CPP 11: INTERNAL SYMPOSIUM Scattering Experiments II

Time: Tuesday 14:00–18:15 Location: H37

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].

[1] R. Steitz, T. Gutberlet, T. Hauß, B. Klösgen, R. Krastev, S. Schemmel, A. C. Simonsen and G. H. Findenegg, Langmuir 19; 2409-2418 (2003). [2] R. Steitz, V. Leiner, R. Siebrecht and R. v. Klitzing, Colloids and Surfaces A. 163, 63-70 (2000). [3] 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 Thomas[1], Wojciechowski Kamil[2], Tikhonov Alexey[3], Schlossman Mark[4], and Buffle Jacques[2] — [1]Lab. f. Neutr. Scattering, ETHZ & PSI, 5232 Villigen PSI, Switzerland — [2]CABE, Dept. of Anal., Inorg. and Appl. Chem., University of Geneva, 1211 Geneva 4, Switzerland — [3]NSLS, Upton, NY, USA — [4]Dept. 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 Seitz[1], Oliver Purrucker[2], Anton Förtig[3], Raimund Gleixner[4], Giovanna Fragneto[5], Rainer Jordan[3], and Motomu Tanaka[1,2] — [1]Physikalisch-Chemisches Institut, Universität Heidelberg, Germany — [2]Physik-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 $1\mu m$ 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

NSF via DMR 0453856.

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-Arriaga[1], Guillermo Orts-Gil[2], •Thomas Hellweg[2], Bela Farago[3], Carlos Menduina[1], and Francisco Monroy[1] — [1]Departamento de Quimica-Fisica I, Facultad de Ciencias Quimicas, Universidad Complutense de Madrid, E-28040 Madrid, Spain — [2]Stranski Laboratorium, TU Berlin, Strasse des 17.Juni 124, D-10623 Berlin, Germany — [3]Institut 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 elasticity of these models of cellular membranes. 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 Ivanova[1], Tune Bonné[1], Kell Mortensen[2], Philipp Pranzas[3], Thomas Komenda[4], Karin Lüdtke[4], Rainer Jordan[4], and Christine Papadakis[1] — [1]Physikdepartment E13, TU München, 85 747 Garching — [2]Risø National Laboratory, Roskilde, Denmark — [3]GKSS, Geesthacht — [4]Department 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 X-ray 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 Sensors — •Jochen S. Gutmann[1,2], Yajun Cheng[1], Mine Memesa[1], Sebastian Nett[1], and Rüdiger Berger[1] — [1]Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany — [2]Institute 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 μm 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.

[1] 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). [3] 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. Roth[1], A. Veligzhanin[1], H. Walter[2], R. Domnick[3], O. Leupold[1], R. Gehrke[1], and P. Müller-Buschbaum[4] — [1]HASYLAB at DESY, Notkestr. 85, D-22607 Hamburg, Germany — [2]CSEM SA, Badenerstrasse 569, CH-8048 Zürich, Switzerland — [3]Ara-Coatings GmbH & Co. KG, Gundstr. 13, D-91056 Erlangen, Germany — [4]TU 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 block-copolymer 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)