

CPP 16: Interfaces and Thin Films II

Time: Tuesday 9:30–13:00

Location: ZEU 114

CPP 16.1 Tue 9:30 ZEU 114

Lipid Monolayers and Adsorbed PSS with Different Degrees of Polymerization: Evidence of Lipid/PSS Complexes — •THOMAS ORTMANN, HEIKO AHRENS, ANDREAS GRÖNING, FRANK LAWRENZ, and CHRISTIANE A. HELM — Inst. f. Physik, Uni Greifswald, 17487 Greifswald, Germany

To gain insight into the equilibrium conformation of adsorbed polyelectrolytes and into their interactions with the supporting surface, lipid monolayers at the air/water interface serve as model substrate with adjustable surface charge.

Monolayers of cationic lipid DODA with adsorbed anionic Polystyrene sulfonate (PSS) are studied by isotherms and X-ray techniques. From salt-free solutions, PSS adsorbs flatly. The lipid monolayer shows a fluid/ordered phase transition. For polymer lengths exceeding 8 nm, PSS adsorbs in a lamellar manner to the lipid monolayer, for both lipid phases. On monolayer compression, the area per lipid molecule and the intermolecular separation of the PSS chains are reduced by a factor of two. On increase of PSS molecular weight, the phase transition pressure of the lipids decreases until the polymer length exceeds the persistence length (27 nm), then it levels off. However, the phase transition enthalpy of the lipids is almost independent of PSS molecular weight. These observations suggest complexes consisting of stiff PSS chains and lipids. If the PSS chains are shorter than 8 nm, the lamellar arranged PSS chains are only found when the lipids are in the ordered phase.

CPP 16.2 Tue 9:45 ZEU 114

Electrostatic nanotemplates: A universal platform for controlled hierarchical particle-deposition. — •TOM WAGNER, LARISA TSARKOVA, and ALEXANDER BÖKER — Chair of Macromolecular Materials and Surfaces / Interactive Materials Research DWI an der RWTH Aachen e.V.

We target nanoscopically functionalized surfaces with potential applications in catalysis, circuitry, molecule-recognition and optoelectronics. Nanocomposite templates with topographically and chemically structured patterns have been prepared using a physicochemical bottom-up technique. As a basic nanopattern we use thin films of microphase separated diblock copolymers, aligned by the application of an electric field. The introduction of positive charges exclusively into one particular block is achieved via inter/intra molecular crosslinking, providing a manifold usable electrostatic nanotemplate. Further, microcontact printing and dipcoating processes allow the selective adsorption of negatively charged nanoparticles, proteins and polyelectrolytes, in order to obtain periodic superstructures. In the course of structuring, the degree of crosslinking (charge-density) as well as the elemental composition of precursors and of the final composites has been monitored by attenuated total reflection infrared spectroscopy (ATR-IR) and by x-ray photoelectron spectroscopy (XPS). AFM- and FESEM-measurements have been used to characterize the topography and particle-arrangement at the composite surface. X-ray reflectivity (XRR) measurements provided information on the inner structure of the film.

CPP 16.3 Tue 10:00 ZEU 114

Scaling theory for compressed polymer-brush bilayers — •TORSTEN KREER — Leibniz Institut für Polymerforschung Dresden, 01069 Dresden, Germany

When linear macromolecules are grafted densely onto a surface, the individual chains are forced to stretch away from the surface plane forming a polymer brush. Polymer brushes allow one to tune surface properties by modification of the functionality or the molecular parameters, i.e., chain length and density of the grafted chains. Thus, they are important in many respects, e.g. for the stabilization of colloidal dispersions, flocculation, wetting phenomena, and (bio-)lubrication. Of particular interest are two polymer brushes compressed against each other (so-called "polymer-brush bilayers"), which play an important role as model systems, e.g. to study biolubrication. Starting from the classical concepts to calculate the interaction free energy of such bilayers, known as the famous theory of Milner, Witten, and Cates and the scaling approach of Alexander and de Gennes, an alternative picture is developed that describes both numerical and experimental data significantly better. To this extent, basic scaling theory and the

strong-stretching limit of the self-consistent mean-field theory will be discussed.

CPP 16.4 Tue 10:15 ZEU 114

Investigation of stretching and force-induced desorption of polymer chain anchored to repulsive and inert surfaces — •ZORYANA USATENKO — Cracow University of Technology, 30-084 Cracow, Poland

The investigation of stretching and force-induced desorption of ideal and real polymer chain with excluded volume interactions in a good solvent anchored to repulsive and inert surface are performed. The calculations of the stretching and desorption force applied to free end of real polymer chain anchored by other end to repulsive and inert surface are performed up to one-loop order of the massive field theory approach in fixed space dimensions $d=3$. The obtained results are in good agreement with previous theoretical results obtained for the stretching force in "Z" ensemble calculated for the case of ideal chain anchored to the surface and have important practical applications for understanding of the elastic properties of the individual macromolecules, networks, gels and brush layers. Besides, the obtained in the framework of the massive field theory approach results are in good agreement with results of density functional theory approach for the region of small applied forces.

CPP 16.5 Tue 10:30 ZEU 114

POLARIZED μ -RAMAN IMAGING SPECTROSCOPY: CRYSTALLINITY AND ORIENTATION OF SHEARED PP FILMS — •KRISZTINA VINCZE-MINYA¹, SABINE HILD¹, SIBYLLE JILG², and REINHARD FORSTNER² — ¹Institut für Polymerwissenschaften, Johannes Kepler Universität Linz, Österreich — ²TCKT Wels, Österreich

Isotactic PP ring-samples were prepared by Pirouette-dilatometer under different pressures and sheared at different temperatures and shear rates. The variations in crystallinity and orientation can be characterized on the microscale using polarized confocal Raman microscopy. For these investigations a method was developed previously by measuring materials with known orientation (iPP thin films), whereby the results were correlated with WAXS. The good agreement of the Raman-results with the WAXS-data was already reported in case of the defined samples. By the means of these findings the investigation method can be applied for the characterization of the samples with undefined orientation prepared with the Pirouette dilatometer.

CPP 16.6 Tue 10:45 ZEU 114

Studying polymer thin films with GISAXS contrast matching at the silicon K-edge — •JAN WERNECKE¹, HIROSHI OKUDA², and MICHAEL KRUMREY¹ — ¹Physikalisch-Technische Bundesanstalt, Berlin, Germany — ²Kyoto University, Kyoto, Japan

Grazing-incidence small-angle X-ray scattering (GISAXS) is an ideal tool to study self-organized nanostructures in block-copolymer thin films as it allows for non-destructive, depth-resolved measurements. However, the strong scattering contribution of the film-substrate interface often makes the evaluation of weak scattering features of nanostructures within the film challenging. The reflection can be minimized by matching the scattering contrast of film and substrate to make the interface virtually 'invisible' for the X-ray beam. The most widely used substrate material is silicon. This requires to record scattering images in vacuum at around 1.8 keV, which is inaccessible for most digital large-area X-ray detectors. The performance of a newly developed in-vacuum PILATUS 1M detector¹ that can be operated down to 1.75 keV is shown in this presentation. The device is used to study structural changes in self-organized PS-b-P2VP thin films under the contrast matching condition at 1827 eV. Depth-resolved GISAXS measurements of the unperturbed scattering features of as-prepared and annealed films are presented and may offer further insights into thermally induced structural modifications along the PS-b-P2VP film thickness.

¹J Wernecke, C Gollwitzer, P Müller & M Krumrey: *Characterization of an in-vacuum PILATUS 1M detector*, submitted to *J. Synchrotron Rad.* (2013) arXiv:1311.5082.

15 min. break

CPP 16.7 Tue 11:15 ZEU 114

An X-ray reflectivity set-up for the study of solid/liquid interfaces under high hydrostatic pressure — FLORIAN J. WIRKERT, ●JULIA NASE, BENEDIKT NOWAK, IRENA KIESEL, SIMON KUJAWSKI, JOHANNES MÖLLER, PAUL SALMEN, MICHAEL PAULUS, CHRISTIAN STERNEMANN, and METIN TOLAN — Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund Germany.

Studying the response of matter to high hydrostatic pressure (HHP) has a long tradition. The knowledge on life at extreme conditions can be broadened if biological systems are investigated under HHP. The importance for studying biological systems at conditions up to 5 kbar lies also in the fact that biologically relevant proteins denature in this pressure regime.

We present the first set-up for in situ X-ray reflectivity studies (XRR) of solid/liquid interfaces at HHP up to 5 kbar [1]. With this new set-up, it is now possible to examine a number of different solid/liquid interfaces under HHP with Angström-resolution. In addition, the influence of a modified water structure (under HHP) on interfaces can be explored.

We present results concerning the structure of hydrophobic interface between OTS and water and discuss first XRR measurements of pressure-induced lysozyme adsorption on hydrophobic silicon wafers. The results demonstrate the enormous potential of the set-up, particularly for the study of biological systems.

[1] F. Wirkert et al, XRR measurements of liquid/solid interfaces at HHP conditions, *J. Synchr. Rad.* 21 (2014)

CPP 16.8 Tue 11:30 ZEU 114

Decontamination of lipophilic hazardous materials on sorptive solid surfaces — SALOMÉ VARGAS RUIZ¹, CHRISTOPH SCHULREICH², REGINE VON KLITZING¹, MARTIN JUNG³, THOMAS HELLWEG², and ●STEFAN WELLERT¹ — ¹Stranski Laboratory, Technical University Berlin, 10623 Berlin, Germany — ²Physical Chemistry III, University Bielefeld, 33615 Bielefeld, Germany — ³Armed Forces Scientific Inst. f. NBC Protection, 29633 Munster, Germany

Modern decontamination media are desired to reconstitute personnel and equipment rapidly. The ability to extract penetrating hydrophobic surface hazards (e.g. pesticides, chemical warfare agents) out of sorptive surfaces and to instantaneously decompose the solubilized compounds is essential. Microemulsions based on natural surfactants and plant and food grade oils possess a soft and "green" performance in a wide temperature range. Additionally, enzymatic degradation of highly toxic organophosphorus compounds inside microemulsions by the enzyme Diisopropyl fluorophosphatase (DFPase) was monitored. The microemulsion structure in the vicinity of model surfaces was investigated by neutron reflectometry. With respect to the desired functionalities, we discuss extraction properties and wetting behaviour of different microemulsions on model and realistic surfaces. Hence, the investigated systems are promising novel environmentally friendly extraction and reaction media providing interesting properties e.g. for biotechnological applications.

CPP 16.9 Tue 11:45 ZEU 114

Tuning the mechanical properties of ultrathin carbon nanomembranes via molecular design — ●XIANGHUI ZHANG¹, POLINA ANGELOVA¹, CHRISTOF NEUMANN¹, ANDRÉ BEYER¹, JÜRGEN SCHNACK², and ARMIN GÖLZHÄUSER¹ — ¹Physics of Supramolecular Systems and Surfaces, University of Bielefeld, Universitätsstr. 25, 33615 Bielefeld — ²Condensed Matter Theory Group, University of Bielefeld, Universitätsstr. 25, 33615 Bielefeld

Self-assembled monolayers (SAMs) of polyaromatic molecules can be cross-linked via low energy electron irradiation and form carbon nanomembranes (CNMs) with a thickness ranging from 0.5 to 3 nm. Freestanding CNMs were fabricated by transferring them onto a Si substrate with an array of orifices and an in-situ bulge test in an atomic force microscope (AFM) was used to characterize mechanical properties of CNMs. A differential pressure was applied to a freestanding CNM and the deflection at the centre of the membrane was recorded by AFM. We observe that the structure of precursor molecules has some effect on the mechanical stiffness of CNMs: CNMs from more rigid condensed polyaromatic precursors like naphthalene and pyrene thiols exhibit higher Young's moduli of 16-18 GPa; CNMs from non-fused oligophenyl molecules like biphenyl and terphenyl thiols possess lower Young's moduli of 8-10 GPa; CNMs from non-condensed hexaphenylbenzene and hexabenzocoronene thiols possess Young's moduli of 13-15 GPa. Finite element method (FEM) was also used to examine the

deformation profiles and simulate the pressure-deflection relationship.

CPP 16.10 Tue 12:00 ZEU 114

Unexpected swelling characteristics of thermoresponsive polymer brush systems based on Poly(2-oxazoline)s — ●STEFAN ADAM^{1,2}, KLAUS-JOCHEN EICHHORN¹, JUAN CARLOS RUEDA³, MANFRED STAMM^{1,2}, MATHIAS SCHUBERT⁴, and PETRA UHLMANN¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V., 01069 Dresden, Germany — ²Technische Universität Dresden, 01062 Dresden, Germany — ³Pontificia Universidad Católica del Perú, Lima, Peru — ⁴University of Nebraska-Lincoln, Lincoln, NE 68588, USA

Responsive polymer coatings or hydrogels are capable to change their structural and physical properties due to changes in the environmental condition (e.g. temperature). Poly(2-oxazoline)s (POX), being structural isomers to polyacrylamides (e.g. poly(N-isopropylacrylamide), PNiPAAm) can exhibit a lower critical solution temperature (LCST) in aqueous solution. Adjusting the molar mass or copolymerization with more hydrophilic/hydrophobic comonomers enables tuning the LCST towards higher/lower temperatures. A combinatorial Quartz Crystal Microbalance with Dissipation and Spectroscopic Ellipsometry setup was used to study quantitatively the swelling characteristics of POX brushes prepared by the "grafting to" method using pre-synthesized polymers with functionalized end groups. The swelling behavior of POX brushes was compared to the phase transition of a corresponding aqueous polymer solution, determined by turbidity measurements. While all POX solutions show sharp transition curves in aqueous solution, an unexpected continuous reversible swelling of grafted POX could be observed over a wide temperature range.

CPP 16.11 Tue 12:15 ZEU 114

Hierarchical multiscale modelling of polystyrene-gold interfaces — ●KAREN JOHNSTON¹, VAGELIS HARMANDARIS², and KURT KREMER³ — ¹Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, United Kingdom — ²Department of Applied Mathematics, University of Crete, Iraklion, Greece — ³Max Planck Institute for Polymer Research, Mainz, Germany

Polystyrene films between two parallel gold surfaces were studied using hierarchical multiscale modelling. Classical all-atom (AA) polymer-surface interface potentials were developed based on density functional theory calculations that account for van der Waals forces [1]. AA molecular dynamics simulations were then used to study the structure and dynamics of 10mer polystyrene thin films up to 10 nm thick [2]. To study longer chains and thicker films a coarse-grained (CG) model was used [3] and the CG surface potentials were developed based on all-atom potential of mean force calculations. The structural properties of the CG and AA simulations were compared for a 5 nm film of 10mer polystyrene and the results were in good agreement. The CG model was used to simulate 10 and 20 nm films for chain lengths of up to 200mer and the dependence of the structure and interphase width on chain length were investigated [4]. The effect of the CG interface potentials on the polymer dynamics near the surface will be discussed.

[1] Johnston and Harmandaris, *J. Phys. Chem. C* 115, 14707 (2011) [2] Johnston and Harmandaris, *Soft Matter*, 8, 6320 (2012) [3] Fritz et al. *Macromolecules*, 42, 7579 (2009) [4] Johnston and Harmandaris, *Macromolecules*, 46, 5741 (2013)

CPP 16.12 Tue 12:30 ZEU 114

Monte Carlo study of polymer adsorption on nanocylinders — JONATHAN GROSS¹ and ●MICHAEL BACHMANN² — ¹Universität Leipzig, Leipzig, Germany — ²The University of Georgia, Athens, GA, USA

The thermodynamic behavior of a coarse-grained flexible polymer model in the vicinity of an attractive nanocylinder is subject of this investigation. We are interested in the structural phases of the polymer and how they change with the surface attraction strength of the nanocylinder. The effective monomer-surface attraction strength is associated with the cylinder radius and its material. Previous studies of polymer adsorption on planar surfaces already provide insight in the structures formed by adsorbed polymer chains. Recently also the adsorption on curved surfaces was investigated. We try to connect the results of the adsorption on curved and planar surfaces, since in the limit of an infinite radius of the cylinder, the surface has the same characteristics as a plane. We construct complete pseudo-phase diagrams of a 30-mer interacting with nanocylinders of five different materials as a function of temperature and radius of the cylinders.

CPP 16.13 Tue 12:45 ZEU 114

Morphology, Mechanical Stability and Protective Properties of Ultrathin Gallium Oxide Coatings — •FRANK LAWRENZ¹, PHILIPP LANGE², NIKOLAI SEVERIN², JÜRGEN P. RABE², CHRISTIANE A. HELM¹, and STEPHAN BLOCK³ — ¹Inst. f. Physik, Uni Greifswald, 17487 Greifswald, Germany — ²Dept. of Physics, Humboldt-Universität zu Berlin, 12489 Berlin, Germany — ³Chalmers University of Technology, Gothenburg, Sweden

Scanning Force Microscopy (SFM) imaging of surfaces treated with liquid gallium shows extended, ultrathin layers, which are attributed to gallium oxide (GaOx) films. These 3 nm thick GaOx layers ex-

hibit high mechanical stability as can be concluded from large forces required to rupture them with the SFM tip. We investigate the permeability of the films to oxygen and water. For this we cover fluorescent thin films made of conjugated polymers with the GaOx layers and investigate the degradation of fluorescence under ambient conditions. We estimated the upper limit of oxygen and water permeation rate of 0.06 molecules/day, this complies with the industrial requirements onto permeation barriers. Similar to other highly functional materials like graphene ultrathin GaOx layers could also be used for prospective transparent barrier applications.