather than plants. Plants do not have muscles, but they are able to pre-stress their tissues in order to actuate their organs. Here, we demonstrate for softwoods that either tensile or compressive stresses can be obtained during swelling of the cell wall. This can be well understood by simple mechanical considerations, taking into account the cell shapes and the observed cellulose fibril orientations. The almost inextensible cellulose fibrils redirect the forces generated by the swelling of the matrix by purely geometrical constraints to produce tension or compression

125

forces according to needs. This principle could be simple enough to be reproduced in artificial systems and one may consider developing fiberreinforced hydrogels as effective microactuators. The main technical challenge would be to reproduce the well controlled fiber orientation found in wood cells.

MM 35.7 Thu 16:30 H16 Bamboo: Mechanical Optimisation and Efficiency — •ULRIKE G.K. WEGST¹ and MICHAEL F. ASHBY² — ¹Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany — ²Cambridge University Engineering Department, Trumpington Street, Cambridge CB2 1PZ, UK

An optimised structure is one which uses the smallest quantity of the best material to perform its function, with adequate safety factor. Structural optimisation occurs not only in mechanical engineering, but also in nature: plants whose stems or stalks approach the optimum shape gain efficiency and a height advantage. Bamboo does this exceptionally. It provides the most efficient material for mechanical performance at minimum mass, supporting large loads due to self-weight and external forces. Bamboo achieves its efficiency in three ways: (i) by using efficient materials such as composites, (ii) by grading the structure, (iii) by shaping the component to form a tube. Investigated here is the material aspect of the structural optimisation of the orthotropic bamboo tube and the role which the microstructure plays in its mechanical performance. Concentrating on the elastic bending behaviour, the stiffness, strength and failure modes of bamboo are reviewed and algorithms and diagrams are proposed which allow the optimum property gradient and section shape to be selected. Man-made materials which exploit all three of bamboo's strategies for mechanical efficiency seem to be very rare. Given the ultimate structural efficiency that this combination allows, developing them in wood-based and other composites, for example, would appear to be worth serious consideration

MM 35.8 Thu 16:45 H16

Hierarchical ceramics from biomimetic processing of wood — •OSKAR PARIS, ATUL DESHPANDE, and INGO BURGERT — Max Planck Institute of Colloids and Interfaces, Department of Biomaterials, Potsdam, Germany

The processing of plant tissues has been used since hundreds of years to obtain useful materials such as paper and activated carbons. The rich structural hierarchy of plant tissues makes them ideal as scaffolds or casting moulds for the synthesis of hierarchically structured inorganic materials based on carbon or ceramics. Besides potential applications as lightweight nanocomposites for structural applications, such materials are typically porous at several length scales, making them interesting candidates for catalysts and filters. A major challenge in the synthesis process of such materials is to preserve the hierarchical plant structure at all levels while retaining the mechanical integrity. We have used wood tissue as a casting mould for the synthesis of hierarchical mesoporous oxide ceramics with directional porosity on the micrometer and the nanometre scale. In particular, we could demonstrate that the entire structure of the wood tissue including the spiralling microfibrillar orientation of the cellulose fibrils can be transformed into a mesoporous Ce0.5Zr0.5O2 ceramic [1]

[1] A. Deshpande, I. Burgert, O. Paris, Small 2 (2006) 994.

$15 { m min \ break}$

MM 35.9 Thu 17:15 H16

TiO2 nanotubes: a bio-inspired and bio-inspiring Material — •SEBASTIAN BAUER¹, JUNG PARK², KLAUS VON DER MARK², EU-GENIU BALAUR¹, and PATRIK SCHMUKI¹ — ¹Department of Materials Science, Friedrich-Alexander-University, Martensstr. 7, 91058 Erlangen. — ²Department of Experimental Medicine I, Friedrich-Alexander-University, Glückstr. 6, 91054 Erlangen.

Self-organized porous structures have had a high impact in surface science due to the simplicity of fabricating nanostructured surfaces. Particularly highly ordered porous Al and Si have attracted significant scientific interest due to the potential applications in different fields. These structures can be achieved essentially by simple anodization under optimized electrochemical conditions. For Titanium we recently reported the preparation of self-organized nanotubular TiO2 layers on titanium surfaces by anodization in various electrolytes containing fluorides. We showed that tailoring the diameter of the formed nanotubes in a wide range (15 - 100 nm) can be achieved by varying the applied potential of the electrochemical setup. The resulting different nanoscale surfaces can be used to evaluate size effects on biorelevant reactions. We will discuss the wetting behavior of these nanoporous surfaces and show that it can be tailored from super-hydrophilic to super-hydrophobic by variation of tube diameter and by light interactions. Furthermore as titanium and its alloys are mainly used as implant materials it is also of interest to see how tissue reacts to the different nanoscales. To evaluate the influence of tube size, tests with rat mesenchymal stem cells were carried out and will be reported.

 $\label{eq:main_matrix} MM 35.10 \ \mbox{Thu 17:30 } H16 \\ \mbox{Material and structural dynamics in trabecular bone} $-$ e. WEINKAMER^1, D. RUFFON1^1, J. DUNLOP^1, M. HARTMANN^2, Y. BRECHET³, P. ROSCHGER⁴, K. KLAUSHOFER⁴, and P. FRATZL¹ - ^1 Max Planck Institute of Colloids and Interfaces, Potsdam, Germany - ^2 C.E.A./Saclay, Gif-sur-Yvette, France - ^3 LTPCM, ENSEEG, Grenoble, France - ^4 Ludwig Boltzmann Institute of Osteology, Vienna, Austria$

In trabecular bone different hierarchical levels contribute to its mechanical performance. In our simulation work we focus on the level of the foam-like architecture and on the inhomogeneity of the material bone itself. Two different processes are responsible for the ongoing changes on the structural and material level: the remodeling where small bone packets are continuously resorbed and deposited and the mineralization process where the mineral content increases in a newly deposited bone packet. The renewal of bone material is mechanically controlled, that is bone is deposited preferentially at mechanically highly loaded sites. Since the details of this control are unknown. a computer model with different realizations of the mechanical feedback loop has been employed, to study their influence on architecture and time evolution. With a separate model, the heterogeneous mineral content of bone at the material level was investigated. An increase in the mineral content results in a stiffer, but also more brittle material. Predictions are presented of the evolution of the frequency distribution of mineral content in situations of increased remodeling like in osteoporosis or in therapies which aim at reducing the remodeling.

MM 35.11 Thu 17:45 H16

Influence of structural principles on the mechanics and efficiency of different biological materials using lobster cuticle as a model material — •CHRISTOPH SACHS, HELGE FABRITIUS, SVETOSLAV NIKOLOV, and DIERK RAABE — Max-Planck-Institut für Eisenforschung, 40237 Düsseldorf, Germany

The cuticle of the lobster Homarus americanus is a nano-composite material consisting of a matrix of chitin-protein fibers associated with various amounts of crystalline and amorphous calcium carbonate and is organized hierarchically on all length scales. The chitin protein fibers are arranged in horizontal planes where the long axes of the fibers are all oriented in the same direction. These planes are stacked with the orientation of the fibers in superimposed layers rotating gradually around the normal axis of the cuticle, thus creating a typical twisted plywood structure. Additionally, the fibers are arranged around the cavities originating from the extremely well developed pore canal system of the lobster which gives the structure a honeycomb-like appearance. Tensile, compression and shear tests performed on both cuticle in its natural hydrated and in the dry state show that both structural principles, twisted plywood and honeycomb, are reflected in the obtained mechanical data of the material. The comparison of hard mineralized cuticle and unmineralized joint membranes shows the influence of the incorporation of minerals on the performance of the material, which is optimized for the role the material has to play in the living organism. The obtained mechanical properties are used to deduce general analytical models describing the mechanics of different biological materials.

MM 35.12 Thu 18:00 H16 Recombinantly produced Spider Silk in a Microfluidic Device — •SEBASTIAN RAMMENSEE¹, UTE SLOTTA², DAVID KEERL², THOMAS SCHEIBEL², and ANDREAS BAUSCH¹ — ¹Technische Universität München, Physik-Department E22-Biophysik, James-Franck-Strasse 1, 85747 Garching — ²Technische Universität München, Department Chemie, Lichtenbergstrasse 4, 85747 Garching

Spider Silks are protein materials which show mechanical properties being superior to all man-made materials in regard to toughness and elasticity. However, commercial applications of natural spider silk are complicated by the highly cannibalistic and territorial behavior of spiders. This problem can be circumvented by recombinant production of spider silk analogous proteins in bacteria. In vivo, the highly complex

spinning process is performed in a specialized organ, being a topic of current research. We study the process of silk fiber formation in microfluidic devices under laminar flow conditions, where mixing occurs only by diffusion. As we have a whole set of recombinantly produced spider silk analogous proteins available for experiments, the influence of different structural features of the proteins on fiber formation can be studied. We present secondary structure information obtained by infrared spectroscopy and Scanning Electron Microscopy images of the produced silk assemblies. We model the elongational flow in the microfluidic channel by Finite Element Simulations, and thus correlate the structure and mechanical properties of the resulting silk structures with the conditions in the spinning channel.

MM 35.13 Thu 18:15 H16

Tension and geometry determine cell and tissue shape — ILKA BISCHOFS¹, DIRK LEHNERT², FRANZISKA KLEIN², MARTIN BASTMEYER², and •ULRICH SCHWARZ³ — ¹University of California at Berkeley, Department of Bioengineering, 717 Potter Street, Berkeley CA 94720, USA — ²University of Karlsruhe, Institute of Zoology I, Haid-und-Neu-Strasse 9, D-76131 Karlsruhe, Germany — ³University of Heidelberg, Im Neuenheimer Feld 293, D-69120 Heidelberg, Germany

Cells adapt their shape in response to the biochemical and physical properties of their environment. Cell shape in turn can determine cell growth and fate. In order to study cell shape as a function of spatially separated ligand patches, we have cultured cells on a square arrangement of fibronectin dots with a large variety of different dots sizes and lattice constants. We found that in any case, cell shape resembles a sequence of circular arcs composed of actin fibers connecting neighboring sites of adhesion. The same morphology has been observed before on the tissue level, namely for fibroblast-populated collagen gels pinned to a flat substrate. Quantitative image analysis revealed that in both cases, a characteristic relation exists between spanning distance and arc radius which can be explained by a mechanical model which includes the effect of both tension and elasticity. Our results suggest that the same universal principles determine the shape of cells and tissues.

MM 35.14 Thu 18:30 H16

The cytoskeleton as an example of a highly adaptive structure — FLORENT DALMAS^{1,2} and •CAMILLA MOHRDIECK^{1,3} — ¹Max Planck Institute for Metals Research, Stuttgart, Germany — ²Present Address: Laboratoire de Recherche sur les Polymères, CNRS - UMR 7581, 94320 Thiais, France — ³Inst. for Physical Metallurgy, University of Stuttgart, Germany

The internal polymer network of eukaryotic cells, the cytoskeleton, is a very interesting example of a smart structure that integrates sensors, actuators and control systems to perform many vital cellular functions. It is able to adapt and respond to a large variety of intra and extracellular stimuli efficiently and often also interactively. This agility is largely due to a variety of molecules that bind to cytoskeletal fibers to execute certain functions, e.g. crosslinking the fibers. To mimic the adaptiveness of the cytoskeleton in engineered structures, it is necessary to identify the components that act as sensors or actuators and how they interplay.

To address this complex issue, we have focused on the effect of crosslinking on the mechanical stability and the adaptiveness of the cytoskeleton. In a new modeling approach, we describe the cytoskeletal fibers and the molecules that crosslink them into a three dimensional network as homogeneous straight beams in a constant volume. The response to a mechanical stimulus is simulated by subjecting the network to a homogeneous shear stress and calculating its shear modulus. New scaling behaviors of the shear modulus are found and analysed. They indicate general design principles of adaptive networks.

MM 35.15 Thu 18:45 H16

Biomimetic mineralization: the effect of polystyrenesulfonate on the growth of calcite crystals — •BARBARA AICHMAYER, HEL-MUT CÖLFEN, OSKAR PARIS, and PETER FRATZL — Max Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany

Macromolecules are of crucial importance for the control of size, shape and arrangement of mineral crystals in biological tissues. Pokroy et al. [1] recently showed that organic molecules in biogenic calcite even induce remarkable lattice distortions. Inspired by the concept of biomineralization, we use a soluble polymeric additive to modify the growth of calcite, which is crystallized from calcium chloride solutions using the CO2 vapor diffusion technique. Polystyrenesulfonate (PSS) was previously shown to have a pronounced effect on the morphology of calcite particles, which were found to be composed of ordered nanocrystalline substructures. According to thermogravimetric analysis, the particles contained a significant amount of polymer (3wt%). [2] By complementing these results and electron microscopy studies with X-ray scattering we aim to get a more detailed picture of the structure of the calcite-PSS particles. Using a microfocus beam (micro-focus beamline at BESSY, Berlin and ID13 at ESRF, Grenoble) enables us to study the wide- and small-angle X-ray scattering behavior of single particles. Our findings on lattice spacings, texture and internal structure of the calcite mesocrystals contribute to a better understanding of biological and biomimetic mineralization.

1 B. Pokroy, A.N. Fitch, E. Zolotoyabko, Adv. Mater. 2006, 18, 2363.

2 T. Wang, M. Antonietti, H. Cölfen, Chem. Eur. J. 2006, 12, 5722.

MM 35.16 Thu 18:45 H16

Diatoms - the source of biotribological inspiration for novel 3D MEMS — ILLE C. GEBESHUBER¹ and •RICHARD M. CRAWFORD² — ¹Institut für Allgemeine Physik, Technische Universität Wien, Wiedner Hauptstrasse 8-10/134, 1040 Wien, Austria & Austrian Center of Competence for Tribology, Viktor Kaplan-Strasse 2, 2700 Wiener Neustadt, Austria — ²Alfred-Wegener Institute for Polar and Marine Research, Bremerhaven, Germany

Diatoms are single-celled organisms with rigid parts in relative motion at the micrometre scale and below. They produce interlocked hydrated silica structures with high precision. These micromechanical parts have been evolutionarily optimized during the last 150 million years or more. It is suggested that MEMS/NEMS researchers meet with diatomists to discuss future common research attempts regarding biomimetic ideas and approaches for novel and/or improved MEMS and NEMS with optimized tribological properties [1,2].

 Gebeshuber I.C. and Crawford R.M. (2006) Micromechanics in biogenic hydrated silica - hinges and interlocking devices in diatoms, Proc. IMechE Part J: J. Eng. Tribol. 220(8), 787-796

[2] Gebeshuber I.C., Stachelberger H. and Drack M. (2005) Diatom bionanotribology - Biological surfaces in relative motion: their design, friction, adhesion, lubrication and wear, J. Nanosci. Nanotechnol. 5(1), 79-87

MM 35.17 Thu 18:45 H16 Investigation of the Orientation Relationship Between α -Chitin and Calcite in Crustacean Cuticle Using Synchrotron x-ray Diffraction — •ALI AL-SAWALMH¹, HELGE FABRITUS¹, SANG-BONG YI², and DIERK RAABE¹ — ¹Max-Planck-Institut f. Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf. — ²Institut für Werkstoffkunde und Werkstofftechnik, Technische Universität Clausthal, 38678 Clausthal-Zellerfeld.

Crustace an cuticle contains α -chitin-protein organic fibers associated with crystallites of calcite and considerable amounts of amorphous calcium carbonate (ACC). In this study, x-ray pole figure analysis was performed to investigate the crystallographic texture (preferred orientation) of the crystalline calcite and α -chitin, with respect to their orientation relationship, in edible crab ${\it Cancer\ pagurus}$ and american lobster Homarus americanus cuticles using synchrotron wide-angle xray diffraction (XRD). It was observed that the *c*-axis of the calcite and the *b*-axis of the α -chitin are firstly preferentially aligned parallel to each other and secondly oriented along the surface normal. The other axes of the α -chit in and calcite are co-aligned with respect to each other throughout the cuticle plane. The synchrotron x-ray crystallographic texture results gave for the first time a statistical description of the orientation relationship between the organic and inorganic components in arthropod cuticle. This result strongly suggests that the fibrous structure of α -chitin assists the growth of calcite crystals in crustacean cuticle, by functioning directly or indirectly as a template for nucleation and subsequent growth of calcite.

MM 35.18 Thu 18:45 H16

Evaluation of different constitutive models for the mechanical behavior of bone at submicron scale — •SVETOSLAV NIKOLOV, HELGE FABRITIUS, CHRISTOPH SACHS, and DIERK RAABE — Max-Planck-Institut für Eisenforchung, 40237 Düsseldorf, Germany

Hard biological tissues, such as vertebrate bone, show a complex hierarchical structure at all length scales. The basic structural unit of bone is a fibrous collagen matrix containing small hydroxyapatite crystals in the form of platelets. Here we focus on the constitutive modeling of a bundle of these mineralized collagen fibrils in order to predict their me-

chanical response. The material is modeled via a two-step homogenization procedure * a first homogenization step at the level of one single mineralized fibril, and a second one at the level of a fibril bundle embedded in an extrafibrillar matrix. We compare different combinations of homogenization models, such as shear-lag models, self-consistent estimates, Mori-Tanaka and double-inclusion homogenization schemes, in order to elucidate which two-step homogenization scheme better reproduce the mechanical data available from experiments. We additionally perform a parametric study on the microstructure parameters, such as the aspect ratio and the volume fraction of collagen fibrils and apatite platelets, the Young*s modulus of the constituents and their density in order to extract some structural optimization principles involved in the natural formation of hard tissues.

MM 35.19 Thu 18:45 H16

Grazing-incidence X-ray scattering investigation on the structure of thin films of recombinant spider silk proteins — •E. METWALLI¹, U. SLOTTA², C. DARKO¹, S. ROTH³, T. SCHEIBEL², and C. PAPADAKIS¹ — ¹Physikdepartment E13, TU München, 85747 Garching — ²Chemiedepartment, TU München — ³HASYLAB at DESY, Hamburg

Protein immobilization on solid supports is important for many potential applications such as protein microarrays. Recombinant spider silk proteins offer the possibility to control the molecular sequence and thus the material properties [1]. Spin-coating was used to prepare films of synthetic spider silk protein derived from the garden spider's (Araneus diadematus) dragline silk protein ADF-4. A transition from alfa-helix to beta-sheet rich structures upon methanol treatment of the films has been detected by IR and circular dichroism spectroscopies [2]. We present here direct evidence for this structural transformation. We have observed crystalline domains within the films after treatment and could determine their size and shape using grazing-incidence Xray diffraction (GIXD) and small-angle scattering (GISAXS). GIXD showed Bragg peaks from beta-sheet poly-alanine crystallites having a size of 8 nm. GISAXS confirmed the presence of crystallites of this size. We conclude that the protein film structure after the methanol treatment consists mainly of crystalline beta-sheet rich regions embedded in an amorphous matrix. [1] Scheibel T., Current Opinion in Biotechnology 16, 427 (2005). [2] Hummerich D., Slotta U., and Scheibel T., Applied Phys. A-Materials Sci. & Processing 82, 219 (2006).

MM 35.20 Thu 18:45 H16

Structural adaptation in trabecular bone — •JOHN DUNLOP¹, MARKUS HARTMANN², YVES BRÉCHET³, PETER FRATZL¹, and WEINKAMER RICHARD¹ — ¹Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Research Campus Golm, 14424, Potsdam, Germany — ²Service de Chimie Moléculaire, C.E.A./Saclay, Bat. 125, 91191 Gif-sur-Yvette cedex, France — ³Groupe Physique du Métal, LTPCM/ENSEEG INPG, Domaine Universitaire de Grenoble, 38402 Saint Martin d'Hères, France

The structure of trabecular bone results from the complex interaction between bone producing cells (osteoblast), bone absorbing cells (osteoclasts) and signalling cells (osteocytes), and the performance of the bone matrix itself. One of the important factors that regulates the trabecular architecture is mechanical loading. This can be generalised by the Wolff-Roux law: that is, bone in general is deposited where it is mechanically needed and removed where it is not. Changes in mechanical loading are clearly seen to affect cellular activity and also to modify the resultant bone architecture. The precise details of how cells "feel" a stimulus and exactly how they respond are not known, although there are many suggestions that have been proposed. Computer simulation techniques are ideally suited to testing these theories. In this contribution a 3D lattice model of trabecular bone is presented and used to investigate the link between individual cell response and trabecular architecture through both the "remodelling" and "stimulus" rules.

MM 35.21 Thu 18:45 H16

Creation and Surface-Functionalization of Microcapsules of Recombinant Spider-Silk Protein — •MARRUS HARASIM¹, TERESA BAUER¹, KEVIN HERMANSON¹, SEBASTIAN RAMMENSE¹, THOMAS SCHEIBEL², and ANDEAS BAUSCH¹ — ¹Physik Department, E22-Biophysik, Technische Universität München, James-Franck-Str.1, 85747 Garching — ²Department Chemie, Lehrstuhl für Biotechnologie, Technische Universität München, Lichtenbergstr. 4, 85747 Garching Micron-size sculpted structures are important for encapsulation and functionalization technologies and as building blocks for larger de vices. Here, spherical capsules are created through the self-assembly of recombinant spider-silk at liquid interfaces and in solution. Due to the natural properties of the spider silk the capsules are mechanically strong and biocompatible. These capsules can be formed either in bulk or through microfabrication using microfluidic devices, which allow for the direct control of capsule size and shell thickness. Functionalization of the capsules can also be achieved using common biochemical techniques. Because of the silk's unique properties, this technique potentially offers a convenient approach to the formation of biologicallycompatible, easily-functionalizable structures.

MM 35.22 Thu 18:45 H16 Effect of calcium concentration on the structure of casein micelles in thin films — •RONALD GEBHARDT¹, ALI EZZELDIN METWALLI², STEPHAN VOLKHER ROTH³, WOLFGANG DOSTER², and PETER MÜLLER-BUSCHBAUM² — ¹European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France — ²TU München, Physik Department LS E13, James-Franck-Str.1, 85748 Garching (Germany) — ³HASYLAB at DESY, Notkestr. 85, 22603 Hamburg (Germany)

Case ins are organized in poly-disperse, roughly spherical aggregates with diameters ranging between 150 and 300 nm. They represent with about 80% the largest protein component in milk. The case in micelle of bovine milk consists of four different phosphor-proteins which can be divided into two groups: the calcium insensitive κ -case in and the calcium sensitive κ -case in a case in micelles are the raw material for the product of gelled and floculated milk products, such as cheese, yog urt and ice-cream. Additionally, case in micelles find a broad application in case in films as adhesives or paint, prepared with solution casting or spray coating techniques.

We have investigated the effect of calcium on the structure of casein micelles in thin films using grazing incidence small angle x-ray scattering (GISAXS) at the BW4 USAXS beamline at HASYLAB/DESY in Hamburg. The GISAXS measurements are complemented with optical microscopy and atomic force microscopy to picture the surface structure [1].

 Müller-Buschbaum P., Gebhardt R., Maurer E., Bauer E., Gehrke R., Doster W. (2006) Biomacromolecules 7, 1773-1780

MM 35.23 Thu 18:45 H16 Hardness anisotropy of crystalline α -chitin: An ab-initio based conformational analysis — •MICHAL PETROV, MARTIN FRIÁK, LIVERIOS LYMPERAKIS, JÖRG NEUGEBAUER, and DIERK RAABE — Max-Planck-Institut für Eisenforschung, Max-Planck-Strasse 1, 402 37, Düsseldorf, Germany

The α -chitin is one of the most abundant biological materials. The complex structure of α -chitin results in a low-weight and high-strength material, which make it a favorable system for potential bio-inspired functional materials applications. In order to gather a deeper understanding of the mechanical properties of α -chitin, study of the elastic properties of pure single-crystalline α -chitin is crucial. We have therefore explored the atomic structure and the hardness anisotropy of crystalline α -chitin. A challenge in identifying the equilibrium structure of α -chitin is the large size of the unit cell consisting of 108 atoms. In order to resolve this complex structure a series of hierarchical approaches/methods is used: A conformational analysis of chitin is performed using computationally fast empirical potentials and tight binding calculations. Based on the conformational analysis a small number of possible atomic configurations could be identified. These structures have then been used as input for accurate ab-initio calculations in order to derive the ground state atomic geometry and the elastic properties of chitin. Finally based on these results we discuss and explain the strong elastic anisotropy of α -chitin in terms of the interplay between covalent and hydrogen bonds.

MM 35.24 Thu 18:45 H16 Micropatterning of ceramics by ion beam sputtering for dental implants — \bullet SEBASTIAN WILLE¹, BIN YANG², and RAINER ADELUNG¹ — ¹Lehrstuhl für Materialverbunde, Technische Fakultät der CAU Kiel, Kaiserstr. 2, 24143 Kiel — ²Universitätsklinikum Schleswig-Holstein Campus Kiel, Klinik für Zahnärztliche Prothetik, Propädeutik und Werkstoffkunde, Arnold-Heller-Strasse 16, 24105 Kiel Due to their attractive esthetics, biocompatibility and mechanical properties, zirconia ceramics are increasingly used for dental implants. But they do not form an osseo-integration due to chemical inertness. In order to improve the osseo-integration of zirconia ceramic implants, a microstructure on the ceramic surface is developed with an ion beam

sputter process through a thin film mask which exhibits low sputtering rates. The thin film masks covering ceramic surface are fractured to obtain a microcrack network . After sputtering, the network of cracks is transferred as a network of micro- and submicro channels. With this, relatively high aspect ratios for the microstructures can be obtained. Moreover, by filling the cracks with another material with a high sputter resistance, it is also possible to obtain the inverted network microstructure on zirconia ceramic surface.

MM 35.25 Thu 18:45 H16

Optical and Structural Characterisation of Metallised Oligonucleotides — ●NADINE HOLZAPFEL¹, GLENN BURLEY², JO-HANNES GIERLICH², DAVID HAMMOND², THOMAS CARELL², GERHARD ABSTREITER¹, and ULRICH RANT¹ — ¹Walter Schottky Institut, Technische Universität München, Am Coulombwall 3, 85748 Garching — ²Ludwig-Maximilians-Universität München, Butenandtstr. 5-13, 81377 München

Metallised DNA structures have received considerable attention recently; mainly for their potential applications in nanoelectronic de-Aside from this, metallised oligonucleotides of nanometer divices. mensions are expected to exhibit intriguing optical properties due to the excitation of collective oscillations of the conducting electrons by visible light (plasmons). In this study, we used two different methods to deposit silver on oligonucleotides of different lengths (23-96 base pairs). The first method involved the specific labelling of nucleotides with aldehyde groups, followed by exposure to Tollens reagens and a developer, whereas the second method relied on the photoinduced deposition of Ag onto unmodified DNA samples. Several preparation parameters (DNA sequence, buffer salt type, Ag concentration, UV illumination time) were varied systematically. The optical properties of the resulting metallised DNA samples were characterised by recording the extinction spectra using a UV/VIS absorption spectrometer. An extinction maximum was found at ca. 410 nm which is indicative of a plasmonic mode. In addition, the metallised DNA structures were deposited on single crystalline Si wafers and imaged by SEM and AFM.

MM 35.26 Thu 18:45 H16

The rate of bone renewal controls its mechanical behavior — \bullet DAVIDE RUFFONI¹, PETER FRATZL¹, PAUL ROSCHGER², KLAUS KLAUSHOFER², and RICHARD WEINKAMER¹ — ¹Max Planck Institute of Colloids and Interfaces, Potsdam, Germany — ²Ludwig Boltzmann Institute of Osteology, Vienna, Austria

At the material level bone is a nano-composite consisting of collagen and mineral particles. A crucial factor for the mechanical behavior is the amount and distribution of mineral. Bone material evolves in time as the result of a remodeling and a mineralization process. In trabecular bone the presence of bone packets with different degrees of mineralization is characterized by a bell-shaped frequency distribution of the mineral content, called the bone mineralization density distribution (BMDD). A tailor-made continuity equation is developed to answer how the rate of bone deposition and bone resorption influence the time evolution of the BMDD. First, the steady state solution of the model equation enables the extraction of information on the mineralization kinetics taking the measured BMDD as starting point. Secondly, the knowledge of the mineralization kinetics can be used to predict the full time evolution of the BMDD. Increasing the remode eling rate causes a less mineralized and more heterogeneous mineral distribution. Conversely, when reducing the turnover the BMDD displays transiently a sharp peak corresponding to bone with an unusual uniformity in its mineral content. Later in time higher and less uniform mineralization distributions are attained. From a mechanical view point this suggests an evolution towards stiffer but more brittle bone.

 $\label{eq:main_state} MM 35.27 \ \ Thu 18:45 \ \ H16$ Mechanical properties of silk: Interplay of deformation on macroscopic and molecular length scales — $\bullet I \rm MKE \ DIDDENS^1$, NADINE HAUPTMANN¹, GESA HELMS¹, IGOR KRASNOV¹, MALTE OGURRECK¹, TILO SEVPLI², SERGIO S. FUNARI³, and MARTIN MÜLLER¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian–Albrechts–Universität zu Kiel — ²Institut Laue–Langevin, Grenoble, France — ³HASYLAB at DESY, Hamburg

Using an *in situ* combination of tensile tests and X–ray fibre diffraction, we have directly determined the mechanical properties of both the crystalline and the disordered phase of the biological nanocomposite silk. We have adapted a model from linear viscoelastic theory, which fully accounts for the semicrystalline morphology of silk. The elastic moduli of the two phases were determined as well as the relaxing modulus and the viscosity of the disordered matrix. The high extensibility of silk results principally from the disordered phase, however, important elastic deformation was also found in the β –sheet protein crystals. The observed interplay between morphology and mechanical properties will have strong impact on the design of novel protein–based high performance fibres.

MM 35.28 Thu 18:45 H16 Fibrillar level deformation mechanisms in antler — •STEFANIE KRAUSS¹, HIMADRI SHIKHAR GUPTA¹, JONG SETO¹, JOHN CURREY², TOMAS LANDETE-CASTILLEJOS³, SERGIO SOUZA FUNARI⁴, STEPHAN VOLKHER ROTH⁴, and PETER FRATZL¹ — ¹Department of Biomaterials, Max Planck Institute of Colloids and Interfaces, Potsdam, Germany — ²Department of Biology, University of York, York, United Kingdom — ³IREC (Sec. Albacete) y ETSI Agronomos, IDR, Univ. Castilla-La Mancha, Albacete, Spain — ⁴HASYLAB-DESY, Hamburg, Germany

In bone and related biomineralized tissues, the combination of a ductile organic matrix (mostly Type I collagen) with stiff mineral crystallites leads to a material with high stiffness and excellent resistance to fracture. As recently shown by us, the mechanisms leading to this in bone involve shearing in the interfibrillar matrix as well as cooperative deformation between mineral and collagen within the fibril. Deer antler is a less mineralized bone type that shows an extremely high toughness, which has obvious advantages for its physiological function as a weapon during dominance fights between male deer in the rutting period. Using in-situ mechanical testing with time-resolved synchrotron X-ray measurements of the meridional collagen small-angle diffraction pattern, we measured the changes in fibril strain while simultaneously stretching the tissue to failure. We compare the fibril and tissue strain and the variation of the 3rd order meridional collagen peak shape with increasing stress. We discuss how these structural changes at the nanoscale may influence the macroscopic toughness of antler.

DPG Jahrestagung und DPG Frühjahrstagung des AKF

Regensburg, 26. - 30. März 2007

Symposium

Scattering experiments on soft-condensed matter systems – new techniques and experimental possibilities

Organisation:

Prof. Dr. Thomas Thurn-Albrecht, Universität Halle

Prof. Dr. Peter Müller-Buschbaum, Technische Universität München,

Special Symposium "Scattering experiments on soft-condensed matter systems – new techniques and experimental possibilities" in Regensburg / Germany at the 27th and 28th March 2007 in the framework of the spring meeting of the Division Condensed Matter of the Deutsche Physikalische Gesellschaft (DPG). The symposium is organized by the division Chemical and Polymer Physics (CPP).

This symposium addresses students, experienced researchers and senior scientists working in the field of and exploiting the potentials of scattering with neutrons and x-rays in the area of chemical and polymer physics. Aim of the symposium is to present the state of the art in scattering experiments with neutrons and x-rays on soft-matter materials (covering chemical and polymer physics aspects) and to highlight new experimental developments in scattering techniques. The symposium will provide information for non-experts in scattering about the potential use of scattering experiments in this field of science and allow for discussions among experts about latest trends and ideas. Central idea is to bring together the community interested in the material aspects of chemical and polymer physics and the community specialized on the experimental techniques of scattering with neutrons and x-rays.

Invited talks will provide an overview of dedicated scattering techniques covering the topics microbeam, coherent, inelastic, surface sensitive and time-resolved scattering. In special contributed lectures each topic will be deepened and illustrated by additional examples. A large poster session concludes the symposium.

The symposium language is English.

Invited speakers (confirmed)

R. May (ILL, Grenoble, France): Time resolved small angle neutron scattering

S. Mochrie (Yale University, New Haven, USA): coherent scattering

D. Richter (Forschungszentrum Jülich, Jülich, Germany): Polymer dynamics: From Synthetic to Biopolymers

C. Riekel (ESRF, Grenoble, France): Synchrotron radiation based micro-beam scattering experiments

R. Steitz (HMI, Berlin, Germany): surface sensitive neutron scattering

Additional info: http://regensburg07.dpg-tagungen.de/index.html?lang=en&

Tuesday

CPP 10: INTERNAL SYMPOSIUM Scattering Experiments I

Location: H37

Time: Tuesday 9:30-12:30

Invited Talk CPP 10.1 Tue 9:30 H37 Polymer dynamics: From Synthetic Polymers to Biopolymers – •DIETER RICHTER – Forschungszentrum Jülich, Institut für Festkörperforschung, 52425 Jülich, Germany

In polymeric materials the structures, the macroscopic mechanical and rheological properties and the phase changes are determined to high degree by thermal motion of the atoms and molecules. Most of the relevant dynamics takes place on mesoscopic lengths and time scales in between the picosecond atomic scale and the macroscopic frame. Offering the proper space time observation window, neutron spin echo (NSE) spectroscopy uniquely addresses these motions. We briefly present some key experimental results on the mesoscopic dynamics of polymer systems. We address briefly the standard model of polymer motion, the Rouse model, the role of topological confinement as expressed in the reptation model and finally, processes limiting the confinement we discuss contour length fluctuations and constraint release of entangled chains. Very recently it became also possible to directly identify large scale internal dynamics of proteins by neutron spin echo. We report the results of these pioneering studies, which most likely will initiate further experiments on the large scale motions of proteins and their relation to the function.

> CPP 10.2 Tue 10:00 H37 Isions and Liquid Dynamics in Soft

Glass-Forming Microemulsions and Liquid Dynamics in Soft Confinement — •THOMAS BLOCHOWICZ¹, TINKA SPEHR¹, ANNIKA FRICKE¹, MARTIN MÜLLER¹, BERNHARD FRICK², and BERND STÜHN¹ — ¹TU-Darmstadt, Germany — ²ILL, Grenoble, France

Recently glass forming liquids have been investigated subject to nanoscale geometrical confinements of various kinds, in order to access changes in the molecular dynamics when the confinement comes close to a characteristic lengthscale of cooperative motion. Most experiments were performed with glass formers confined in nanopores in case of which, however, actual finite size effects are superposed with pressure effects or interactions with the confining walls. A different situation can be found in microemulsions, where, droplets of a hydrophillic substance are stabilized by surfactant molecules in a hydrophobic environement. When the substances involved are chosen properly vitrification in a so-called "soft confinement" can be observed. In our particular case we study droplets of glycerol in a matrix of toluene and m-xylene stabilized by the ionic surfactant AOT. The temperature dependent structure of these systems is investigated by small-angle X-ray and neutron scattering, whereas for the dynamical behaviour quasielastic neutron scattering techniques are particularly useful due to their nanoscale spatial resolution. We present time-of-flight and backscattering measurements to access the dynamics of glycerol inside the emulsion droplets. As compared to bulk glycerol pronounced acceleration of the dynamics is observed whereas comparison of core and shell dynamics of the micelles yields almost identical behaviour.

CPP 10.3 Tue 10:15 H37

Starlike dendrimers in solutions: Structural properties and internal dynamics — \bullet SILKE RATHGEBER¹, MICHAEL MOKENBUSCH², JAMES L. HEDRICK³, MIKAEL TROLLSAS³, and AL-ICE P. GAST⁴ — ¹Max-Planck Institut für Polymerforschung, Polymer Physik, D-55128 Mainz, Germany — ²Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425 Jülich, Germany — ³IBM Almaden Research Center, San Jose, California 95120-609, USA — ⁴Department of Chemical Engineering, Masschusetts Institute of Technology, Cambridge, Massachusetts 0213, USA

We measured the shape and the internal dynamics of starlike dendrimers under good solvent conditions with small-angle neutron scattering and neutron spin-echo spectroscopy, respectively. [1] Architectural parameters such as the spacer length and generation were varied in a systematic manner. Structural changes occurring in the dendrimers as a function of these parameters are discussed. A first cumulant evaluation of the NSE spectra for each scattering vector qseparately yields the length scale dependent relaxation rates $\Omega(q)/q^3$ on length scales corresponding to the overall dendrimer dimension. The dynamics is discussed within a Rouse-Zimm approach generalized to the case of starlike dendrimers of arbitrary geometry. The model allows an identification of the modes contributing to the relaxation of the dendrimer. The local minimum is due to collective breathing motions of (parts of) the dendrons relative to each other. Shape fluctuations are not observed. [1] S. Rathgeber et. al., J. Chem. Phys. **125**, 204908 (2006)

CPP 10.4 Tue 10:30 H37

Neutron Spectroscopy on nono-confined polymers in comparison with dielectric and thermal results — •ANDREAS SCHOENHALS¹, BERNHARD FRICK², MARIA MAYOROVA³, and REINER ZORN³ — ¹Federal Institute of Materials Research and Testing, Unter den Eichen 87, D-12205 Berlin — ²Institut Laue-Langevin, B.P. 156, F-38042 Grenoble — ³Research Center Jülich, Institute for Solid State Research, D-52425 Jülich

The effect of a nanometre confinement on matter is an interesting problem of soft-matter physics. Neutron scattering (NS) is valuable tool to investigate such systems because of the high penetration depth of neutrons. Incoherent NS was carried out on poly(dimethyl siloxane) and poly(methyl phenyl siloxane) confined to Sol/Gel-glasses (7.5, 5.0, 2.5 nm). To cover a broad dynamical range of the scattering function $\mathrm{S}(\mathbf{Q},\!\mathbf{E})$ time-of-flight and backscattering are combined. For the Boson peak the vibrations at lowest frequencies are depressed by the confinement. The mean square displacement msd was calculated from elastic scanes. Above Tg the characteristic increase of the msd found for the bulk is strongly influenced by the confinement but for both materials in a different manner. The main influence of the confinement on S(Q,t)=FT(S(Q,E)) is an broadening of S(Q,t) with increasing confinement. These results are discussed together with dielectric measurements. This comparison gives strong evidence that (1) the thermodynamic state in a nanometer confinement is different from that of the bulk and that (2) an inherent length scale might exist for the glass transition.

A theory of vibrational excitations in disordered materials¹ and their observation by inelastic light, neutron, X-ray² and nuclear γ -ray scattering³, based on a model with fluctuating shear moduli is presented. The enhancement of the vibrational density of states (DOS) $g(\omega) \propto ver$ Debye's $g(\omega) \propto \omega^2$ law ("boson peak") is shown to be a direct consequence of the disorder. The observed spectra in coherent scattering experiments do not in general reveal the DOS directly. Only in incoherent neutron experiments and in nuclear resonant scattering of synchrotron radiation the scattering law is proportional to $g(\omega)$. Raman spectra are shown to reveal the imaginary part $\Sigma''(\omega)$ of the disorder-induced self energy, which is only indirectly related to the DOS, namely to its enhancement over the Debye DOS. The high-frequency sound damping, observed as broadening of the Brillouin line, is also proportional to $\Sigma''(\omega)$. It is shown that the existing spectra can be consistently interpreted in the light of this theory.

[1] W. Schirmacher, Europhys. Lett. **73**, 892 (2006)

- [2] W. Schirmacher, G. Ruocco, T. Scopigno, submitted to
- Phys. Rev. Lett.
- [3] A. I. Chumakov et al. Phys. Rev. Lett. 92, 245508 (2004)

15 min. break

Invited TalkCPP 10.6Tue 11:15H37Time-resolved small-angle neutron scattering — •ROLAND MAY— Institut Max von Laue - Paul Langevin, BP 156, F-38042 GrenobleCedex 9, France

Small-angle neutron scattering has a history of about 40 years, but only with the advent of modern fast electronics has it become feasible to penetrate into time regimes that are compatible with reaction rates and process times of biomolecules, polymers and colloids at full detector resolution. Neutron sources cannot compete with the flux or brilliance of X-ray sources. Therefore they are limited as far as the observation of very fast processes is concerned, unless if they can

Tuesday

be easily and often repeated, as in cyclic events. Of course, neutrons heave the special advantage of neutron contrast variation, allowing one to highlight parts of a structure, and they do not produce any radiation damage. This contribution will address these technical issues and give a number of examples from the slow kinetics of oil droplet formation to the observation of the photocycle of photo-active yellow protein in the tens of milliseconds range, and also mention how one can reach even shorter times with sophisticated time-of-flight techniques.

${\rm CPP} \ 10.7 \quad {\rm Tue} \ 11{\rm :}45 \quad {\rm H37}$

Protein Interactions in Aqueous Solution Studied by Small-Angle X-ray Scattering — •FAJUN ZHANG¹, MAXIMILIAN SKODA^{1,2}, ROBERT JACOBS³, RICHARD MARTIN⁴, CHRISTOPHER MARTIN⁵, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen, Germany — ²PTCL, University of Oxford, UK — ³CRL, University of Oxford, UK — ⁴Department of Physics, University of Bath, UK — ⁵SRS, Daresbury, Warrington, UK

We have studied protein interactions in two related systems by smallangle x-ray scattering: a series of pure protein solutions with various salt and protein concentrations, and mixtures of protein with oligo(ethylene glycol) (OEG) thiol decorated gold colloids. Structure factors derived from hard sphere potential, screened Coulomb potential, and square well potential, combined with an oblate ellipsoid form factor are used to fit the scattering intensities. An interaction phase diagram has been constructed as a function of ionic strength and protein concentration [1]. For the mixture of protein with functional gold colloid, we present evidence for an attractive interaction between OEGdecorated gold colloids and a repulsive interaction between gold colloid and protein. The attractive potential originates from a depletion force which strongly depends on the size of colloids and the concentration of protein, while the repulsive potential is due to the protein resistance of the OEG monolayer. Indeed, we observed the aggregation of gold colloids, when protein concentration is higher than a critical value

[1] Zhang, F.; Skoda, M.W.A.; Jacobs, R.M.J.; Martin, R.A.; Martin, C.M.; Schreiber, F. J. Phys. Chem. B 2006, in press.

${\rm CPP} \ 10.8 \quad {\rm Tue} \ 12{:}00 \quad {\rm H37}$

Surfactant Phase Transitions: New Insights From Timeresolved Small-angle Scattering Experiments — ANNINA SALONEN¹, JACQUES LENG², PETER SCHURTENBERGER³, and •STEFAN EGELHAAF⁴ — ¹Institute of Chemistry, Karl Franzens University, 8010 Graz, Austria — ²LOF unité mixte CNRS/Rhodia/Bordeaux, 33608 Pessae, France — ³Department of Physics, University of Fribourg, 1700 Fribourg, Switzerland — ⁴Condensed Matter Physics Labora tory, Heinrich-Heine-University, 40225 Düsseldorf, Germany

Most early studies on surfactant systems have addressed their equilibrium behaviour. These remain a prerequisite for further progress, but attention is turning to nonequilibrium phenomena. I plan to present two recent projects in this area:

First, time-resolved small-angle neutron scattering is used to investigate the intermediate structures during the growth of mixed micelles. The growth of the micelles is induced by a reduction in total surfactant concentration, which is realized by rapid mixing of a surfactant solution with buffer. The subsequent structural changes are followed by time-resolved small-angle neutron scattering.

Second, structural changes during the dissolution of lamellar phase are studied with small-angle x-ray scattering. After contact with water, lamellar phase can form fascinating interface instabilities, so-called myelins. Using time and space resolved small-angle x-ray scattering we investigate the changes in the lamellar phase during the formation and growth of these structures.

CPP 10.9 Tue 12:15 H37 Mapping the local nanostructure inside a specimen by tomographic small-angle x-ray scattering — •JAN M. FELDKAMP¹, CHRISTIAN G. SCHROER¹, MARION KUHLMANN², STEPHAN V. ROTH²,

CHRISTIAN G. SCHROER¹, MARION KUHLMANN², STEPHAN V. ROTH², RAINER GEHRKE², NORBERT STRIBECK³, ARMANDO ALMENDAREZ-CAMARILO³, and BRUNO LENGELER⁴ — ¹Institute for Structural Physics, Dresden University, D-01062 Dresden, Germany — ²HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg, Germany — ³Institute of Technical and Molecular Chemistry, Hamburg University, Bundesstrasse 45, D-20146 Hamburg, Germany — ⁴II. Physikalisches Institut, Aachen University, D-52056 Aachen, Germany

Small-angle x-ray scattering is combined with scanning microtomography to reconstruct the small-angle diffraction pattern in the direction of the tomographic rotation axis at each location on a virtual section through a specimen. These data yield information about the volumeresolved local nanoscale structure of the sample. With rotational symmetry present in the diffraction patterns, e.g., for isotropic or fibertextured local nanostructure, the full reciprocal space information in the small-angle scattering regime can be reconstructed at each location inside the specimen. The resolution in real space is determined by the size of the x-ray beam. The experiments were performed with the microbeam option at HASYLAB beamline BW4.

Using this new method, we prove the existence of a skin-core structure in injection molded samples, which cannot be detected in classical tomography.

Tuesday

CPP 11: INTERNAL SYMPOSIUM Scattering Experiments II

Location: H37

Time: Tuesday 14:00-18:15

Invited Talk CPP 11.1 Tue 14:00 H37 Surface sensitive neutron scattering — ●R. STEITZ — Hahn-Meitner-Institut, SF1, Glienicker Str. 100, D-14109 Berlin

Current problems in soft matter science often require insight on the nanometer scale. In this contribution we will show how neutron reflectivity (NR) and grazing incidence small angle neutron scattering (GISANS) can be utilized to reveal details on thin films at solid-liquid and solid-gas interfaces. The first chapter will investigate the structure of the boundary of a hydrophobic polymer film and its adjacent water phase [1]. Chapter two will demonstrate that NR is an excellent tool for monitoring water uptake and respective structural changes in hydrophilic polyelectrolyte films [2] and chapter three will illustrate that application of GISANS can help to clarify transient lateral structures in molecular surfactant layers that are not detectable otherwise[3].

R. Steitz, T. Gutberlet, T. Hauß, B. Klösgen, R. Krastev, S. Schemmel, A. C. Simonsen and G. H. Findenegg, Langmuir 19; 2409-2418 (2003).
 R. Steitz, V. Leiner, R. Siebrecht and R. v. Klitzing, Colloids and Surfaces A. 163, 63-70 (2000).
 R. Steitz, P. Müller-Buschbaum, S. Schemmel, R. Cubitt, and G. H. Findenegg, EPL 67, 962-968 (2004).

CPP 11.2 Tue 14:30 H37

X-ray reflectivity study of the adsorption of azacrown ethers and palmitic acid at the hexane-water interface — •GUTBERLET THOMAS¹, WOJCIECHOWSKI KAMIL², TIKHONOV ALEXEV³, SCHLOSSMAN MARK⁴, and BUFFLE JACQUES² — ¹Lab. f. Neutr. Scattering, ETHIZ & PSI, 5232 Villigen PSI, Switzerland — ²CABE, Dept. of Anal., Inorg. and Appl. Chem., University of Geneva, 1211 Geneva 4, Switzerland — ³NSLS, Upton, NY, USA — ⁴Dept. of Phys. and Chem., University of Illinois, Chicago, IL, USA

Azacrown ethers substituted with different alkyl chain length (decyl, palmitoyl, tetracosanoyl) and palmitic acid have been investigated at the aqueous-organic hexane-water interface by means of x-ray reflectivity. These systems are of interest in Permeation Liquid Membrane techniques to separate aqueous solutions by a hydrophobic membrane to select chemical species. The x-ray reflectivity measurements reveal the presence of a dense interfacial layer at the hexane-water interface. The longer alkyl chain substituted azacrown ethers show a diminished interfacial roughness. Here, the experimental set-up and results will be presented in detail and discussed.

CPP 11.3 Tue 14:45 H37

Annexin binding to solid supported membranes: a neutron and synchrotron scattering study — KIRSTIN SEIDEL, JOACHIM RÄDLER, and •BERT NICKEL — Dep. für Physik, Ludwig-Maximilians-Universität, München

We have developed a microfluidic setup which allows to prepare and observe solid supported membranes by fluorescence microscopy. Two variants exist, one allows for complementary x-ray reflectivity experiments [1], while the other allows for complementary synchrotron studies at 20 keV. The amount of liquid needed is about 2 ml. As a model system, we have chosen Annexin II, which binds in a Ca dependent way to negatively charged membranes. Here, we report neutron reflectivity experiments at Amor (PSI) and Refsans (FRM-2) and compare them with respective synchrotron studies performed at Hasylab Hamburg and ESRF. The goal of these experiments is to find the configuration of the membrane and the Annexin from the diffraction experiments. while the microscopy experiments allow to determine membrane fluidity with and without Annexin present. Experiments were performed in collaboration with B. Windschiegel and C. Steinem (U. Göttingen). Experiments at Refsans were done in collaboration with GKSS (R. Kampmann et al.)

[1] C. Reich, M. Hochrein, B. Krause, B. Nickel, Review of Scientific Instruments 76, 095103 (2005)

CPP 11.4 Tue 15:00 H37

Influence of spacer length and density on the vertical structures of supported membranes studied by neutron reflectivity — •PETER SEITZ¹, OLIVER PURRUCKER², ANTON FÖRTIG³, RAIMUND GLEIXNER⁴, GIOVANNA FRAGNETO⁵, RAINER JORDAN³, and MOTOMU TANAKA^{1,2} — ¹Physikalisch-Chemisches Institut, Universität Heidelberg, Germany — ²Physik-Department E22, Technische Universität

München, Germany — 3 Institut für Technische Chemie, Technische Universität München, Germany — 4 Max Planck Institute of Biochemistry, Martinsried, Germany — 5 Institut Laue-Langevin, Grenoble, France

We studied the structure of a new class of polymer-supported membranes, which are separated from the solid substrate via poly(2-methyl-2-oxazoline) spacers of defined length, functionalized with a surface coupling group and hydrophobic membrane anchors. The proximal leaflet was deposited via Langmuir-Blodgett transfer, followed by vesicle fusion to deposit the distal layer. Precise control of the polymer chain length and its lateral density enables the quantitative adjustment of the thickness and the viscosity of the polymer interlayer. Previously, we measured the membrane-substrate distance with fluorescence interference contrast microscopy (FLIC). To gain a deeper insight to the vertical structure of the membrane, we conducted specular neutron reflectivity experiments under a systematic variation of the spacer length and density, and calculated the static roughness and the volume fraction of water in the polymer interlayer.

CPP 11.5 Tue 15:15 H37

Nanotemplate fabrication and macroscopic alignment of nanoscale domains using self-organized diblock copolymers — •DENIS KOROLKOV, PETER BUSCH, EMMANUEL KENTZINGER, LUTZ WILLNER, and THOMAS BRUECKEL — Forschungszentrum Jülich GmbH, Institut für Festkörperforschung, D-52425, Jülich

Fabrication of macroscopic domains of periodic nanoscale structures using self-organizing systems promises to be a simple and low cost method with potential to produce high-density arrays of magnetic devices [1]. A block-copolymer can self-assemble into microphase separated domains with a spacing of 10-100 nm which strongly depends on molecular weight, segment size, and the strength of interaction between the blocks. Without further constraint, the domains have no preferred orientation and form a disordered "fingerprint" structure.

In this study self-organization of polystyrene-polybutadiene (dPS-PB) diblock copolymer with various thicknesses and molecular weights was investigated. Using pre-structured Si wafer with gratings[2] of μm period and depth of 60 nm we were able to achieve a macroscopic alignment of polymer domains.

Structural characterization, in particular the degree of long-range order was done by combining a surface-sensitive technique like atomic force microscope (AFM) with grazing incidence small angle scattering (GISAS).

[1] I. W. Hamley Nanotechnology 14 (2003) R39-R54

[2] D. Sundrani, S.B. Darling, S.J. Sibener Nano Lett., Vol. 4, No. 2, 2004

15 min. break

Invited Talk CPP 11.6 Tue 15:45 H37 Coherent x-ray studies of polymer membrane fluctuations and colloidal dynamics near the glass transitions — •SIMON MOCHRIE — Department of Physics and Applied Physics, Yale University, New Haven, CT 06520, USA

This talk will briefly review the emerging technique of x-ray photon correlation spectroscopy (XPCS). Then, it will describe XPCS measurements of the dynamics of self-assembled block copolymer membranes within a dilute vesicle (L4) phase and within in a sponge (L3) phase which occur in homopolymer-triblock copolymer blends. In the L4 phase, the results are consistent with predictions for the dynamics of isolated membranes. In the L3 phase, there is a crossover from stretched exponential relaxations to highly-unusual compressed exponential relaxations. In the third part of the talk, the results of very recent measurements will be presented of the dynamics within a dense colloidal suspension in a binary fluid mixture. These measurements reveal the existence of re-entrant glassy behavior in this system, and further highlight the promise of the XPCS method at the next generation of high-brightness x-ray sources, such as PETRA III.

This work was carried out at beamline 8-ID at the Advanced Photon Source at Argonne National Laboratory in collaboration with Xinhui Lui, Peter Falus (Yale), Matt Borthwick (MIT), Suresh Narayanan, Alec Sandy, and Michael Sprung (APS) and is supported by the US

CPP 11.7 Tue 16:15 H37

Speckle echo-technique for diffusing-wave spectroscopy of soft solids — • PAVEL ZAKHAROV and FRANK SCHEFFOLD — University of Fribourg, Fribourg, Switzerland

We present a detection scheme for diffusing-wave spectroscopy (DWS) based on a two-cell geometry that allows efficient multi-speckle averaging with a single-mode detection. This is achieved by placing a fast-rotating diffuser in the optical path between laser and sample. We show that the recorded (multispeckle) correlation echoes provide an ensemble averaged signal without lengthy time averaging. Furthermore, combined with traditional two-cell DWS, the full intensity autocorrelation function can be measured with a single experimental setup. The scheme provides access to a large range of correlation times thus opening an experimental window for the study of slowly relaxing and arrested systems, such as viscoelastic complex fluids, colloidal glasses, and gels. We also demonstrate how the technique can be used to monitor dynamic properties of samples that evolve in time

CPP 11.8 Tue 16:30 H37

Bending elasticity of DPPC vesicles with changing cholesterol content — LAURA RODRIGUEZ-ARRIAGA¹, GUILLERMO ORTS-GIL², •THOMAS HELLWEG², BELA FARAGO³, CARLOS MENDUINA¹, and FRANCISCO MONROY¹ — ¹Departamento de Quimica-Fisica I, Facultad de Ciencias Quimicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain — ²Stranski Laboratorium, TU Berlin, Strasse des 17. Juni 124, D-10623 Berlin, Germany — ³Institut Laue-Langevin, Grenoble, France

A combination of neutron spin-echo spectroscopy and photon correlation spectroscopy (PCS) can be used to determine motions in colloidal particles in the nanosecond time range [1](e.g. film deformation modes). In the present study we used this approach to discriminate membrane shape fluctuations of DPPC vesicles with different cholesterol content from their translational diffusion. The relative amplitude of the translational contribution to the intermediate scattering functions is found to decrease as q increases and the vesicle deformation mode becomes the main contribution to the relaxation function at times short enough, like the ones probed by the NSE technique. We have performed experiments on vesicles with different lipid composition and we have gained some insight in the compositional grounds of the bending elastic constant κ is calculated using the Zilman-Granek approach.

[1] Th. Hellweg, D. Langevin; PRE, **57** (1998) 6825.

CPP 11.9 Tue 16:45 H37

Micellar hydrogels of poly(2-oxazoline) copolymers containing fluorophilic, hydrophilic and lipophilic blocks — •RUZHA IVANOVA¹, TUNE BONNÉ¹, KELL MORTENSEN², PHILIPP PRANZAS³, THOMAS KOMENDA⁴, KARIN LÜDTKE⁴, RAINER JORDAN⁴, and CHRISTINE PAPADAKIS¹ — ¹Physikdepartment E13, TU München, 85 747 Garching — ²Risø National Laboratory, Roskilde, Denmark — ³GKSS, Geesthacht — ⁴Department Chemie, TU München, 85 747 Garching

The self-assembly of novel amphiphilic poly(2-oxazoline) di- and triblock copolymers containing hydrophilic and fluorophilic and/or lipophilic blocks in aqueous solutions was studied. Small-angle neutron scattering together with contrast matching was used to study the size and the shape of the micelles as well as the effect of the copolymer concentration and the length of the hydrophilic block on the structure. It was shown that lipophilic-hydrophilic and hydrophilic-fluorophilic diblock copolymers do not form common micelles. This result is an important prerequisite for the formation of multi-compartment micelles and hydrogels in aqueous poly(2-oxazoline) systems. The triblock copolymers aggregate into micelles, and at higher concentrations, hydrogels are formed. We could show that the scattering curves of the hydrogels can be described by a coexistence of spherical lipophilic and elongated fluorophilic micellar cores linked by the hydrophilic blocks. Thus the studied poly(2-oxazoline) copolymers have large practical potential as multi-compartment vehicle systems in e.g. medicine or cosmetics.

15 min. break

Invited Talk CPP 11.10 Tue 17:15 H37 Microbeam Synchrotron Radiation Scattering Experiments in Soft Condensed Matter — •CHRISTIAN RIEKEL — ESRF, B.P.220, F-38043 Grenoble Cedex France

The talk will review scientific applications of small- and wide-angle Xray scattering (SAXS/WAXS) techniques with micron- and submicron-sized X-ray beams at the ESRF. The two complimentary techniques are scanning-SAXS/WAXS and single crystal diffraction. I will show a number of scanning applications for synthetic polymers and biopolymers, which allow the generation of "diffraction images" based on the extraction of specific parameters such as local orientation, strain or crystallinity from a series of diffraction patterns. Single crystal microdiffraction has found many applications in protein crystallography but can also be used for small unit-cell biopolymers. This has allowed in the case of A-amylose replacing the combination of fiber diffraction&molecular modeling by atomic scale structural refinement. Microbeams are also very convenient for in-vivo studies of biological processes like silk extrusion, for studying protein aggregation in microfluidic environments or for grazing-incidence scattering (GISAXS) studies on small sample areas. The examples discussed in the review will show the strong interdisciplinary character of synchrotron radiation research.

CPP 11.11 Tue 17:45 H37 **Micro-focus GISAXS Investigations of Microcantlever Sen sors** — **•** JOCHEN S. GUTMANN^{1,2}, YAJUN CHENG¹, MINE MEMESA¹, SEBASTIAN NETT¹, and RÜDIGER BERGER¹ — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany — ²Institute for Physical Chemistry, Johannes Gutenberg University Mainz, Welderweg 11, D-55099 Mainz

Microcantlever sensors (MC) are a versatile class of sensors, with the potential for a high spatial integration of very different analyte sensitivity into a single sensor unit. Polymeric coatings on MC sensors allow for a facile variation in analyte detection due the ease of functional chemical modification of the polymer layer. While homopolmyer coatings are easily applied to the MC surface, polymer brushes extend the use of MC sensor technology into liquid environments. [1,2] In order to investigate the lateral structures of the polymer layers on the μ m sized cantilevers, we used a micro-focus set-up for X-ray scattering under grazing incidence (μ -GISAXS), at the BW4 beam line of the HASYLAB. [3] The structural information obtained from the grazing incidence scattering experiments is then used to separate the mechanical sensing response of the MC sensor to its changes in structure and surface energy.

 Bumbu G.-G., Kircher G., Wolkenhauer M., Berger R., Gutmann J.S., Macromol. Chem. Phys. 2004, 205 (13): 1713-1720 [2] J. Zhao, R. Berger, J. S. Gutmann, Applied Physics Letters, 89, 033110 (2006).
 M. Wolkenhauer, G.-G. Bumbu, Y. Cheng, S. V. Roth, J. S. Gutmann, Applied Physics Letters, 89, 054101 (2006).

CPP 11.12 Tue 18:00 H37

Polymer-based nanocomposites investigated with micro-GISAXS — •S.V. ROTH¹, A. VELIGZHANIN¹, H. WALTER², R. DOMNICK³, O. LEUPOLD¹, R. GEHRKE¹, and P. MÜLLER-BUSCHBAUM⁴ — ¹HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg, Germany — ²CSEM SA, Badenerstrasse 569, CH-8048 Zürich, Switzerland — ³Ara-Coatings GmbH & Co. KG, Gundstr. 13, D-91056 Erlangen, Germany — ⁴TU München Physik Department LS E13, James-Franck-Str.1, D-85747 Garching, Germany

Polymer-based nanocomposites allow to combine the extraordinary features of the individual materials forming the nanocomposite. Especially the richness of polymer structures in blend as well as blockcopolymer systems in thin film geometry gives rise to new classes of nanocomposite materials. Annealing as a second step in nanocomposite preparation allows for further nanostructuring the polymer film inducing e.g. a definite roughness or particle distribution. In our approach we combine the richness of the polymer structure with a metal coating [1,2]. Such polymer-based metal nanocomposites are widely used in many optical and biotechnological applications. As experimental method to study such nanocomposites, we used microbeam grazing incidence small-angle x-ray scattering at the beamline BW4 of HASYLAB (Hamburg). Our results reveal the dominating influence of the polymer layer in the structure of this nanocomposite.

[1] S.V. Roth et al., Appl. Phys. Lett. 82, 1935 (2003)

[2] S.V. Roth et al., Appl. Phys. Lett. 88, 021910 (2006)

Tuesday

Monday

Location: Poster B

CPP 7: POSTER: INTERNAL SYMPOSIUM Scattering Experiments

Time: Monday 16:00-18:00

3 the case in micelle structures.

 $\label{eq:CPP 7.1 Mon 16:00 Poster B} \end{tabular} Electric field effects on alignment of lamellar structures in diblock copolymer thin films studied by neutron scattering <math display="inline">-\bullet$ XIULI JIANG¹, THOMAS GUTBERLET², MUKUL GUPTA², THOMAS GEUE², and THOMAS THURN-ALBRECHT¹ — ¹Department of Physics, Martin-Luther-University, Halle, Germany — ²Laboratory for Neutron Scattering, ETH Zürich & PSI, Villigen, Switzerland

Self-assembled block copolymers have attracted much attention in recent years for their potential use as nanostructure templates. In this context, it is of interest to control the order and orientation of block copolymer thin films by means of external electric fields. In order to gain additional understanding of the alignment process, we studied the effect of a weak electric field on a lamellar microphase structure oriented perpendicular to the electric field by neutron diffuse scattering in reflection geometry. It has been predicted that the electric field induces periodic structural undulations which lead to a disruption of the original structure and facilitate reorientation to set in. In our experiments on lamellar PS-PMMA block copolymers these field-induced undulations were not observed. Rather, already after preparation the films displayed a diffuse intensity interpreted as corresponding to a mosaic structure of domains with a typical correlation length of about $1-2\,\mu\text{m}$. This diffuse intensity increases after the application of the field, even if the field is too weak to induce alignment. The lateral length scale of the mosaicity remains unaffected by the electric field.

CPP 7.2 Mon 16:00 Poster B

Extending the possibilities of a Kratky-Compact-Camera by use of focussing multilayer X-ray optics — •THOMAS HENZE, KLAUS SCHRÖTER, and THOMAS THURN-ALBRECHT — Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, Polymerphysik

The use of focussing multilayer x-ray optics in laboratory x-ray equipment offers the potential of a substantial gain in primary beam intensity without a significant loss of resolution. We present the result of a refurbishment of Kratky-Compact-Camera, a classical setup for small angle x-ray scattering on isotropic samples, with an elliptically bent focussing multilayer. The advantages of the Kratky collimation system are ease of alignment, high intensity and low background. A further gain in intensity is highly desirable for time dependent experiments as well as for measurements of weakly scattering samples. The performance of the revised setup is analyzed quantitatively by comparing intensity and full width at half maximum of the primary beam, as well as the minimal accessible scattering vector with the corresponding parameters of the simple setup without optics. A gain in intensity of a factor of 2 up to 10 is achieved, depending on the details of the alignment. In addition the multilayer produces a monochromatic beam. First measurements on exemplary polymer systems are shown.

CPP 7.3 Mon 16:00 Poster B

Structural investigation of casein micelles in thin films — •E. METWALLI¹, R. GEBHARDT¹, A. TOLKACH², J.-F. MOULIN¹, V. KÖRSTGENS¹, S.V. ROTH³, R. CUBITT⁴, and P. MÜLLER-BUSCHBAUM¹ — ¹Physikdepartment E13, TU München, 85747 Garching. — ²Chair for Food Process Engineering and Dairy Technology, TU München, Weihenstephan — ³HASYLAB at DESY, Hamburg — ⁴Institut Laue-Langevin, Grenoble, France

Case n micellar films on solid supports have interesting applications in labeling of glass containers and adhesion technology. Gaining structural information on these films will help to optimize the appropriate physical properties for the desired application. Casein micelles thin films were applied from aqueous solutions on pre-cleaned glass slides by spin coating technique. The effect of transglutaminase enzyme concentrations on the thin film structures was investigated using atomic force microscopy (AFM) and grazing incidence small-angle X-ray scattering (GISAXS). The AFM images can only give information on the top surface structure with low statistical significance. In contrary, GISAXS provides information on the in-plane structures of the casein thin film with much higher statistical significance. The GISAXS data on the thin films were compared with those obtained by dynamic light scattering from the solution phase. The swelling behavior of some selected casein films in deuterated water vapor was also investigated using grazing incidence small-angle neutron scattering (GISANS). The results were discussed and compared with various proposed models on

The liquid crystals E7 and 8CB are confined to the nanopores of the molecular sieve Al-MCM-41 with a mean diameter of the pores of 2.5 nm. Dielectric spectroscopy shows that for the confined system one relaxation process is observed. Its characteristic relaxation time is much lower compared to that of the bulk. The temperature dependence of the relaxation time of this relaxation process shows some similarities to glassy dynamics. Moreover excess contributions to the vibrational densities of state (Boson-Peak) were found by neutron scattering using the time-of-flight spectrometer IN4 at the ILL in Grenoble. The Boson- Peak is a characteristic feature of glassy behaviour. In addition elastic scans are carried out at the backscattering spectrometer IN10 (ILL) These measurements show a signature for glass transition.

CPP 7.5 Mon 16:00 Poster B

Influence of spacer length and density on the vertical structures of supported membranes studied by neutron reflectivity — •PETER SEITZ¹, OLIVER PURRUCKER², ANTON FÖRTIG³, RAIMUND GLEIXNER⁴, GIOVANNA FRAGNETO⁵, RAINER JORDAN³, and MOTOMU TANAKA^{1,2} — ¹Physikalisch-Chemisches Institut, Universität Heidelberg, Germany — ²Physik-Department E22, Technische Universität München, Germany — ³Institut für Technische Chemie, Technische Universität München, Germany — ⁴Max Planck Institute of Biochemistry, Martinsried, Germany — ⁵Institut Laue-Langevin, Grenoble, France

We studied the structure of a new class of polymer-supported membranes, which are separated from the solid substrate via poly(2-methyl-2-oxazoline) spacers of defined length, functionalized with a surface coupling group and hydrophobic membrane anchors. The proximal leaflet was deposited via Langmuir-Blodgett transfer, followed by vesicle fusion to deposit the distal layer. Precise control of the polymer chain length and its lateral density enables the quantitative adjustment of the thickness and the viscosity of the polymer interlayer. Previously, we measured the membrane-substrate distance with fluorescence interference contrast microscopy (FLIC). To gain a deeper insight to the vertical structure of the membrane, we conducted specular neutron reflectivity experiments under a systematic variation of the spacer length and density, and calculated the static roughness and the volume fraction of water in the polymer interlayer.

CPP 7.6 Mon 16:00 Poster B

Formation of lateral structures in thin diblock copolymer films by vapor treatment — •CHRISTINE PAPADAKIS¹, PETER ČERNOCH², CHARLES DARKO¹, EZZ METWALLI¹, PETR ŠTĚPÁNEK², DETLEF-M. SMILGIES³, and STEPHAN V. ROTH⁴ — ¹Physikdepartment E13, TU München, James-Franck-Str. 1, 85747 Garching — ²Inst. Macromolecular Chemistry, Prague, Czech Republic — ³Cornell University, Ithaca NY, USA — ⁴HASYLAB at DESY, Hamburg

Diblock copolymers in the melt spontanously self-organize into mesoscopically ordered structures. In order to understand their response to changes of the environment, in-situ and real-time methods are of great value. We have performed grazing-incidence small-angle X-ray scattering (GISAXS) measurements on 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 [1]. The solvent quality and selectivity were found to have a strong influence on the inner film structure. Solvents which are poor for one block and good for the other block preferentially lead to the formation of lateral structures. Time-resolved in-situ GISAXS measurements allowed us to follow the formation of lateral structures in the vapor, giving insight into the time scales and the mechanisms involved.

Monday

1. P. Černoch, P. Štěpánek et al., Eur. Polym. J., accepted.

CPP 7.7 Mon 16:00 Poster B

Recent developments at BW4 / HASYLAB — •A. TIMMANN, S.V. ROTH, R. GEHRKE, S. HU, F.-U. DILL, M. DOMMACH, R. DÖHRMANN, and T. SCHUBERT — HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg, Germany

The beamline BW4 of HASYLAB, Hamburg (Germany), is a dedicated materials science beamline [1]. The main experimental techniques used are transmission small-angle x-ray scattering (TSAXS) and grazing-incidence SAXS (GISAXS). With the implementation of the microfocus option at BW4 scanning experiments have become possible [1]. After the major refurbishment of the beamline in 2004 and 2005, we focussed on upgrading and introducing necessary sample environments. This includes a new stretching cell allowing to draw film shaped samples to elongations up to 640mm with drawing velocities from 0.1 up to 1200 mm/min keeping the beam position on the sample fixed. Presently, several force sensors with a measuring range up to 500N are available now, which will be upgraded to 1kN. For GISAXS, a heating stage for polymeric samples has been commissioned. In-situ sample observation is now possible with a high-resolution video camera. Based on recent experimental results, we present the upgraded capabilities of BW4.

[1] S.V. Roth et al., Rev. Sci. Instr. 77, 085106 (2006)

CPP 7.8 Mon 16:00 Poster B Structure and changes of thin block copolymer films during vapor treatment — •zHENYU DI¹, CHRISTINE PAPADAKIS¹, DORTHE POSSELT², and DETLEF-M SMILGIES³ — ¹Physikdepartment E13, TU München, 85747 Garching, Germany — ²IMFUFA, Roskilde University, Dänemark — ³CHESS, Cornell University, Ithaca NY, USA

The mesoscopic structures formed by diblock copolymers in thin film geometry are interesting for a variety of applications. However, selfassembly leads to domain structures with domain walls and defects. Vapor treatment has been shown to be an efficient way to increase the long-range order.

We have studied the structural changes in thin films of poly(styreneb-butadiene) (PS-PB) diblock copolymers and their kinetics during vapor treatment. In this system, the initial lamellar orientation (parallel or perpendicular) can be controlled by the block copolymer molar mass [1]. We have investigated both initial orientations as well as the influence of the solvent selectivity and the film thickness. Insitu grazing-incidence small-angle x-ray scattering (GISAXS) is ideally suited because of its good time resolution ("sec) [2]. We found that in addition to swelling of the films, lamellar reorientation takes place on the time scale of minutes. Complex processes and transient states were encountered. In some cases, improved long-range order was achieved. [1] P. Busch, D. Posselt, D.-M. Smilgies, C.M. Papadakis et al.

Macromolecules 36, 8717 (2003) and Macromolecules, in press.

[2] D.-M. Smilgies, P. Busch, C.M. Papadakis, D. Posselt, Synchr. Rad. News 15(5), p. 35 (2002).

CPP 7.9 Mon 16:00 Poster B

Thin films of diblock copolymers having one crystalline block — ●CHARLES DARKO¹, EZZELDIN METWALLI¹, IOAN BOTIZ², GÜNTER REITER², DAG W BREIBY³, STEPHAN V ROTH⁴, DETLEF-M SMILGIES⁵, and CHRISTINE M PAPADAKIS¹ — ¹Physikdepartment E13, TU München, James-Franck-Str. 1, D-85747 Garching — ²Institut de Chimie de Surfaces et Interfaces, CNRS, Mulhouse, France — ³Niels Bohr Institute, University of Copenhagen, Denmark — ⁴Hasylab at DESY, Hamburg — ⁵CHESS, Cornell University, Ithaca NY, USA

In thin films of semicrystalline diblock copolymers, the final structure formed depends on the competition between (i) the order-disorder transition of the diblock copolymer, (ii) the crystallization of the crystallisable block, and (iii) the virification of the amorphous block. We have studied lamellae-forming poly(styrene-b-ethylene oxide) diblock copolymers differing in molar mass. Combining grazing-incidence small and wide-angle X-ray scattering with high-resolution grazingincidence X-ray diffraction, we obtain information on the inner structures on a large range of length scales and can compare them to the surface textures from optical and atomic-force microscopy. For the lowest molar mass sample, we find that the surface textures are different from the ones of poly(ethylene oxide) homopolymer films and that, depending on crystallization temperature, confined crystallization or breakout occur.

CPP 7.10 Mon 16:00 Poster B

The microfocus SAXS/WAXS beamline at PETRA III / DESY — •S.V. ROTH, R. DÖHRMANN, H. FRANZ, R. GEHRKE, U. HAHN, R. RÖHLSBERGER, H. SCHULTE-SCHREPPING, N. SCHWARZ, and E. WECKERT — HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg, Germany

Among the first beamlines to be built at PETRA III is the microfocus small- and wide-angle x-ray scattering beamline μ SAXS/WAXS. This beamline will exploit the excellent photon beam properties of the low emittance source PETRA III to provide micro- and nanofocused beams in dedicated end-stations with ultra-high intensity and resolution in real and reciprocal space. Targeting at scanning investigations at multiple length scales, the areas of research include in-situ experiments as well as brilliance demanding novel methods like microbeam grazing incidendence small-angle x-ray scattering (μ GISAXS) [1] and microbeam SAXS tomography [2]. The current layout foresees a largeoffset double crystal monochromator and compound refractive on-axis optics for microfocusing. The projected beam sizes for routine user operation range from 110 nm- 40μ m. The design of the beamline especially allows for combining ultra small-angle x-ray scattering (USAXS) with a microfocused beam (μ USAXS). We will present the present layout of the μ SAXS/WAXS beamline introducing the projected capabilities of this new micro- and nanofocus scattering beamline at PETRA III.

S.V. Roth et al., Appl. Phys. Lett. 88 (2006) 021910
 C.G. Schroer et al., Appl. Phys. Lett. 88 (2006) 164102

CPP 7.11 Mon 16:00 Poster B High Pressure SAXS/WAXS using a Diamond Anvil Cell — •RONALD GEBHARDT, MANFRED BURGHAMMER, MICHAEL HAN-FLAND, MOHAMED MEZOUAR, and CHRISTIAN RIEKEL — European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France

The possibility of using a diamond anvil cell for SAXS/WAXS studies on small confined volumes has been explored at the ESRF ID13 beamline. As a demonstration experiment, single potato starch granules were pressurized up to 700 MPa at 20°C. In this pressure range a two-phase process was proposed (1,2). Scanning SAXS/WAXS experiments were performed with an about 1 micron beam. A Raman spectrometer was used to determine the pressure from the ruby fluorescence. The experimental setup is explained and first experimental results are shown. 1) Svensson E., Eliasson A. C. (1995) Carbohydrate Research, 26, 171-176 2) Rubens P., Heremans K. (2000) Biopolymers, 54, 524-530

CPP 7.12 Mon 16:00 Poster B Spin-Echo Neutron Reflectivity on Diblock-Copolymer Films — •MAX NÜLLE, ADRIAN RÜHM, MARTON MAJOR, JÁNOS MAJOR, and HELMUT DOSCH — Max Planck Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart

SERGIS (Spin-Echo Resolved Grazing Incidence neutron Scattering) is a recently developed novel neutron scattering technique which we employ at the new neutron/X-ray reflectometer N-REX+ at FRM II. In contrast to conventional scattering methods, SERGIS measures the lateral structure and morphology of surfaces and thin film systems in real space. The spatial resolution is achieved by measuring the total polarization of the scattered beam, without the usual need to collimate the beam in the direction of interest. Therefore SERGIS combines a high neutron flux with the ability to characterize structures from the nanometer scale up into the micron range, and can thus yields novel information about both equilibrium and time-dependent phenomena on these length scales. As an example, we employ SERGIS to study morphologies produced by dewetting phenomena in thin polymer films. These experiments are complemented by detailed atomic force microscopy investigations. First results on thin diblock-copolymer films will be presented.

CPP 7.13 Mon 16:00 Poster B Ellipsometric Light Scattering: The Spectroscopic Approach — •ARNE STARK¹, ANDREAS ERBE², KLAUS TAUER¹, and RENNARD SIGEL¹— ¹MPI of Colloids and Interfaces, D-14476 Golm — ²Institute of Physics, Academia Sinica, Taiwan

We present first results obtained by Spectroscopic Ellipsometric Light Scattering (SELS). The discussion is complemented by an analysis of the general robustness of ELS against polydispersity effects.

Ellipsometric light scattering is based on Mie theory to analyze the scattering of polarized light by suspended particles in the colloidal range. Similar to standard ellipsometry this technique has an enhanced sensitivity to interface effects, allowing to investigate e.g. (multiple) coatings on particles or adsorbed surface layers.

First experimental results obtained with a multi-wavelength apparatus are presented: augmenting the method to a spectroscopic technique extends the resolution considerably. The camera detector allows a simultaneous investigation of a range of scattering angles and speeds up the measurements. Light of different wavelengths is selected by interference filters from a mercury lamp. Thus, it is established experimentally that coherence of the light source is not required.

All ellipsometric methods yield ratios of eigenvalues of the optical system under investigation. Consequently ELS exhibits an averaging behavior that is distinctly different from normal static light scattering. It is shown theoretically and experimentally that information regarding structural details of the suspended particles is robustly preserved in the presence of moderate sample polydispersity.

CPP 7.14 Mon 16:00 Poster B $\,$

Polymer coated micro mechanical cantilever arrays — •SEBASTIAN K. NETT^{1,2}, GUNNAR KIRCHER¹, and JOCHEN S. GUTMANN^{1,2} — ¹Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany — ²Institute for Physical Chemistry, Johannes Gutenberg University, Jakob-Welder-Weg 10, D-55099 Mainz

Functional layers can turn micro mechanical sensors consisting of an array of eight cantilevers into specific sensing systems for chemical or biological applications. We showed before that tethered polymers are robust and sensitive for analytes. To access individual cantilevers inkjet printing is a versatile approach. Using the automatic pipetting system, Nano-PlotterTM (GeSiM) the solution for tethering is applied contact less in small droplets directly onto the cantilever. Small droplets tend to evaporate in a few seconds. On the other hand anchoring the molecules to the surface need some time due to kinetic and diffusion processes. Therefore room temperature Ionic Liquids which have a negligible vapour pressure are incorporated in the coating step. The small geometry of the cantilever (500 to 1000 μ m length, 90 μ m width, 1 to 5 μ m of thickness) rises problems with the standard techniques for characterising the functional layer. To overcome these characterization problems, we used the μ -focus option at the GISAXS Line BW4 at the HASYLAB in Hamburg for detailed studies.

CPP 7.15 Mon 16:00 Poster B

Investigation of lubrication in natural joints by neutron reflectometry — •THOMAS KALTOFEN¹, THOMAS GUTBERLET², MAXIMILIAN WOLFF³, ROLAND STEITZ⁴, and REINER DAHINT¹ — ¹Angewandte Physikalische Chemie, Universität Heidelberg — ²Paul-Scherrer-Institut, Villigen, Schweiz — ³Experimentalphysik IV - Festkörperphysik, Universität Bochum — ⁴Hahn-Meitner-Institut, Berlin

Despite their high medical relevance, the principles of lubrication in natural joints are still unclear. It is generally accepted, that the pres ence of hyaluronic acid (HA), the main component of the synovial liquid, plays an important role for the low friction observed. Furthermore, it is assumed that surface active lipids participate in the lubrication. Using a model system of lipid bilayers deposited on a polyelectrolyte (PE) cushion and in contact with HA solution, we started to investigate the effects of pressure and shear forces, as experienced by natural joints, on the internal structure of the SiO₂/PE/lipid/HA interface and the bulk HA solution by neutron reflectometry (NR), complemented by in situ ellipsometry and quartz crystal microbalance (QCM-D) measurements. Only on positively charged polyelectrolyte surfaces, the successful build-up of the model system could be demonstrated. By NR, the existence of an irreversibly absorbed, highly hydrated HA layer on top of the lipid membrane was proven. For shear rates above $2.5~\mathrm{min^{-1}}$ a swelling of the HA layer has been observed. Pressure dependent studies are presently underway.

CPP 7.16 Mon 16:00 Poster B

Influence of degree of branching in LLDPE on its physical properties — \bullet STEFAN FISCHER¹, DIETER MEINHARDT², BERNHARD RIEGER², and OTHMAR MART1¹ — ¹Institute of Experimental Physics, University of Ulm, 89069 Ulm, Germany — ²Institute of Inorganic Chemistry II, University of Ulm, 89069 Ulm, Germany

Novel metallocene catalysts allow the polymerization of linear low density polyethylene (LLDPE) with controlled molecular weight directly from ethylene without the need for (more expensive) higher alkanes [1]. The influence of the degree of branching and the molecular weight on the physical properties has been analyzed with several methods, including tensile tests, AFM (atomic force microscopy), DSC (differential scanning microscopy), WAXS (wide angle x-ray scattering) and SAXS (small angle x-ray scattering). The LLDPE samples have been compared with commercially available high and low density polyethylenes (HDPE and LDPE). The results will be presented.

[1] Dieter Meinhard, Marcus Wegner, Georgy Kipiani, Andrew Hearley, Peter Reuter, Stefan Fischer, Othmar Marti and Bernhard Rieger; JACS; submitted

CPP 7.17 Mon 16:00 Poster B Modelling the structure of fillers in rubber and their small angle scattering — •KLAUS NUSSER, GERALD JOHANNES SCHNEIDER, and DIETMAR GÖRITZ — Universität Regensburg, Universitätsstr. 31, 93053 Regensburg

Silicas are technically important fillers for elastomers with respect to several applications. In such a filler-rubber system the mechanical properties strongly depend on the kind and the concentration of the filler. Despite being cruciable for the adjustment of high performance materials, the exact correlation between the morphology of the filler and the related reinforcement of the material is still unknown.

An up-to-date constitutive model suggests that isotropic silica primary particles form fractal clusters, which work as a basic unit for larger cluster structures. This notion was gained by the analysis of small angle X-ray scattering curves, which show regions of constant slope in a log-log plot. However, conclusions from scattering curves are not unique. In order to examine the assumptions made in constitutive models, numerical investigations were performed. Scattering structures were generated and their scattering curves were calculated by means of a computer. In particular, the origin of regions of constant slope in log-log depicted scattering curves was investigated.

CPP 7.18 Mon 16:00 Poster B

Side chain crystallization in soft and rigid confinement — •E. HEMPEL¹, H. BUDDE², M. HAHN², and M. BEINER¹ — ¹Martin-Luther-Universität Halle-Wittenberg, Institut für Physik, D-06099 Halle (Saale), Germany — ²Fraunhofer Pilotanlagenzentrum für Polymersynthese und -verarbeitung, Value Park, Bau A74, D-06258 Schkopau, Germany

The side chain crystallization of poly(n-octadecyl methacrylate) [PODMA] under confinement is studied in a series of microphaseseparated block copolymers containing PODMA cylinders with diameters in the range 10-20nm. The glass temperature of the matrix is systematically varied in the range 50...-30°C by choosing a morphous poly(n-alkyl methacrylates) with three to eight alkyl carbons per side chain as second component of the block copolymer. Since the crystallization temperature of the PODMA block is about 25°C crystallization occurs either in a glassy or in a highly viscous environment. The influence of the matrix properties on crystallization kinetics and internal structure of the PODMA domains is investigated by DSC and X-ray scattering. A central question of this study is whether or not the block copolymer morphology is changing due to side chain crystallization in the PODMA domains under conditions where the matrix material is soft and chemically not too different from the crystallizable component.

CPP 7.19 Mon 16:00 Poster B Reversible Tuning of Block Copolymer Domain Spacings via Electric Fields — •KRISTIN SCHMIDT¹, HEIKO SCHOBERTH¹, HELMUT HÄNSEL¹, THOMAS WEISS², VOLKER URBAN³, ALEXANDER BÖKER¹, and GEORG KRAUSCH¹ — ¹Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany — ²European Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France — ³Oak Ridge National Lab (ORNL), Oak Ridge, TN 37831, USA

We investigate the influence of electric fields on the domain spacing of a lamellar forming diblock copolymer solution by time-resolved synchrotron small angle X-ray scattering. As a model system we use a polystyrene-b-polyisoprene block copolymer dissolved in toluene or tetrahydrofurane. We find a significant dependence of the characteristic spacing on the electric field strength. For lamellae aligned parallel to the electric field direction we observe a decreasing lamellar distance with increasing field strength, while for perpendicularly orientated lamellae the domain size is increasing. We investigate the influence of the electric field strength, the degree of phase separation, molecular weight, composition and the polarity of the solvent. Furthermore we monitor the relaxation kinetics and show the revesibility of the changes in domain spacing on application and turn off of the electric field.

Monday

CPP 7.20 Mon 16:00 Poster B Scaling behavior of the reorientation kinetics and changes in the phase behavior of block copolymers exposed to elec-- •Heiko G. Schoberth¹, Kristin Schmidt¹, Thomas tric fields -M. WEISS², AGUR SEVINK³, ANDREI V. ZVELINDOVSKY⁴, ALEXANDER BÖKER¹, and GEORG KRAUSCH¹ — ¹Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany — $^2\rm European$ Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France — ³Leiden Institute of Chemistry, Universiteit Leiden, The Netherlands — ⁴Department of Physics, Astronomy & Mathematics, University of Central Lancashire, Preston PR1 2HE, United Kingdom We have followed the reorientation kinetics of various block copolymer solutions exposed to an external electric DC field by time-resolved svnchrotron small-angle X-ray scattering (SAXS). The characteristic time constants follow a power law indicating that the reorientation is driven by a decrease in electrostatic energy. Moreover, the observed exponent suggests an activated process in line with the expectations for a nucleation and growth process. When properly scaled, the data collapse onto a single master curve spanning several orders of magnitude both in reduced time and in reduced energy. The power law dependence of the rate of reorientation derived from computer simulations based on dynamic density functional theory (MesoDyn) agrees well with the experimental observations. In addition, we observe an influence of the electric field on the order disorder temperature and phase separation in our block copolymer solutions. For further investigations we study this effect by birefringence and SAXS.

CPP 7.21 Mon 16:00 Poster B Characterisation of structural changes during deformation and relaxation of semi-crystalline polymers by SAXS — •KONRAD SCHNEIDER¹ and PETER BÖSECKE² — ¹Leibniz-Institut für Polymerforschung Dresden, Hohe Str. 6, 01069 Dresden — ²European Synchrotron Radiation Facility (ESRF), BP 220, F38043 Grenoble, France

Time resolved small angle x-ray scattering using synchrotron radiation allows to follow up structural changes during deformation and relaxation of semi-crystalline polymers. On the example of polypropylene as well as high-density polyethylene copolymers the changes of the structure in the crystalline and in the amorphous domains were followed during the three characteristic stages of the load-displacement curves: The elastic stage and the plastic range composed of the stage of the lowering load in the force-displacement-curve (yielding) and the strain hardening. It is found that most rigorous changes are observed during yielding, whereas changes on a scale of second during relaxation are more pronounced than during the loading steps.

CPP 7.22 Mon 16:00 Poster B Upgrades of two SANS diffractometers at the Munich reactor FRM-II — •HENRICH FRIELINGHAUS, AUREL RADULESCU, PETER BUSCH, VITALY PIPICH, ALEXANDER IOFFE, DIETEMAR SCHWAHN, and DIETER RICHTER — Forschungszentrum Jülich GmbH, Jülich Centre of Neutron Science, D-52425 Jülich

Political decisions made the Jülich reactor FRJ-2 shut down, and the high performance instruments are moved to Munich now. The two SANS diffractometers are transferred, and refurbished in a second step in order to meet the world leading machines. Neutron polarization and polarization analysis will be possible to study magnetic samples. Supermirrors and ³He filters will be installed. Aspherical neutron MgF₂ lenses aim at two goals: 10 to 20 times higher intensity and a resolution of $\Delta Q = 10^{-4}$ Å. The lenses will be cooled to minimize the thermal diffuse scattering. A high resolution detector ($\Delta x = 0.5$ mm) allows to collect the high resolution scattering patterns. To operate with high resolution at finite Q a chopper placed behind the selector will reduce the wavelength uncertainty to 1% and better by a TOF analysis. The newly developed TiSANE mode will be possible: The neutron pulses will be triggered by a periodic external field at the sample in concert with the projected time-dependent scattering collected by the detector. We expect to resolve kinematic processes in the range of 2μ s to 5ms and above. In this mode the Q-resolution typically is not improved. The GISANS option allows to study the lateral structure of thin films in the range of 10 to 1000Å with a free depth resolution. Here we aim at soft condensed matter and magnetic films.

CPP 7.23 Mon 16:00 Poster B

Focusing-mirror ultra-small-angle neutron scattering (US-ANS) instrument of Research Centre Jülich at FRM-2 Reactor — EMMANUEL KENTZINGER¹, •AUREL RADULESCU^{1,2}, ALEXAN- DER IOFFE^{1,2}, PETER-PAUL STRONCIWILK^{1,2}, JÖRG STELLBRINK¹, DI-ETMAR SCHWAHN¹, THOMAS BRÜCKEL^{1,2}, and DIETER RICHTER^{1,2} — ¹Institute for Solid State Research, Research Centre Jülich, 52425 Jülich, Germany — ²Jülich Centre for Neutron Sciences (JCNS), Research Centre Jülich, 52425 Jülich, Germany

Biological, colloidal and macromolecular samples presenting characteristic length scales from nanometer up to micron-scale are usually investigated by combining USANS at double-crystal diffractometers (DCD) and SANS at conventional pinhole cameras. In principle, the Q-range of both classes of instruments overlaps but the required instrumental settings push both techniques to their limits, mainly due to signal-to-noise level and the reduced flux at sample position. The KWS3 USANS instrument of Research Centre Jülich is the worldwide unique instrument running on the principle of a one-to-one image of an entrance aperture on a two-dimensional position sensitive detector by neutron reflection from a double-focusing toroidal mirror. The instrument is just relocated at the FRM-2 reactor in Garching where it will permit to perform SANS studies within a Q-range between $4x10^{-5}$ and 10^{-3} Å⁻¹ with considerable advantages over the DCD and conventional SANS instruments. The working principle and recent use of KWS3 in investigations of multiscale aggregates formed by poly(ethylene-butene) random copolymers in solution are reported.

 $\begin{array}{c} \mbox{CPP 7.24} & \mbox{Mon 16:00} & \mbox{Poster B} \\ \mbox{Microbeam GISAXS investigation of sol-gel templated} \\ \mbox{nanccomposite films } & - \bullet J. \mbox{PERLICH}^1, \mbox{M. MEMESA}^2, \mbox{J.S.} \\ \mbox{GUTMANN}^{2,3}, \mbox{S.V. ROTH}^4, \mbox{and P. MÜLLER-BUSCHBAUM}^1 & - {}^1 TU \\ \mbox{München, Physik-Department LS E13, James-Franck-Str. 1, D-85748} \\ \mbox{Garching (Germany)} & - {}^2 \mbox{Max-Planck Institute for Polymer Research,} \\ \mbox{Ackermannweg 10, D-55128 Mainz (Germany)} & - {}^3 \mbox{Institute for Physical Chemistry, Johannes Gutenberg University, Jakob-Welder-Weg 10, D-55099 Mainz (Germany) & - {}^4 \mbox{HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg (Germany)} \\ \end{array}$

We focus on the creation of nanostructured TiO2 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. For the preparation of the ${\rm TiO2}$ nanocomposite films we combine the amphilic diblock-copolymer PS-b-PEO with an inorganic sol-gel chemistry. Under these conditions a so-called good-poor-solvent pair induced phase separation leads to the formation of the nanostructures by film preparation via spin-coating. 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 synchrotron beamline BW4 of the DESY HASYLAB. The investigation is complemented by surface and thin film sensitive probes. We acknowledge financial support by the project MU 1487/5-1.

CPP 7.25 Mon 16:00 Poster B The new Jülich Neutron Spin Echo Spectrometer J-NSE at the FRM-II — •OLAF HOLDERER^{1,2}, MICHAEL MONKENBUSCH^{1,2}, REINHARD SCHÄTZLER^{1,2}, and DIETER RICHTER^{1,2} — ¹Jülich Centre for Neutron Science (JCNS), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany — ²Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany

Neutron spin echo (NSE) spectroscopy is a well-suited method for studying the dynamics of soft matter systems such as glasses, polymers and complex liquids and paramagnetic properties of e.g. spin glasses. The Jülich NSE spectrometer has been in operation at the Jülich research reactor FRJ-2 since 1996. It has been transferred now to the new research reactor FRM-II of the TU München, where it is in the comissioning phase and will continue with user service this year. The J-NSE will operate at an neutron guide end position, giving access to the wavelength band of about 4.5 to 16 Å. New correction coils have been designed and manufactured, allowing to use higher currents in the main precession coils.

A larger neutron guide exit of 60x60 mm, the higher neutron flux and the better correction elements push the performance of the instrument to fourier times $\lambda{=}1$ ps to about 350 ns, with a q-range of q=0.02 - 1.5 1/Å.

 $\begin{array}{c} CPP \ 7.26 \quad Mon \ 16:00 \quad Poster \ B \\ \textbf{GISAXS studies on titania ultrathin films with different morphologies — YAJUN CHENG¹, MARKUS WOLKENHAUER¹, GINA BUMBU¹, \\ STEPHAN ROTH³, JOCHEN GUTMANN^{1,2}, and •YAJUN CHENG¹ — ¹Max \\ \end{array}$

Monday

Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany — ²Institute for Physical Chemistry, Johannes Gutenberg University, Welder Weg 11, D-55099 Mainz — ³HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg

Ultrathin TiO2 films showing rich morphologies are achieved by using sol-gel chemistry coupled with an amphiphilic polystyrene-blockpoly (ethylene oxide) (PS-b-PEO) diblock copolymer as a structuredirecting agent. The block copolymer undergoes a good-poor-solvent pair induced phase separation in a mixed solution of 1,4-dioxane, concentrated hydrochloric acid (HCl) and Titanium tetraisopropoxide (TTIP). By adjusting the weight fractions of 1,4-dioxane, HCl, and TTIP, inorganic-block-copolymer composite films containing a variety of different morphologies are obtained. Through calcination the amorphous Titania composite films can be converted to crystalline anatase phase. Based on the local characterization of AFM and SEM on the various different morphologies of the film. Grazing incidence small angle x-ray scattering (GISAXS) is further conducted to study the lateral structure of the film over large length scale. As a complementary method, x-ray reflectivity experiment is made to investigate the electron density gradient normal to the substrate. As a result, the combination of local imaging characterization and average x-ray scattering experiment provide a deep insight into the structure of the film.

 $\label{eq:CPP 7.27} \begin{array}{c} {\rm CPP \ 7.27} & {\rm Mon \ 16:00} & {\rm Poster \ B} \end{array}$ Beitrag abgesagt — •XXX XXX —

CPP 7.28 Mon 16:00 Poster B Nanostructure evolution during melting and oriented crystallization of polypropylene studied by in-situ SAXS — •ULRICH NÖCHEL¹, ARMANDO ALMENDÁREZ CAMARILLO¹, NORBERT STRIBECK¹, and STEPHAN VOLKHER ROTH² — ¹University of Hamburg, Institute TMC, Hamburg, Germany — ²HASYLAB at DESY, Hamburg, Germany

Polypropylene film with high uniaxial orientation and lamellar structure is melt-annealed at temperatures between $168^\circ\mathrm{C}$ and $175^\circ\mathrm{C}$ followed by different cooling programs during which 2D SAXS patterns are continuously taken in order to identify the mechanisms of crystallization. Peculiar "cross-patterns" observed during the early stages of crystallisation clearly demonstrate the mechanism of "building of lamellae from blocks" as proposed by Strobl. The evolution of the patterns under quiescent conditions shows that the complementary model of a "cross-hatched structure" cannot be applied. 2D SAXS data from various crystallization series[1] are evaluated by means of the CDF method[2] for a quantitative description of the crystallization mechanisms.

[1] Fibr. Text. EE (2005), 13(5), 27-29

[2] J. Appl. Cryst. (2001), 34(4), 496-503

CPP 7.29 Mon 16:00 Poster B $\,$

Optical diffraction measures the filling of superhydrophobic surfaces. — **HELMUT RATHGEN and FRIEDER MUGELE** — University of Twente, Physics of Complex Fluids, Postbus 217, 7500AE Enschede, The Netherlands

A hydrophobic surface with a periodic texture of period of order $1\mu m$ is a superhydrophobic surface and an optical grating at the same time. A drop deposited on such a superhydrophobic optical grating can float on the texture like a fakir (Cassie-Baxter state) or it can penetrate the texture, soaking the grooves of the grating completely (Wenzel state). In the prior case, micrometer size liquid-gas interfaces are formed at the rims of the grooves. The diffractive properties of the optical grating (diffraction efficiencies of all diffraction orders) now depend on position and curvature of these micro menisci. Realspace information can be obtained by comparing measured diffraction data to a theoretical model based on Multilayer Rigorous Coupled Wave Analysis. We use this to investigate filling state and microscopic curvature at a superhydrophobic surface for a true water-vapor two phase system as a function of external pressure. We find: 1. The surfaces fill (transition from Cassie-Baxter to Wenzel state) at a critical pressure that depends on geometry and hydrophobicity in agreement with a prediction based on capillary theory. 2. Filling cannot be reversed by decreasing the external pressure to the vapor pressure. Our method is relevant as a technique of optical detection for a range of problems in micro- and nanofluidics, such as tracer free liquid detection in nanochannels or surface cavitiation.

 $CPP\ 7.30 \ \ Mon\ 16:00 \ \ Poster\ B$ Microemulsion-Polymer Systems Studied with Elastic and

Inelastic Neutron Scattering — •TINKA SPEHR^{1,2}, BERNHARD FRICK¹, and BERND STUEHN² — ¹Institut Laue-Langevin, Grenoble, FRICK¹, and BERND STUEHN² — ⁻²Institute of Solid State Physics, TU Darmstadt, Germany France -We study a microemulsion consisting of water, decane or toluene and AOT forming water-in-oil droplets. The addition of amphiphilic triblock copolymer leads to the interconnection of the droplets. We are investigating the structural and dynamical behavior of this model system for a transiently linked network with different neutron scattering techniques. Also this system is used to realize soft confinement of the water. Neutron Small Angle Scattering showed increasing ordering of the droplets upon polymer addition. Measurements on pure microemulsions have been carried out on a time-of-flight and a neutron backscattering instrument to study the effect of spatial soft confinement on water. Two different droplet sizes have been investigated (diameters of about 3 and 10 nm). Elastic scans from 315 K to 2 K showed a deeper undercooling of the water confined in the smaller droplets. Inelastic scans have been carried out at temperatures between 300 K and 250 K. The dynamic structure factor displays a complex shape clearly deviating from one single Lorentzian. The combination of spatial restriction and wall effects on the dynamics will be discussed. Neutron Spin Echo can probe shape fluctuations of the droplet shell [3]. We investigated the effect of polymer addition on the elastic properties of the surfactant shells.

[2] J. Huang, S. Milner, B. Farago, D. Richter (1987), PRL 59, 2600

 $\begin{array}{c} \mbox{CPP 7.31} & \mbox{Mon 16:00} & \mbox{Poster B} \\ \mbox{Water uptake and exchange kinetics of polyelectrolyte films:} \\ \mbox{A neutron reflectometry study} & - \mbox{eRegINE V. KLITZING^1, JOHN} \\ \mbox{WONG^1, and ROLAND STEITZ}^2 & - \mbox{^1TU Berlin, Stranski-Laboratorium,} \\ \mbox{Straße des 17. Juni 124, D-10623 Berlin} & ^2\mbox{Hahn-Meitner-Institut,} \\ \mbox{SF1, Glienicker Str. 100, D-14109 Berlin} \\ \end{array}$

The sequential layer-by-layer adsorption of polyanions and polycations to build polyelectrolyte multilayers has triggered enormous interest in their potential uses in a wide range of fields, from photonic to pharmaceutical applications. We will show that the conformation of the solvent swollen films - prior to drying - is determined by the initial adsorption conditions, but can be altered ex-situ by exposure to a liquid phase of very high ionic strength. Recently it has been observed that the swelling depends on the charge of the outermost layer. In the PAH/PSS system we saw that assemblies with PSS as the outermost layer swell more than those with PAH outside. A neutron reflectivity study of this effect in addition indicated the existence of two kinds of water, bound with different strength within the films. Beside an unexpected two-step kinetics of swelling, the reflectivity curves of the layers against vacuum before and after re-hydration in D2O vapor did not agree. It was only after subsequent re-hydration in saturated H2O vapor that the initial and final reflectivity curves against vacuum superimposed. We will discuss our findings in the context of polyion complex formation, interdigitation and film imperfections.

CPP 7.32 Mon 16:00 Poster B

Horizontal ToF-Neutron Reflectometer REFSANS at FRM II Munich: Potential and First Experimental Results — •REINHARD KAMPMANN¹, MARTIN HAESE-SEILER¹, VALERI KUDRYASHOV¹, BERT NICKEL², PETER MÜLLER-BUSCHBAUM⁴, CHRIS-TINE PAPADAKIS⁴, WILHELM FENZL², ANDREAS SCHREYER¹, ERICH SACKMANN³, and JOACHIM RÄDLER² — ¹GKSS-Forschungszentrum Geesthacht GmbH, D-21502 Geesthacht, Germany — ²Department für Physik, Ludwig-Maximilians-Universität, D-80539 München, Germany — ³Physik-Department E22, TU-München, D-85748 Garching, Germany — ⁴Physik-Department E13, TU-München, D-85748 Garching, Germany

The reflectometer REFSANS allows to perform comprehensive analyses of vertical and lateral surface and interface structures by means of specular and off-specular neutron reflectivity as well as small-angle neutron scattering at grazing incidence (GISANS). All measurements can be performed on the air-water interface (horizontally aligned sample). REFSANS has been put into operation in 2005/06. Its performance is demonstrated by results of first reflectivity as well as GISANS measurements on nanostructured polymer and metallic films. The potential of this novel instrument for measuring weak off-specular scattering, GI-SANS and extremely low specular reflectivity including the case of a strongly incoherently scattering substrate is discussed.

This work has been supported by the German Federal Ministry of Education, Research and Technology (BMBF) under contracts 03-KA5FRM-1 and 03-KAE8X-3.

Bilateral Colloquium TUM- HASYLAB

The polymer-metal interface (Real-time observation of metal-on-polymer deposition kinetics)

Tagunsort: TU München, Garching, Physics Department, room 3734 Datum: 25.09.2007, 10:00 am

Speaker:	(30min)
10:00-10:30	C. Papadakis - Introduction to polymer films and surfaces
10:30-11:00	R. Röhlsberger - Introduction to metal films and interfaces
11:00-11:30	P. Müller-Buschbaum - Introduction to GISAXS
11:30-12:00	H. Graafsma - Detector developments at DESY
12:00-13:30	Lunch break
13:30-14:00	Schlage oder S. Couet - Sputtering technique
14:00-14:30	S.V. Roth - Metal polymer interfaces using μ GISAXS at P3
14:30-15:00	E. Metwalli Ali - Structure formation of metals at patterned surfaces
15:00-15:30	G. Kaune - Metal contact on polymer films for photovoltaic applications
15:30-16:00	Coffee break
16:00-16:30	W. Wang - Metal-hydrogel composites
16:30-17:00	A.Timmann - Outlook on future real time investigations at BW4
17:00-17.30	R. Gehrke - Future sources
19:00	Dinner



2nd Workshop "GISAXS - An Advanced Scattering Method"

May 09, 2007 - May 11, 2007 at HASYLAB / DESY, Notkestr. 85, D-22607 Hamburg (Germany)

Programme

Wednesday, May 09, 2007

08:00-09:00 Registration

Section 1 – Lectures

Welcome

140

09:00-09:30	Current and Future Photon Science at DESY	
	R. Gehrke (DESY Hamburg, Germany)	

Session Modelling

09:30-10:15	Theoretical Foundations of GISAXS
	M. Rauscher (MPI Metallforschung, Stuttgart, Germany)
10:15-11:00	Simulation of Grazing Incidence Small-Angle X-ray
	Scattering from Nanostructures
	R. Lazzari (Univ. Paris, France)

Break

15:15-15:45

Session Quantum	Objects
11:15-12:00	GIXD on Quantum Dots
	T. Metzger (ESRF Grenoble, France)
12:00-12:30	GISAXS Studies on Dielectric Thin Films
	J.P. Simon (CNRS & Univ. J. Fourier Grenoble, France)
12:30-13:00	GISAXS on Quantum Dots
	H. Okuda (Univ. Kyoto, Japan)
13.00-14.30	Lunch
Session Polymer-	Engineered Thin Films
14:30-15:15	Kinetic Investigations in Thin Polymer Films
	A. Gibaud (Univ. Le Mans, France)

and µm-Length Scales

Pushing the Limits of GISAXS - Nanobeams

P. Müller-Buschbaum (TU Munich, Germany)

15:45-16:15	GISAXS on Ordered Polymer Films G. Fritz (Univ. Graz, Austria)
Break	
16:30-18:30	Poster Session (contributed presentations)
19:00-22:00	Workshop Dinner
	Thursday, May 10, 2007
Session Biophy 09:00-09:45	sics & Sensors GISAXS & Biophysics
09:45-10:15	J. Salditi (Univ. Gollingen, Germany) Surface Sensors Investigated with µGISAXS J.S. Gutmann (MPI f. Polymer research, Mainz, Germany)
Break	
Session Nanoco	omposite thin films
10:30-11:15	Nanostructured Thin Films
11:15-11:45	GISAXS on Advanced Nanostructured Materials A. Frömsdorf (Univ. Hamburg, Germany)
Session Instrum	nentation
11:45-12:15	Introduction to BW4 A Timmann (DESY Hamburg, Germany)
12:15-12:45	GISAXS at BW4 & Future Possibilities S.V. Roth (DESY Hamburg, Germany)
12:45 - 14:15	Lunch
14:15-14:45	30 min Safety Course S.V. Roth (DESY Hamburg, Germany)
14:45-15:00	Organization into Groups
Section 2 - Prac 3 groups up to 1(3h with including	tical training) persons, rotating between (1), (2), (3) each part: 20min break to change between stations
15:15 - 18:15	Practical training part 1 (1) Measurement @ BW4 Tutors: P. Müller-Buschbaum / S.V. Roth (2) Data tractment: LS, Cutmann / A. Timmann

(2) Data treatment: J.S. Gutmann / A. Timmann(3) Simulation: R. Lazzari / R. Gehrke

	Physik-Department E13	ANNUAL REPORT 2007
18:30-20:30	Poster Session (contributed presentations) Refreshments	
	Friday , May 11, 2007	,
09:00-12:00	Practical training part 2	
12:00-13:00	Lunch	
13:00-16:00	Practical training part 3	

Conference website: <u>https://indico.desy.de/conferenceDisplay.py?confld=111</u>

Wissenschaftlerinnen am Physikdepartment

Wege zur Finanzierung einer Nachwuchsgruppe

Dienstag 16. Januar 2007 um 17.15 Uhr HS2 im Physikdepartment Technische Universität München 85748 Garching

> Eine Initiative der Frauenbeauftragten des Physikdepartments

Prof. Christine Papadakis

144						PHYSIK	-Depa	RT	MENT	E13			ANNU	AL REP	ORT T	2007
Thursday 26.7.05	Breakfast	9:00 Departure					13:00 Return									
Wednesday 25.7.05	Breakfast	Material Science (Neuhaus) P. Kudejova G. Vanue	J. Reper S. Stüber	F. Yang Theorie W. Schirmacher	Break	Biophysics/Proteins (Nickel) B. Nickel (25 min) M-S. Appavou W. Doster /S. Busch	A. Oaspar A. Ostermann	Lunch	Methods (Georgii) H. Breitkreuz W Klein	K. Lorenz D. Visser	J. Wudtke	Coffee	Positrons (Schreckenbach) C. Hugenschmidt (25 min) J. Mayer	Ph. Phkart B. Löwe K. Schreckenbach	Dinner 20:00 B. Löper: n-Bestrahlung	
Tuesday 24.7.05	Breakfast	Polymers 3 (Frielinghaus) H. Frielinghaus (25 min) V. Divich	R. Ivanova Ch. Smuda	A. Kulkarnı A. Radulescu	Break	Magnetism (Pfleiderer) Ch. Pfleiderer (25 min) T. Keller (25 min) M. Abul Kashem	1. Menadaene A. Sazonov	Lunch		14:30 Exentsion: Hiking into the	"Hafenlohr Tal"				Dinner 20:00 S. Paul: UCN (E18, TUM)	
Monday 23.7.05		8:00 Departure (Bus at the Pforte FRM-II)				12:00 Arrival		Lunch	Polymers 1 (Müller-Busch.) P. Müller-Buschbaum (25 min) F. Merwalli	Z. Di M. Nülle	C. Darko	Coffee	JF. Moulin Polymers 2 (Papadakis) Ch. Papadakis (25 min)	J. Perlich W. Wang M. Ruderer	Dinner	
	8:00	8-30_10-30	00.01 -00.0		10:30 -11:00	11:00 -13:00		13:00 -14:30	06.71_05.41	07.01_00.11		16:20 -16:40	16:40 -18:30		18:30	

3rd FRM-II Workshop on Neutron Scattering – 23.7-26.7.05 Burg Rothenfels am Main
ANNUAL REPORT 2007

Abul Kashem M.	Magnetic nanoparticles in supported polymer structure probed with GISAXS
Appavou M-S.	Influence of pressure on the dynamics of Human hemoglobin. A quasi-elastic neutron scattering study
Breitkreuz, H.	Spektrale Charaktersierung des Spaltneutronenstrahls
Darko C.	Thin films from crystalline diblock copolymers studied using GIXD and GISAXS
Doster W. (/Busch S.)	Protein Diffusion in Biological Cells
Frielinghaus, H.	Tailormade Microemulsions with Polymer Additives
Gaspar A.	Using polarized neutrons for the study of the dynamical structure of proteins
Häußler, W.	Struktur und Dynamik von Proteinen in Lösung
Hugenschmidt, C.	Positron annihilation spectroscopy at NEPOMUC
Ivanova R.	Multicompartment polymeric hydrogels studied using SANS
Kaune G.	GISAXS Investigation of Organic-Anorganic Nanostructures for Photovoltaics
Keller, T.	Introduction to Larnor diffraction
Klein, W.	Mo2B5 vs. Mo2B4 - Strukturlösung mit allen Mitteln
Kudejova, P.	PGAA and PGAI for the ANCIENT CHARM project and other applications
Kulkarni,A.	Smart hydrogels from amphiphilic triblock copolymers
Lorenz, K.	First measurements with the new multi filter at ANTARES
Löwe, B.	Beam brightness enhancement with a gas-moderator
Mayer, J.	Positron annihilation induced Auger-electron spectroscopy on Cu-covered Si(100) and on Au-covered copper
Mehaddene, T.	Dynamics of magnetic shape memory alloys investigated by inelastic neutron scattering
Metwalli Ali E.	Water-vapor swelling response of thin casein films: A GISANS study
Moulin JF.	In situ characterisation of a fluidic cell by means of GISAXS
Müller-Buschbaum P.	TOF-GISANS at REFSANS
Nickel, B.	Reflectivity experiments on membranes and membrane associated protein layers
Nülle, M.	Investigation of the dewetting of thin diblock copolymer films with SERGIS and complementary methods
Ostermann, A.	Dynamical properties of the hydration shell of proteins
Papadakis C.	The inner structure of thin block copolymer films studied using NR ans GISANS
Perlich J.	Investigation of the solvent content in spin-coated thin polymer films by neutron reflectometry at MIRA
Pfleiderer, C. Pikart, Ph.	Magnetism Coincident Doppler-broadening sepctroscopy on Al-Sn-layers
Pipich, V.	The diblock copolymer as an external field in A/B/A-B polymer mixtures
Radulescu, A.	Wide-Q SANS investigation of hierarchical morphologies formed by crystalline and semi-crystalline polymers in soloutions
Repper, J.	Residual stress analysis on IN718 samples
Ruderer M.	Characterisation of semi-conducting polymer blend thin films for photovoltaic applications
Sazonov, A.	Crystallographic and magnetic study of synthetic cobalt-olivine
Schirmacher W.	Theory of scattering from vibrational excitations of disordered solids
Schreckenbach, K.	Production and lifetime determination of the negatively charged Positronium ion
Smuda, Ch.	QENS und PFG-NMR-Untersuchungen zur Diffusion in Schmelzen mittelkettiger Moleküle
Stüber S.	Em levitation for time-of-flight spectroscopy - studying the dynamics of metallic melts
Visser,D.	Ancients objects investigated with neutron beams
Wang W.	Swelling of Diblock and Triblock Copolymer Thin Hydrogel Films probed with x-ray and neutron scattering
Wudke, J.	Erste Messungen und neue Perspektiven am Höchstfluss-Rückstreuspektrometer SPHERES
Yang F.	Hydrous silicates: structure and dynamics
Zhenyu D.	Time-resolved GISAXS on thin diblock copolymer films

9 Publications, talks and funding

9.1 Publications

M. M. Abul Kashem, J. Perlich, L. Schulz, S.V. Roth, W. Petry, P. Müller-Buschbaum *Maghemite nanoparticles on supported diblock Copolymer* Macromolecules, **40**, 5075-5083 (2007)

S. V. Adichtchev, N. V. Surovtsev, J. Wiedersich, A. Brodin, V. N. Novikov, E. A. Rössler *Fast relaxation processes in glasses as revealed by depolarized light scattering* J. Non-cryst. Solids, **353**, 1491 (2007)

M. Allalen, T. Mehaddene, H. Bouzar Monte Carlo simulations of the $L1_0$ long-range order relaxation in dimensionally reduced systems

J. Phys.: Condens. Matter 19, 36218 (2007)

M. Appavou, W. Doster, S. Busch and T. Unruh *The effect of packing on internal motions of hydrated myoglobin* MRS Bulletin (Material Research Science, 2007) Quasielastic Neutron Scattering Conference 2006, p.117-116 Editors: P. Sokol, H. Kaiser, D. Baxter, R.Pynn, D. Bossev, M. Leuschner

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, W. Petry, P. Müller-Buschbaum *Maghemite nanoparticles on supported diblock copolymer nanostructures* Macromolecules, **40**, 5075-5083 (2007)

T.B. Bonné, K. Lüdtke, R. Jordan, C.M. Papadakis Effect of Polymer Architecture of Amphiphilic Poly(2-oxazoline) Copolymers on the Aggregation and Aggregate Structure Macromol. Chem. Phys. **208**, 1402 (2007)

T.B. Bonné, C.M. Papadakis, K. Lüdtke, R. Jordan Role of the Tracer in Characterizing the Aggregation Behavior of Aqueous Block Copolymer Solutions Using Fluorescence Correlation Spectroscopy Colloid Polym. Sci. **285**, 491 (2007)

S. Busch, W. Doster, S. Longeville, V.G. Sakai and T. Unruh *Protein diffusion in concentrated solutions and biological cells* MRS Bulletin (Material Research Science, 2007) Quasielastic Neutron Scattering Conference 2006, p.117-116 Editors: P. Sokol, H. Kaiser, D. Baxter, R.Pynn, D. Bossev, M. Leuschner

P. Busch, D. Posselt, D.-M. Smilgies, M. Rauscher, and C.M. Papadakis The Inner Structure of Thin Films of Lamellar Poly(Styrene-b-Butadiene) Diblock Copolymers as Revealed by Grazing-Incidence Small-Angle Scattering Macromolecules **40**, 630 (2007)

Y.-J. Cheng, P. Müller-Buschbaum, J. S. Gutmann Ultrathin anatase TiO₂ films with stable vesicle morphology templated by PMMA-b-PEO** Small, **3**, 1379-1382 (2007) W. Doster and S. Longeville *Microscopic diffusion and hydrodynamic interactions in red blood cells* Biophys.J. (2007) 93:1360-1368

W. Doster *The dynamical transition of proteins, concepts and misconceptions* Eur.Biophys.J. (2007) accepted

W. Doster *The new Munich neutron source FRM 2, overview and uses for biological studies* American Institut of Physics (AIP) Conference Proceedings (2007) p. 16

A. M. Gaspar, M. S. Appavou, S. Busch, T. Unruh, W. Doster Dynamics of well-folded and natively disordered proteins in solution: a time-of-flight neutron scattering study Eur.Biophys.J., 2007

A. M. Gaspar

Methods for analytically estimating the resolution and intensity of neutron time-of-flight spectrometers The case of the TOFTOF spectrometer **arXiv:0710.5319v1, physics.ins-det (2007)**

R. Gilles, A. Ostermann, W. Petry Monte Carlo simulations of the new Small-Angle Neutron Scattering instrument SANS-1 at the Heinz Maier-Leibnitz Forschungsneutronenquelle J. Appl. Cryst. 40, s428 - s432 (2007)

C. Jarousse, P. Lemoine, P. Boulcourt, A. Röhrmoser, W.Petry *Monolithic UMO Full Size Prototype Plates for IRIS V Irradiation'* **Proceeding of IGORR - RRFM**, March 11. - 15.2007, Lyon, France

R. Jungwirth, N. Wieschalla, W. Schmid, A. Röhrmoser, W. Petry, Ch. Pfleiderer *Thermal Conductivity of Heavy-Ion-Bombarded U-Mo/AL Disperion Fuel* Proceedings on the 11th International Topical Meeting in Research Fuel Management (RRFM) 2007, Lyon, 7

M. Memesa, Y. Cheng, J. Perlich, P. Müller-Buschbaum, J. S. Gutmann *Integrated spin-on barrier layers a reasonable idea?* Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, **37**, 315-320, (2007)

E. Metwalli, U. Slotta, C. Darko, S. V. Roth, T. Scheibel, C. M. Papadakis *Structural changes of thin film from recombinant spider silk proteins upon post-treatment* Appl. Phys. A **89**, 655 (2007)

J.F. Moulin, S. V. Roth, P. Müller-Buschbaum *Flow at interfaces: A new device for x-ray surface scattering investigations* **Rev. Sci. Instr., accepted for publication (2007)**

P. Müller-Buschbaum, J. Perlich, M. M. Abul Kashem, L. Schulz, S.V. Roth, Y.J. Cheng, J. S. Gutmann

Cominatorial investigation of nanostructures formed in a titanium dioxide based nanocomposite

film on top of flour-doped tin oxide layers Phys.stat.sol (RRL) **1**, 119-121 (2007)

P. Müller-Buschbaum, E. Bauer, E. Maurer, A. Nelson, R. Cubitt In-situ neutron reflectometry probing competitive swelling and de-swelling of thin polystyrene films Phys.stat.sol (RRL) **1**, R68-R70 (2007)

P. Müller-Buschbaum, E. Bauer, E. Maurer, S. V. Roth, R. Gehrke, M. Burghammer Large-scale and local-scale structures in polymer-blend films: a grazing-incidence ultra-smallangle X-ray scattering and sub-microbeam grazing-incidence small-angle X-ray scattering investigation

J. Appl. Cryst., 40, S341-S345 (2007)

P. Müller-Buschbaum, R. Gebhardt, S. V. Roth, E. Metwalli, W. Doster *Effect of calcium concentration on the structure of casein micelles in thin films* Biophys. J., **93**, 960-968 (2007)

P. Müller-Buschbaum, T. Ittner, E. Maurer, V. Körstgens, W. Petry *Pressure-sensitive adhesive blend films for low-tack applications* Macromol. Mater. Eng., **292**, 825-834 (2007)

J. Neuhaus, W. Petry *Forschungsneutronenquelle Heinz Maier-Leibnitz (FRM II)* Neutron News **18**, 2, 13 - 15 (2007)

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**, s361 (2007)

J. Perlich, L. Schulz, M.M. Abul Kashem, Y.-J. Cheng, M. Memesa, J.S. Gutmann, S.V. Roth, P. Müller-Buschbaum *Modification of the morphology of P(S-b-EO) templated thin TiO2 films by swelling with PS homopolymer* Langmuir **23**, 10299-10306 (2007)

W. Petry, J. Neuhaus *Neutronen nach Maß* Physik-Journal 6/7, 31-37 (2007)

V. V. Ponkratov, J. Wiedersich, J. Friedrich, J. M. Vanderkooi *Experiments with proteins at low temperature: What do we learn on properties in their functional state?* J. Chem. Phys., **126**, 166104 (2007)

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 Macromol. Rapid Commun. **28**, 579 (2007)

S. Rajagopalan, T. Asthalter, V. Rabe, U. van Bürck, F. E. Wagner. S. Laschat *Mössbauer spectroscopy and nuclear inelastic scattering studies on polynuclear oxo-bridged iron*

catalysts - first results Hyperfine Interactions, in print 2007

A. Röhrmoser, W. Petry, C. Jarousse, J. Falgoux, A. Chabre, P. Lemoine *Results of UMO dispersive fuel plates irradiations for FRM II* **Proceedings of IGORR - RRFM 2007, March 11 - 15, 2007, Lyon, France**

A. Röhrmoser, W. Petry, P. Boulcourt, A. Chabre, S. Dubois, P. Lemoine, Ch. Jarousse, J.L. Falgoux *Status of UMo full size plates irradiation program IRIS-TUM* Proceedings of the RRFM - IGORR 2007, March 11 - 15, 2007, Lyon –, 8

S. V. Roth, T. Autenrieth, G. Grübel, C. Riekel, M. Burghammer, R. Hengstler, L. Schulz, P. Müller-Buschbaum In situ observation of nanoparticle ordering at the air-water-substrate boundary in colloidal solutions using x-ray nanobeams Applied Physics Letters **91**, 091915 (2007)

S. V. Roth, P. Müller-Buschbaum, A. Timmann, J. Perlich, R. Gehrke *Structural changes in gradient colloidal thin gold films deposited from aqueous solution* J. Appl. Cryst. **40**, S346-S349 (2007)

W. Schirmacher, G. Ruocco, T. Scopigno *Acoustic attenuation in glasses and its relation with the boson peak* Phys. Rev. Lett. **98**, 025501 (2007)

I. Sergueev, A.I. Chumakov, T.H. Deschaux Beaume-Dang, R. Rüffer, C. Strohm, U. van Bürck *Nuclear forward scattlering for high energy Mössbauer transitions* Phys. Rev. Lett. **99**, 097601 (2007)

G.V. Smirnov, U. van Bürck, J. Arthur, G.S. Brown, A.I. Chumakov, A.Q.R. Baron, W. Petry, S.L. Ruby *Currents and fields reveal the propagation of nuclear polaritons through a resonant target* Phys. Rev. A **76**, 043811 (2007)

C. Smuda, G. Gemmecker, T. Unruh *Quasi-elastic and inelastic neutron scattering study of methyl group rotation in solid and liquid pentafluoroanisole and pentafluorotoluene* J. Phys. Chem. submitted

M. M. Somoza, J. Wiedersich, J. Friedrich *Protein elasticity determined by pressure tuning of the tyrosine residue of ubiquitin* J. Chem. Phys., **127**, 095102, (2007)

T. Unruh, A. Meyer, J. Neuhaus, W. Petry, W. *The Time-of-flight Spectrometer TOFTOF* Neutron News **18**, 22 - 24 (2007)

T. Unruh, J. Neuhaus, W. Petry *The high-resolution time-of-flight spectrometer TOFTOF* Nuclear Instruments and Methods in Physics Research **A 580**, 1414-1422 (2007) F.M. Wagner, P. Kneschaurek, S. Kampfer, A. Kastenmüller, B. Loeper-Kabasakal, W. Waschkowski, H. Breitkreutz, A. Röhrmoser, W. Petry *The Munich Fission Neutron Therapy Facility MEDAPP at FRM II* Radiotherapy and Oncology (2007)

J. Wiedersich, S. Köhler, A. Skerra, J. Friedrich *Temperature and pressure dependence of thermodynamic protein stability: the engineered fluorescein-binding lipocalin FluA shows an elliptic phase diagram* **Proc. Natl. Acad. Sci. USA, submitted**

9.2 Talks given by members of E13

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, P. Müller-Buschbaum Investigation of structures in diblock copolymer film containing magnetic nanoparticles DPG Frühjahrstagung, Regensburg, March 2007

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, P. Müller-Buschbaum *Correlated roughness in polymer film containing magnetic nanoparticles* 2007 NSTI Nanotechnology and Trade Show (Nanotech 2007), Santa Clara, USA, May 2007

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, P. Müller-Buschbaum *Magnetic nanoparticles in supported polymer structure* 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

S. Busch, W. Doster, S. Longeville, V. Garcia Sakai, T. Unruh *Microscopic protein diffusion at high concentration* DPG Frühjahrstagung, Regensburg, March 2007

C. Darko, C.M. Papadakis *Thin films of crystalline diblock copolymers: studied by GISAXS and GIWAXS* **3rd FRM II workshop on neutron scattering, Rothenfels, July 2007**

Z. Di, C.M. Papadakis Structural changes of thin block copolymer films in solvent vapor 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

W. Doster *Picosecond dynamics of proteins and function* Workshop Proteins at Work, Perugia, Italy, June 2007

W. Doster *The new Munich neutron source FRM2: Overview and biological applications* Summer School, Nuclear Physics Methods and Accelerators in Biology and Medicine, Prague, July 2007

W. Doster *Neutron scattering applications to biology* Summer School, Nuclear Physics Methods and Accelerators in Biology and Medicine, Prague, July 2007

W. Doster

Protein diffusion in concentrated solutions and biological cells 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

W. Doster

Neutron scattering analysis of protein dynamics International Workshop, Light-induced Dynamcis of Proteins, Freising, October 2007

W. Doster Wie erzeugt man Energie? Physik kompakt für Anfänger Wissenschaftsnacht Garching, 13.10. 2007

A. M. Gaspar, W. Doster, M.-S. Appavou, S. Busch, M. Diehl, W. Haeussler, R. Georgii, S. Masalovich

Using polarization analysis to separate the coherent and incoherent scattering from protein samples

3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

J. S. Gutmann, P. Müller-Buschbaum,

Hierarchisch strukturierte Filme aus selbstkapselnden anorganisch-organischen Hybridmaterialien

DFG Schwerpunktbegutachtung SPP1181, NANOMAT, Darmstadt, July 2007

R. Ivanova

Micellar hydrogels of poly(2-oxazoline) copolymers containing fluorophilic, hydrophilic and lipophilic blocks

DPG Frühjahrstagung, Regensburg, March 2007

R. Ivanova *Multicompartment polymer hydrogels studied using SANS*3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

C. Jarousse, P. Lemoine, P. Boulcourt, A. Röhrmoser, W. Petry Monolithic UMO full size prototype plates for IRIS V irradiation IGORR - RRFM 2007, Lyon, France, March 2007

R. Jungwirth, N. Wieschalla, W. Schmid, W. Petry, Chr. Pfleiderer *Thermal conductivity of heavy-ion-bombarded U-Mo/Al dispersion fuel* RRFM conference 2007, Lyon, France, March 2007

G. Kaune GISAXS characterisation of gold deposition on composite films for photovoltaics 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

G. Kaune Metal contact on polymer films for photovoltaic applications Bilateral colloquium TUM-HASYLAB: The polymer-metal interface, Garching, September 2007

G. Kaune, J. Perlich, M. Memesa, S. V. Roth, J. S. Gutmann, P. Müller-Buschbaum *Creating nano-structured films from self-encapsulated inorganic-organic hybrid materials* International Soft Matter Conference 2007, Aachen, October 2007 G. Kaune

Anorganische-organische Hybridmaterialien - Neue Lösungen für die Photovoltaik Seminar "Struktur und Eigenschaften kondensierter Materie", TU Chemnitz, November 2007

A. Kulkarni, K. Troll, C.M. Papadakis *Stimuli-sensitive self-organizing polymeric hydrogels*3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

A. Kulkarni SAXS investigation of stimuli-sensitive block copolymer micelles Workshop of the SPP 1259 'Intelligent Hydrogele', Berlin, October 2007

T. Mehaddene Inelastic neutron scattering in Ni₂MnGa shape memory alloys DPG Frühjahrstagung, Regensburg, March 2007

T. Mehaddene *Phonon investigations in the austenitic and martensitic phases of NiMnGa* **3rd FRM II workshop on neutron scattering, Rothenfels, July 2007**

T. Mehaddene Lattice dynamics in Ni- and Cu-based shape memory alloys from inelastic neutron scattering (Invited Talk) EUROMAT 2007, Nürnberg, September 2007

T. Mehaddene *Dynamical properties of magnetic NiMnGa and NiMnSn shape memory alloys* Klausur DFG-Schwerpunktprogramm 1239, Wessling, September 2007

E. Metwalli, J.-F. Moulin, P. Müller-Buschbaum Structural characterization of copolymer thin films using TOF-GISANS at REFSANS REFSANS workshop, Garching, 16.03.2007

E. Metwalli

Aminosilane treated glass substrates for DNA microarrays 6th International Symposium on Silane and other Coupling Agents, University of Cincinnati, Ohio, USA, June 2007

E. Metwalli, V. Körstgens, P. Müller-Buschbaum
Evaluation of interfacial adhesion between a model pressure sensitive adhesive and chemically modified surfaces using the probe tack method
6th International Symposium on Polymer Surface Modification, University of Cincinnati, Ohio, USA, June 2007

E. Metwalli, P. Müller-Buschbaum Nanopattering of gold particles using a polymer template: in-situ GISAXS study Bilateral Colloquium, TUM - HASYLAB: The polymer-metal interface, Garching, 25.09.2007

E. Metwalli, J.-F. Moulin, M. Rauscher, P. Müller-Buschbaum Structural investigation of diblock copolymer thin films using TOF-GISANS at REFSANS 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007 E. Metwalli, J.-F. Moulin, . Müller-Buschbaum, Structural characterization of polystyrene-block-polyisoprene diblock copolymer thin films with TOF- GISANS at REFSANS REFSANS workshop, Garching, 16.03.2007

J.-F. Moulin, P. Müller-Buschbaum A scattering approach to fluidics Meeting of the SPP 1164 Nano- and Microfluidics, Bad Honnef, August 2007

P. Müller-Buschbaum *Probing long-ranged correlations with high resolution GIUSAXS* Satellite meeting - status and perspectives of SAXS/WAXS/GISAXS, Hamburg, 25.01.2007

P. Müller-Buschbaum, Exploring local structures with micro- and nano-beams (Keynote Lecture ESRF Users' Meeting, Grenoble, France, February 2007

P. Müller-Buschbaum *Pushing the limits of GISAXS - nanobeams and micro-length scales* **2nd GISAXS workshop, HASYLAB at DESY, Hamburg, May 2007**

P. Müller-Buschbaum Nano-structured polymer films - relation between structure and function Kolloquium der Montanuniversität Leoben, Österreich, 21.05.2007

P. Müller-Buschbaum Development of instrumentation and methods for the investigation of surfaces and thin films Kolloquium der TU Berlin, 01.06.2007

P. Müller-Buschbaum, M.M. Abul Kashem, L. Schulz, S.V. Roth, V. Lauter-Pasyuk, W. Petry *Magnetic particles in supported polymer nano-structures* Seminar, Jülich Center of Neutron Science, Garching, 03.07.2007

P. Müller-Buschbaum, V. Körstgens Probe tack with oscillations Schwarzkopf, Hamburg, 09.07.2007

P. Müller-Buschbaum, Structural investigation of thin polymer films with TOF-GISANS at REFSANS 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

P. Müller-Buschbaum, J. Perlich, M. Memesa, J. S. Gutmann *Creating nano-structured films from self-encapsulated inorganic-organic hybrid materials* EUROMAT 2007, Nürnberg, September 2007

P. Müller-Buschbaum, E. Metwalli, W. Wang *Film thickness dependence of water storage in thin hydrogel films*11th Dresden Polymer Discussion Meeting, Meissen, September 2007

P. Müller-Buschbaum Introduction into GISAXS Bilateral colloquium TUM-HASYLAB: The polymer-metal interface, Garching, 25.09.2007

P. Müller-Buschbaum Magnetic and structural properties of thin polymer films with embedded super-paramagnetic γ - Fe_2O_3 nano-particles Nanoworkshop - 3rd International Workshop on Polymer/Metal Nanocomposites, Kobe, Japan, October 2007

P. Müller-Buschbaum *Probing lateral structures at interfaces with GISANS* Workshop on Neutron Scattering in Strongly Correlated Electron Systems, Garching, October 2007

P. Müller-Buschbaum, V. Körstgens *Probe tack with oscillations* Diskussionstreffen "Haftklebstoffe", Düsseldorf, 29.10.2007

P. Müller-Buschbaum Structural investigation of thin polymer films with TOF-GISANS at REFSANS 1st User Meeting of the FRM II, Garching, 30.10.2007

P. Müller-Buschbaum

Correlation between morphology and photophysical properties in photoactive polymer blend films Gutachtertreffen zum SPP 1355 "Elementary processes of Organic Photovoltaics", Bad Honnef, November 2007

P. Müller-Buschbaum Correlation between structure and adhesive properties at the interface of a solid with a copolymer melt Gutachtertreffen zum SPP 1369 "Polymer-Solid Contacts: Interfaces and Interphases", Bonn, November 2007

P. Müller-Buschbaum, V. Körstgens Probe tack and hot melt PSAs Diskussionstreffen "Haftklebstoffe", Düsseldorf, 10.12.2007

P. Müller-Buschbaum, V. Körstgens Probe tack on casein films - some ideas Diskussionstreffen "Haftklebstoffe", Düsseldorf, 10.12.2007

J. Neuhaus, W. Petry, T. Mehaddene Magnetic, magnetoelastic and dynamical properties of martensitic Heusler alloys: phonon spectra Klausur DFG-Schwerpunktprogramm 1239, Wesseling/Bonn, September 2007

C.M. Papadakis Structure and stability of thin block copolymer films JCNS Seminar, Garching, 14.03.2007 C.M. Papadakis

Nanostrukturierte Blockcopolymerfilme: Matrizen für die Nanotechnologie 18th Edgar-Lüscher-Seminar, Klosters, Switzerland, February 2007

C.M. Papadakis, P. Müller-Buschbaum, A. Laschewsky *Responsive selbstorganisierte polymere Hydrogele* Workshop of the SPP1259 'Intelligente Hydrogele', Aachen, 07.03.2007

C.M. Papadakis *Thin films of lamellar block copolymers* **REFSANS workshop, Garching, 16.03.2007**

C.M. Papadakis Vom nanostrukturierten dünnen Film zum responsiven Hydrogel - Blockcopolymere, eine flexible Materialklasse Festkörperkolloquium, Physikdepartment, TU München, 26.04.2007

C.M. Papadakis Fluorescence correlation spectroscopy - a tool to investigate micelle formation 8th International Congress on Optical Particle Characterization, Graz, 09.07.2007

C.M. Papadakis *The inner structure of thin block copolymer films: GISAXS and NR* **3rd FRM II workshop on neutron scattering, Rothenfels, July 2007**

C.M. Papadakis *Thin block copolymer films - interaction of polymers with solids* Bilateral colloquium TUM-HASYLAB: The polymer-metal interface, Garching, September 2007

C.M. Papadakis *Fluorescence correlation spectroscopy (Tutorial)* Workshop of the SPP 1259 'Intelligente Hydrogele', Berlin, 04.10.2007

C.M. Papadakis

Distinct time regimes during vapor treatment of thin diblock copolymer films: a time-resolved in-situ grazing-incivence SAXS study

The II Workshop on Applications of Synchrotron Light to Non-Crystalline Diffraction in Materials and Life Sciences, Madrid, 15.10.2007

J. Perlich *Polymer nanocomposite films for photovoltaic applications* 18th Edgar Lüscher Seminar, Klosters, Switzerland, February 2007

J. Perlich, M. Memesa, Y.-J. Cheng, J.S. Gutmann, P. Müller-Buschbaum Investigation of sol-gel templated polymer nanocomposite films for photovoltaic applications 3rd International Workshop on Polymer/Metal Nanocomposites, Kobe, Japan, October 2007

W. Petry Die Entwicklung hochdichter Brennstoffe für den FRM II Vortrag im Bundesministerium für Bildung und Forschung (BMBF), Bonn, 07.03.2007

W. Petry

Licht im Dunkeln - Neutronen für Forschung, Medizin und Industrie Carl-Orff-Gymnasium Unterschleißheim in der Reihe: Faszination Physik, Spitzenforschung in und um München, 09.05.2007

W. Petry

Podiumsdiskussion - Die Verwendung von Nukleartechniken: Verfolgen Deutschland und Frankreich die gleichen Ziele und Strategien?

Café Sciences et Culture - gemeinsame Veranstaltung des Bayerisch-Französischen Hochschulzentrums und des Institut Français München, 10.05.2007

W. Petry

Podiumsdiskussion: Technologie- und Energiepolitik für Europa. Weitere Teilnehmer: Etienne Klein (CEA), Prof. Dr. Detlev Ganten (Charité Berlin), Prof. Dr. Dr. h.c.F. Mayinger (LMU) Sommeruniversität Bayerisch-Französisches Hochschulzentrum (BFHS), Frauenchiemsee, 20.07.2007

W. Petry

The neutron source Heinz Maier-Leibnitz, a contribution by TUM to strengthen the European research area

T.I.M.E. at TU München, 04.10.2007

W. Petry

Neutronen als Sonde für wissenschaftliche und industrielle Anwendungen Neutronenstrahlen für angewandte Forschung im Bereich Materialentwicklung und Werkstofftechnik - RWTH Aachen, 10.10.2007

W. Petry

Podiumsdiskussion - Klimawandel, nein danke! Nuclear-Free Future Award - Symposium 2007, Salzburg

W. Petry

50 Jahre Neutronenforschung in Garching - und ihre Zukunft Festveranstaltung: 50 Jahre Neutronenforschung in Garching, 31.10.2007

W. Petry

Kernenergie in Deutschland - vom Winde verweht? Deutsche Bank Kapitalmarktforum - Investoren diskutieren mit Experten "Deutschland im Jahre 2020", 07.11.2007

W. Petry *FRM II - A brilliant new neutron source for materials science* Institut für Materialphysik im Weltraum, DLR, Köln, 13.11.2007

W. Petry *Research at FRM II*5th European Winter School NESY 2007, Research with Neutron and Synchrotron Radiation, Planneralm, Austria, March 2007

A. Röhrmoser, W. Petry, C. Jarousse, J. Falgoux, P. Boulcourt, A. Chabre, P. Lemoine *Results of UMO dispersive fuel plates irradiations for FRM II* IGORR - RRFM 2007, March 11-15, Lyon, France S.V. Roth, R. Gehrke, G. Jakopic, R. Röhlsberger, H. Walter, R. Domnick, M.M. Abul Kashem, P. Müller-Buschbaum

Structure and morphology of nanostructured noble metal-polymer bilayers for optical applications

3rd International Workshop on Polymer/Metal Nanocomposites, Kobe, Japan, May 2007

S. V. Roth, A. Veligzhanin, G. Jakopic, H. Walter, R. Domnick, O. Leupold, M. Kuhlmann, C. Schroer, B. Lengeler, R. Gehrke, M. M. Abul Kashem, P. Müller-Buschbaum, *Tailored polymer - metal nano-composites for optical applications* EUROMAT 2007, Nürnberg, September 2007

M. Ruderer

Characterisation of semi-conducting polymer blend thin films for photovoltaic applications **3rd FRM II workshop on neutron scattering, Rothenfels, July 2007**

W. Schirmacher Anomale Schwingungseigenschaften amorpher Festkörper Seminar, Freie Universität Berlin, 12.01.2007

W. Schirmacher, B. Schmid, G. Ruocco, T. Scopigno *The boson peak: theory of scattering from vibrational excitations in disordered materials* DPG Frühjahrstagung, Regensburg, March 2007

W. Schirmacher Spectral properties of disordered solids Seminar, TU Eindhoven, 15.05.2007

W. Schirmacher Sound waves in the presence of correlated disorder International Conference on Interacting Disordered Systems, Marburg, August 2007

W. Schirmacher Anomalous vibrational excitations in disordered materials Seminar, DESY, Hamburg, 06.12.2007

W. Schirmacher *Magnetic properties of small magnetic particles* Seminar, DESY, Hamburg, 07.12.2007

L. Schulz, S. Vallopilly, J. Perlich, M. M. Abul Kashem, S. V. Roth, P. Müller-Buschbaum, Magnetic and structural properties of thin polymer films with embedded superparamagnetic γ -Fe203 nanoparticles DPG Frühjahrstagung, Regensburg, March 2007

C. Smuda Dynamics of medium-chain molecules in colloidal drug carrier systems by QENS and PFG-NMR 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

S. Stüber, A. Meyer, T. Unruh *Quasielastic Neutron Scattering on Ni-Zr melts* DFG SPP "Phase Transitions in Multicomponent Melts" meeting, Bad Honnef, March 2007 S. Stüber, A. Meyer, D. Holland-Moritz, H. Hartmann, T. Unruh Interplay of structure and dynamics in liquid and undercooled AlNi melts DPG Frühjahrstagung, Regensburg, March 2007

S. Stüber, A. Meyer, D. Holland-Moritz, T. Unruh Electromagnetic levitation for time-of-flight spectroscopy 3rd FRM II workshop on neutron scattering, Rothenfels, July 2007

S. Stüber, A. Meyer, D. Holland-Moritz, T. Unruh Electromagnetic levitation - dynamics of metallic melts International Symposium on Time-Resolved Processes in Condensed Matter, Göttingen, September 2007

S. Stüber

Electromagnetic levitation for quasielastic neutron scattering Seminar, Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt, Köln, 09.10.2007

K. Troll

Stimuli-sensitive micelles from diblock copolymers (Keynote Lecture) Workshop of the SPP 1259 'Intelligente Hydrogele', Berlin, 04.10.2007

U. van Bürck

Coherence in nuclear resonant scattering of synchrotron radiation 37th Winter Colloquium on the Physics of Quantum Electronics, Snowbird, Utah, USA, 05.01.2007

W. Wang

Characterization and swelling behavior of diblock copolymer thin hydrogel films **3rd FRM II workshop on neutron scattering, Rothenfels, July 2007**

W. Wang

Characterization of hydrogel and metal-hydrogel composites Bilateral colloquium TUM-HASYLAB: The polymer-metal interface, Garching, 25.09.2007

J. Wiedersich, V. Ponkratov, M. Somoza, J. Vanderkoi, J. Friedrich *Proteins under pressure: spectroscopic determination of compressibilities* DPG Frühjahrstagung, Regensburg, March 2007

F. Yang, A. Meyer, J. Kaplonski, T. Unruh *Hydrous silicates: structure and dynamics - a neutron scattering study* **3rd FRM II workshop on neutron scattering, Rothenfels, July 2007**

F. Yang, A. Meyer, T. Unruh, J. Kaplonski In-situ study of dynamics in hydrous silicate melts with quasielastic neutron scattering 8th Silicate Melt Workshop, La Petite Pierre, October 2007

9.3 Poster

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, P. Müller-Buschbaum *Nanostructures in ultra-thin diblock copolymer film containing magnetic nanoparticles* HASYLAB Users' Meeting, DESY, Hamburg, Germany, 26.01.2007

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, W. Petry, P. Müller-Buschbaum Magnetic nanoparticles in supported polymer nanostructures 18th Edgar-Lüscher-Seminar, Klosters, Switzerland, February 2007

M. M. Abul Kashem, J. Perlich, L. Schulz, S. V. Roth, W. Petry, P. Müller-Buschbaum *Magnetic nanoparticles in supported polymer nanostructures* 2nd GISAXS workshop, HASYLAB at DESY, Hamburg, May 2007

C. Darko, E. Metwalli, I. Botiz, G. Reiter, D.W. Breiby, S.V. Roth, C.M. Papadakis *Thin films of crystalline diblock copolymers* HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

C. Darko, E. Metwalli, I. Botiz, G. Reiter, D.W. Breiby, S.V. Roth, C.M. Papadakis *Thin films of crystalline diblock copolymers* 18th Edgar-Lüscher-Seminar, Klosters, Switzerland, February 2007

C. Darko, E. Metwalli, I. Botiz, G. Reiter, D. W. Breiby, S. V. Roth, D.-M. Smilgies, C.M. Papadakis *Thin films of diblock copolymers having one crystalline block* DPG Frühjahrstagung, Regensburg, March 2007

C. Darko, I. Botiz, G. Reiter, D.W. Breiby, J.W. Andreasen, D.-M. Smilgies, S.V. Roth, C.M. Papadakis

Thin films of crystalline diblock copolymers: structure and nano-pore formation 2nd GISAXS Workshop, HASYLAB at DESY, Hamburg, May 2007

Z. Di, C. M. Papadakis, D. Posselt, D.-M. Smilgies *Transient states during vapor treatment of thin block copolymer films* 18th Edgar-Lüscher-Seminar, Klosters, Schwitzerland, February 2007

Z. Di, C.M. Papadakis, D. Posselt, D.-M. Smilgies *Structure and changes of thin block copolymer films during vapor treatment* DPG Frühjahrstagung, Regensburg, March 2007

Z. Di, C. M. Papadakis, D. Posselt, D.-M. Smilgies *Structure and changes of thin block copolymer films during vapor treatment* 2nd GISAXS workshop, HASYLAB at DESY, Hamburg, May 2007

A. M. Gaspar, M.-S. Appavou, S. Busch, W. Doster *Neutron scattering studies on the dynamical structure of disordered proteins: the case of caseins* **Proteins at Work 2007, Perugia, Italy, May 2007**

A. M. Gaspar, M.-S. Appavou, S. Busch, W. Doster *Time-of-flight neutron scattering studies on the dynamical structure of disordered proteins: the case of caseins*

4th European Conference on Neutron Scattering, Lund, Sweden, June 2007

R. Gebhardt, E. Metwalli, S. V. Roth, W. Doster, P. Müller-Buschbaum *Effect of calcium concentration on the structure of casein micelles in thin films.* DPG Frühjahrstagung, Regensburg, March 2007

R. Jungwirth, N. Wieschalla, W. Schmid, W. Petry, Chr. Pfleiderer *Thermal conductivity of heavy-ion-bombarded U-Mo/Al dispersion fuel* RRFM conference 2007, Lyon, France, March 2007

R. Kampmann, M. Haese-Seiller, V. Kudryashov, B. Nickel, P. Müller-Buschbaum, C.M. Papadakis, W. Fenzl, A. Schreyer, E. Sackmann, J. Rädler Horizontal ToF-Neutron reflectometer REFSANS at FRM II Munich: potential and first experimental results DPG Frühjahrstagung, Regensburg, March 2007

G. Kaune, M. Ruderer, P. Müller-Buschbaum Comparison between polymer-polymer and polymer-inorganic hybrid thin films for photovoltaic applications EUROMAT 2007, Nürnberg, September 2007

V. Körstgens, C.-C. Hsu, D. Paneque, E. Lorenz, P. Müller-Buschbaum Characterization of colloids, polymer solutions and nanoparticles suspensions flow by surface sensitive scattering DPG Frühjahrstagung, Regensburg, March 2007

T. Mehaddene, J. Neuhaus, W. Petry, K. Hradil, Ph. Bourges *Phonon measurements in magnetic shape memory alloys* 1st User Meeting of the FRM II, Garching, 30.10.2007

T. Mehaddene, J. Neuhaus, W.Petry

Interplay of magnetism and vibrational degrees of freedom in magnetic shape memory alloys Focus meeting of the SPP1239 "Magnetic field induced modification of microstructure and form of solid materials", Ringberg, February 2007

M. Memesa, Y. Cheng, S. Nett, J. Perlich, P. Müller-Buschbaum, J. S. Gutmann Integrated approaches in self assembled nanomaterials for photovoltaic applications EUROMAT 2007, Nürnberg, September 2007

E. Metwalli, U. Slotta, C. Darko, S. Roth, T. Scheibel, C. Papadakis Structural investigation of recombinant spider silk protein films HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

E. Metwalli, U. Slotta, C. Darko, S. Roth, T. Scheibel, C.M. Papadakis *Grazing-incidence X-ray scattering investigation on the structure of thin films of recombinant spider silk proteins* DPG Frühjahrstagung, Regensburg, March 2007

E. Metwalli, R. Gebhardt, A. Tolkach, J.-F. Moulin, V. Körstgens, S.V. Roth, R. Cubitt, P. Müller-Buschbaum Structural investigation of casein micelles in thin films DPG Frühjahrstagung, Regensburg, March 2007 E. Metwalli, R. Gebhardt, A. Tolkach, J.-F. Moulin, V. Körstgens, S.V. Roth, R. Cubitt, P. Müller-Buschbaum Structural investigation of casein micelles in thin films 2nd GISAXS workshop, HASYLAB at DESY, Hamburg, May 2007

E. Metwalli, R. Gebhardt, A. Tolkach, J.-F. Moulin, V. Körstgens, S.V. Roth, R. Cubitt, U. Kulozik, P. Müller-Buschbaum *Water-vapor swelling response of thin casein films* International Soft Matter Conference, Aachen, Germany, October 2007

E. Metwalli, J.-F. Moulin, M. Rauscher, P. Müller-Buschbaum Structual investigation of diblock copolymer thin films using TOF-GISANS 1st User Meeting of the FRM II, Garching, 30.10.2007

A. Meyer, S. Stüber, D. Holland-Moritz, O. Heinen, T. Unruh *Quasielastic neutron scattering on liquid Ni* 1st User Meeting of the FRM II, Garching, 30.10.2007

J.-F. Moulin, P. Müller-Buschbaum Surface scattering characterisation of colloid, polymer solutions and nanoparticle suspensions flow

DPG Frühjahrstagung, Regensburg, March 2007

J.-F. Moulin, S. V. Roth. and P. Müller-Buschbaum *Flows at interfaces : a scattering approach.* International Soft Matter Conference, Aachen, October 2007

J.-F. Moulin, S. V. Roth, P. Müller-Buschbaum A fluidic setup for GISAXS investigations of fluid/solid interfaces under flow. HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

J.-F. Moulin, P. Müller-Buschbaum, P. Uhlmann, M. Stamm In-situ investigation of non-equilibrium flow on gradient surfaces HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

J.-F. Moulin, V. Körstgens, E. Metwalli, W. Wang, S. V. Roth, P. Müller-Buschbaum Structure of polymer coatings established for advanced quantum efficiency of photomultiplier tubes

DPG Frühjahrstagung, Regensburg, March 2007

P. Müller-Buschbaum, S. V. Roth, R. Cubitt, M. Burghammer, C. Riekel Probing thin polymer films: A comparative GISAXS and GISANS investigation HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

P. Müller-Buschbaum, E. Metwalli, J.-F. Moulin, R. Cubitt Surface versus interface induced order in triblock copolymer films investigated with GISANS European Conference on Neutron Scattering (ECNS), Lund, Sweden, June 2007

P. Müller-Buschbaum

Correlation between morphology and photophysical properties in photoactive polymer blend films Gutachtertreffen zum SPP 1355, Elementary Processes of Organic Photovoltaics, Bad Honnef, November 2007 P. Müller-Buschbaum

Correlation between structure and adhesive properties at the interface of a solid with a copolymer melt

Gutachtertreffen zum SPP 1369, Polymer-Solid Contacts: Interfaces and Interphases, Bonn, November 2007

C.M. Papadakis, P. Černoch, C. Darko, E. Metwalli, S.V. Roth Effect of treatment with solvent vapor on the structure of thin diblock copolymer films HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

C.M. Papadakis, Z. Di, P. Busch, D. Posselt, D.-M. Smilgies Intermediate states in thin block copolymer films during treatment with solvent vapor Makromolekulares Kolloquium, Freiburg, 23.02.2007

C.M. Papadakis, P. Černoch, C. Darko, E. Metwalli, P. Štěpánek, D.-M. Smilgies, S. V. Roth

Formation of lateral structures in thin diblock copolymer film by vapour treatment DPG Frühjahrstagung, Regensburg, March 2007

C.M. Papadakis, Z. Di, E. Kentzinger, L. Willner, R. Kampmann, M. Haese-Seiller *Thin films of lamellar block copolymers studied by high-resolution neutron reflectrometry and GISANS*

Workshop on Neutron Scattering in Strongly Correlated Electron Systems, Garching, October 2007

C.M. Papadakis, Z. Di, E. Kentzinger, L. Willner, R. Kampmann, M. Haese-Seiller *TOF neutron reflectometry and TOF GISANS from thin, lamellar diblock copolymer films* **1st User Meeting of the FRM II, Garching, 30.10.2007**

J. Perlich, M. Memesa, Y.-J. Cheng, J.S. Gutmann, S.V. Roth, P. Müller-Buschbaum $\mu GISAXS$ investigation of sol-gel templated nanocomposite films at beamline BW4 HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

J. Perlich, M. Memesa, Y.-J. Cheng, J.S. Gutmann, S.V. Roth, P. Müller-Buschbaum *Microbeam GISAXS investigation of sol-gel templated nanocomposite films at beamline BW4* DPG Frühjahrstagung, Regensburg, March 2007

J. Perlich, M. Memesa, Y.-J. Cheng, J.S. Gutmann, S.V. Roth, P. Müller-Buschbaum *Microbeam GISAXS investigation of sol-gel templated nanocomposite films* 2nd GISAXS Workshop, HASYLAB at DESY, Hamburg, May 2007

J. Perlich, M. Memesa, Y.-J. Cheng, J.S. Gutmann, S.V. Roth, P. Müller-Buschbaum *Characterization of nanostructured films of inorganic-organic hybrid materials with X-ray scattering under grazing incidence* EUROMAT 2007, Nürnberg, September 2007

J. Perlich, V. Körstgens, E. Metwalli, L. Schulz, R. Georgii, P. Müller-Buschbaum *Solvent content in thin spin-coated polymer films* 1st User Meeting of the FRM II, Garching, 30.10.2007

T. Pöpperl, G. J. Schneider, P. Müller-Buschbaum, D. Göritz Macroscopically thick silica-rubber systems investigated using GISAXS DPG Frühjahrstagung, Regensburg, March 2007 S. V. Roth, A. Veligzhanin, H. Walter, R. Domnick, O. Leupold, R. Gehrke, P. Müller-Buschbaum

Polymer-based nanocomposites investigated with micro-GISAXS DPG Frühjahrstagung, Regensburg, March 2007

M. Ruderer, J.-F. Moulin, P. Müller-Buschbaum *Thin polymer blend films of conducting homopolymers* DPG Frühjahrstagung, Regensburg, March 2007

M. Ruderer, G. Kaune, P. Müller-Buschbaum Comparison between semi-conducting polymer-polymer and polymer-inorganic hybrid thin films

EUROMAT 2007, Nürnberg, September 2007

B. Sandow, D. Brossell, O. Bleibaum, W. Schirmacher Break-junction tunnel spectroscopy in the hopping regime DPG Frühjahrstagung, Regensburg, March 2007

B. Schmid, W. Schirmacher Theory of low-frequency Raman-spectroscopy in disordered solids DPG Frühjahrstagung, Regensburg, March 2007

 L. Schulz, S. Vallopilly, W. Schirmacher, S. V. Roth, R. Gehrke, M. Burghammer, C. Rieker, J. Perlich, M. M. Abul-Kashem, P. Müller-Buschbaum
 Structural and magnetic properties of polystyrene-b-polyisoprene copolymer films with embedded γ-Fe₂O₃ nanoparticles
 18. Edgar-Lüscher Seminar, Klosters, Switzerland, February 2007

L. Schulz, S. Vallopilly, W. Schirmacher, S. V. Roth, R. Gehrke, M. Burghammer, C. Rieker, J. Perlich, M. M. Abul-Kashem, P. Müller-Buschbaum *Structural and magnetic properties of polystyrene-b-polyisoprene copolymer films with embedded* γ -Fe₂O₃ *nanoparticles* Workshop Nanostructured Anvanced Materials, IFW Dresden, May 2007

I. Sergueev, T. Asthalter, U. van Bürck, A.I. Chumakov, C. Strohm, R. Rüffer, G.V. Smirnov, W. Petry *SRPAC: Basic features and first applications* 37th Winter Colloquium on the Physics of Quantum Electronics, Snowbird, Utah, USA, January 2007

I. Sergueev, T. Asthalter, U. van Bürck, A.I. Chumakov, C. Strohm, R. Rüffer, G.V. Smirnov, W. Petry *SRPAC: Basic features and first applications* NRS/IXS Workshop for PETRA-III, September 2007

C. Smuda, S. Busch, A. Gaspar, J. Neuhaus, W. Petry, T. Unruh *Quasielastic and inelastic neutron scattering at the time-of-flight spectrometer TOFTOF* 1st User Meeting of the FRM II, Garching, 30.10.2007

S. Stüber, A. Meyer, D. Holland-Moritz, H. Hartmann, T. Unruh *Quasielastic neutron scattering on refractory Al-Ni melts* 1st User Meeting of the FRM II, Garching, 30.10.2007 F. Varnik, B. Wu, D. Raabe, P. Truman, P. Uhlmann, M. Stamm, J.-F. Moulin, P. Müller-Buschbaum

Non-equilibrium flow on gradient surfaces: Fluid kinetics of droplets and particle motion Gutachtertreffen zum SPP 1164 Nano- & Microfluidics, Bonn, December 2007

W. Wang, P. Müller-Buschbaum Preparation and characterization of thermo-responsive polymer thin films HASYLAB Users' Meeting, DESY, Hamburg, 26.01.2007

W. Wang, J.-F. Moulin, J. Perlich, M. M. Abul Kashem, S.V. Roth, P. Müller-Buschbaum *Preparation and characterization of thermo-responsive polymer thin films* DPG Frühjahrstagung, Regensburg, March 2007

W. Wang, J.-F. Moulin, J. Perlich, M. M. Abul Kashem, S.V. Roth, P. Müller-Buschbaum *Preparation and characterization of thermo-responsive polymer thin films* 2nd GISAXS Workshop, HASYLAB at DESY, Hamburg, May 2007

W. Wang, A. Laschewsky, P. Müller-Buschbaum Preparation and characterization of nanocomposite films with switch effect DPG Frühjahrstagung, Regensburg, March 2007

J. Wiedersich, S. Köhler, J. Friedrich, A. Skerra Spectroscopy of protein denaturation: FluA reveals an elliptic phase diagram DFG Symposium, Freising, October 2007

F. Yang, A. Meyer, T. Unruh, J. Kaplonski *In-situ quasielastic neutron scattering on hydrous silicate melts* 1st User Meeting of the FRM II, Garching, 30.10.2007

9.4 Invited talks at E13

Dr. Fathollah Varnik, MPI Düsseldorf Lattice Boltzmann studies of liquid-vapor systems beyond equilibrium

Dr. Johannes Wiedersich, TU München (Weihenstephan) "Optical spectroscopy of proteins: Thermodynamic stability and mechanical properties"

Dr. Jens Wenzel Andreasen, Risø National Laboratory *X-ray scattering at Risø*

Prof. Friedrich Kremer, Universität Leipzig Experimente mit einzelnen Polymeren und einzelnen Kolloiden

Nora Kristen, Technische Universität Berlin Polyelectrolytes in Thin Films

Dr. Amit Kulkarni, Universität Potsdam Enzymatic Degradation Studies of Polymers for Biomedical Applications Prof. Jens-Uwe Sommer, Institut für Polymerforschung Dresden Equilibrium of Polymer Crystals

Prof. Bernd Stühn, Technische Universität Darmstadt Competition of Crystallization and Microphase Separation in Semicrystalline Confinement

Alexander Diethert, Universität Regensburg Numerical Analysis of a variational principle in discrete space-time

Robert Meier, Universität Ulm Hole mobility of CdTe MEH-PPV film

Florian Selmaier, LMU München Ultra-fast decay of the excited electronic state in a thin pentacen film

9.5 Funding

Deutsche Forschungsgemeinschaft:

Im Rahmen des SFB 533: Lichtinduzierte Dynamik von Biopolymeren Teilprojekt B11 "Proteindynamik unter Hochdruck" Leiter: Dr. Wolfgang Doster

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

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. Winfried Petry

Inelastische Neutronenstreuung bei hohen Temperaturen und Drücken zur Aufklärung der Lösungs- und Transportmechanismen von Wasser in wasserhaltigen Silikatschmelzen Förderkennzeichen: ME 1658/8-2 Leiter: Prof. Winfried Petry

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 1487/4-1 Leiter: Prof. Peter Müller-Buschbaum Im Rahmen des DFG Schwerpunktprogramm SPP 1181: Nanostrukturierte Filme aus selbstkapselnden anorganisch-organischen Hybridmaterialien Förderkennzeichen: MU 1487/5-1 Leiter: Prof. Peter Müller-Buschbaum

Im Rahmen des DFG Schwerpunktprogramm SPP 1181: Hierarchisch strukturierte Filme aus selbstkapselnden anorganisch-organischen Hybridmaterialien Förderkennzeichen: MU 1487/5-2 Leiter: Prof. Peter Müller-Buschbaum

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

Im Rahmen des DFG priority program SPP 1259: *Struktur und Kinetik stimuli-rexponsiver, dünner Hydrogelfilme aus amphiphilen Blockcopoly mern* Förderkennzeichen: MU 1487/8-1 Leiter: Prof. Peter Müller-Buschbaum

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

Copenhagen Munich Center of Soft, Nanostuctured Material (CMC-SNN) Incentive Fund for Research Collaborations between Technische Universität München and the Danish Technical University Leiter: Prof. Christine Papadakis, PD Dr. Rainer Jordan (Department Chemie, Techni-

sche Universität München), Prof. Martin E. Vigild (Department of Chemical Engineering, Danish Technical University)

Crystalline, mesoscopic and long-range order in thin films of crystalline block copolymers Incentive Fund for Research Collaborations between Technische Universität München and the Danish Technical University Leiter: Prof. Christine Papadakis. Dr. Jens Wenzel Andreasen (Risg National Laboratory)

Leiter: Prof. Christine Papadakis, Dr. Jens Wenzel Andreasen (Risø National Laboratory, Danish Technical University)

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: SPP 1259 'Intelligente Hydrogele': Struktur und Kinetik stimuli-responsiver, dünner Hydrogelfilme aus amphiphilen Blockcopolymeren Förderkennzeichen: PA 771/4-1 Leiter: Prof. Christine Papadakis Rolle der Mikrospannungen bei der Eigenspannungsanalyse mittels Neutronenbeugung in mehrphasigen Hochleistungslegierungen Förderkennzeichen: PE 580/7-1 Leiter: Prof. Winfried Petry

Bundesministerium für Bildung und Forschung:

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

Entwicklung und Aufbau von muSISAXS am muSAXS/WAXS Instrument am Synchroton PETRA III Förderkennzeichen: 05KS7WO1 Leiter: Prof. Peter Müller-Buschbaum

ESRF: Methodische Entwicklungen zum SRPAC Spektrometer: Gestörte Winkelkorrelation mit Synchrotronstrahlung Förderkennzeichen: 05KS4WOC/3 Leiter: Prof. Winfried Petry

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

Im Rahmen des Internationalen Graduiertenkollegs: Material Science of Complex Interfaces *Magnetic particles in supported polymer structures* Leiter: Prof. Peter Müller-Buschbaum

Im Rahmen des Internationalen Graduiertenkollegs: Material Science of Complex Interfaces Strukturelle Änderungen in nanostrukturierten Blockcopolymerfilmen - Zeitaufgelöste in-situ-Untersuchungen mit Röntgenkleinwinkelstreuung unter streifendem Einfall Leiter: Prof. Christine Papadakis

10 The chair

10.1 Graduations

Accomplished diploma thesis Matthias Ruderer Strukturierung von halbleitenden Polymerfilmen für die Anwendung in der Photovoltaik

Accomplished PhD thesis

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

10.2 Staff

Chair: Univ.-Prof. Dr. Winfried Petry

Head: Univ.-Prof. Dr. Peter Müller-Buschbaum

Fellows

Dr. Ezzeldin Metwalli Ali Dr. Marie-Soussai Appavou PD Dr. Wolfgang Doster Dr. Ana Gaspar Dr. Rusha Ivanova Dr. Volker Körstgens Dr. Amit Kulkarni Dr. Valeria Lauter-Passiouk (ILL) Dr. Peter Link Dr. Jean-François Moulin Dr. Jürgen Neuhaus (FRM II) Prof. Dr. Christine Papadakis Prof. Dr. Walter Schirmacher Dr. Cornelius Strohm Dr. Tobias Unruh Dr. Uwe van Bürck Dr. Johannes Wiedersich

PhD students

Mottakin Abul Kashem Sebastian Busch Charles Darko Zhenyu Di Alexander Diethert Christian Hesse Gunar Kaune Tarik Mehaddene Andreas Meier-Koll Jan Perlich Julia Repper Christoph Smuda Sebastian Stüber Weinan Wang Fan Yang

Diploma students

Christoph Geissinger Stefan Guldin Matthias Ruderer Bernhard Schmid Kordelia Troll

Bachelor students

Matthias Hirzinger

Students assistants

Stefan Aschauer Katharina Diller Jin Han Jinming Lu Steven Nyabero Reinhard Roßner Constantin Tomaras

Technical/administrative staff

Monika Antoniak Ricarda Baumhoer Joachim Dörbecker Petra Douglas Reinhold Funer Lukas Hein Raffael Jahrstorfer Josef Kaplonski Dieter Müller Jandal Ringe Cornelia Simon

10.3 Guests

Nora Kristen, Technische Universität Berlin (August 2007) Prof. Dorthe Posselt, Roskilde University, Denmark (March and August 2007) Prof. Dr. Gennadi Smirnov, Russian Research Center Kurchatov Institute, Russia