

CPP 5: Interfaces

Time: Monday 10:30–12:45

Location: ZEU 160

CPP 5.1 Mon 10:30 ZEU 160

Tracing physio-chemical changes at the solid liquid interface with single molecule microscopy. — ●TÄUBER DANIELA, SCHUSTER JÖRG, and VON BORCZYKOWSKI CHRISTIAN — TU-Chemnitz, Institut für Physik, 09107 Chemnitz, and FOR 877

Hydrodynamics at the solid-liquid interfaces are subject of recent studies in experiment and simulations. Scaling down to nanoscience X-ray and other investigations revealed structural ordering of liquids close to interfaces. However on the molecular level there are still open questions which interactions with the solid interface are accountable for dynamic and structural effects. In previous single molecule tracking experiments [1] we were able to show that diffusion within ultrathin liquid films is vertically heterogeneous and drastically slowed down in comparison to the bulk behavior. Furthermore it is characterized by adsorption events interrupting the diffusional motion.

In series of recent experiments we focussed on details of molecular interactions. By the use of charged and neutral dyes we could reveal spontaneously occurring physio-chemical changes at the solid liquid interface within days leading to a decrease in adsorption probability and thus enhancement of dye diffusion. A simple surface chemistry model is presented to explain those observations.

[1] J. Schuster, F. Cichos, Ch. von Borczykowski: Euro. Phys. J. E. 12 (2003), 75-80

CPP 5.2 Mon 10:45 ZEU 160

Wetting and surface tension dynamics of aqueous anionic surfactant/cationic polyelectrolyte mixtures — RADOMIR SLAVCHOV^{1,2}, BORJAN RADOEV¹, GUDRUN PETZOLD², BURKHARD BREITZKE³, and ●VICTORIA DUTSCHK² — ¹Faculty of Chemistry, University of Sofia, Bulgaria — ²Leibniz Institute of Polymer Research — ³Sasol Germany, Marl

Surfactant-polyelectrolyte interactions in aqueous mixtures were studied using dynamic surface tension, polyelectrolyte titration, nephelometric turbidity and dynamic light scattering. A cationic polyelectrolyte (hydroxyethylcellulose, HEC) was used in combination with two anionic surfactants in surfactant classes AS (alkyl or fatty alcohol sulphates) and LES (lauryl ether sulphates) of similar structure but different hydrophobicity.

Systematic studies of the dynamic surface tension and contact angles of aqueous solutions of single components as well as of their mixtures led to an indirect estimation of the interactions both at the liquid-vapour and solid-liquid (highly hydrophobic) interfaces. Here, differences in the wetting kinetics depend on adsorption mechanisms.

Evidently, hydrophobic surfaces show the same or similar adsorption kinetics at the solid-liquid interface as to be expected in the case of the liquid-vapour interface. Besides, the current state of the air interface (dynamic surface tension) at the instance of the drop-surface contact determines the contact angles on hydrophobic surfaces.

CPP 5.3 Mon 11:00 ZEU 160

Large molecules near metal surfaces: A density functional based scale-bridging approach — ●LUIGI DELLE SITE — Max-Planck-Institute for Polymer Research, PO Box 3148, D-55021 Mainz

We present a hierarchical quantum-classical scale-bridging approach for modeling and simulating large molecules, in bulk and in solution, on inorganic (metal) surfaces. Some examples of its application are illustrated, in particular the study of the adsorption of oligopeptides on a Pt(111) in solution.

CPP 5.4 Mon 11:15 ZEU 160

A thermodynamically consistent view of ion adsorption at interfaces — ●DOMINIK HORINEK, NADINE SCHWIERZ, and ROLAND R. NETZ — Physik Department, Technische Universität München, 85748 Garching, Germany

The implications of ion adsorption at water/solid interfaces are relevant in many biological, chemical, and physical processes. The adsorption shows a very ion-specific behavior, which leads to the so-called Hofmeister series. In recent years this subject has moved into the focus of atomistic computer simulations. In such simulations, one key problem is the proper choice of the ionic force field: the bulk solvation properties and the affinity to interfaces are very sensitive on the ion parameterization. We demonstrate that a thermodynamically consistent

description of bulk solvation is compatible with ion adsorption of large anions at hydrophobic interfaces even if the force field is free of atomic polarizabilities. At polar interfaces, the Hofmeister series is reversed, and small ions have a higher affinity to the interface than large ions.

CPP 5.5 Mon 11:30 ZEU 160

Polymer Adsorption Transitions at Attractive Substrates: Analysis from Canonical and Microcanonical Perspectives — ●MONIKA MÖDDEL, MICHAEL BACHMANN, and WOLFHARD JANKE — Institut für Theoretische Physik, Universität Leipzig

Multicanonical simulations allow not only for a precise determination of canonical expectation values over a wide range of temperatures, they also provide a very precise estimation of the density of states. We used thermal fluctuations of energetic and structural quantities to identify the variety of pseudophases of a semiflexible off-lattice homopolymer near an attractive substrate [1]. Introducing a solvent parameter related to the strength of the surface attraction, the solubility-temperature phase diagram is constructed and discussed. Apart from the adsorption transition, several other structural transitions such as the freezing transition between energy-dominated crystalline low-temperature structures and globular entropy-dominated structures as well as the layering transition between single- and double-layered conformations are identified. With the density of states, we then performed a microcanonical analyses focused on the adsorption transition, where a convex intruder of the microcanonical entropy can be observed for short chains, which is a typical signal for a phase separation process. However, for longer chains, the latent heat decreases and seems to vanish in the thermodynamic limit. Thus, we interpret the adsorption process as a second-order phase transition.

[1] M. Möddel, M. Bachmann, and W. Janke, submitted to J. Phys. Chem. B (2008).

CPP 5.6 Mon 11:45 ZEU 160

Lateral structures of buried interfaces in ABA-type tri-block copolymer films — ●PETER MÜLLER-BUSCHBAUM¹, LEANDER SCHULZ², EZZELDIN METWALLI¹, JEAN-FRANCOIS MOULIN^{1,3}, and ROBERT CUBITT⁴ — ¹TU München, Physikdepartment E13, James-Frank-Str.1, 85747 Garching (Germany) — ²Uni. de Fribourg, Phys. Dept., Chemin du Musée 3, 1700 Fribourg (Switzerland) — ³Inst. für Werkstofforschung, GKSS, 21502 Geesthacht (Germany) — ⁴ILL, 6 rue Jules Horowitz, 38042 Grenoble (France)

The lateral structure of an A-B-A type tri-block copolymer polyparamethylstyrene-block-polystyrene-block-polyparamethylstyrene at the buried silicon substrate interface is studied as a function of different substrate surface energies. With grazing incidence small angle neutron scattering (GISANS) high interface sensitivity is reached. With GISANS the orientation and the degree of order of the morphology are probed. The powder-like oriented lamellar structure in the bulk becomes oriented along the surface normal in the vicinity of the substrate. A modification of the short-ranged interface potential of the substrate introduces a stretching of the lateral spacing of this lamellar structure up to 8 % as compared to the bulk. The decay of the stretching towards the volume structure is probed with depth profiling. It extends at least up to a distance of 51 nm from the solid surface. [1]

[1] P.Müller-Buschbaum, et al.; Langmuir Letter, 24, 7639-7644 (2008) and P.Müller-Buschbaum, et al.; Langmuir ASAP (DOI 10.1021/la802471p)

CPP 5.7 Mon 12:00 ZEU 160

Free volume distribution at a polymer-solid interface investigated by a slow positron beam — ●STEPHAN HARMS¹, KLAUS RÄTZKE¹, VLADIMIR ZAPOROJTCHEKNO¹, FRANZ FAUPEL¹, WERNER EGGER², and PETER SPERR² — ¹Technische Fakultät der CAU, Lehrstuhl für Materialverbunde, Kaiserstr. 2, 24143 Kiel, Germany — ²Universität der Bundeswehr München, Neubiberg, Germany and FRM II München

Polymer-solid contacts are important for many applications such as adhesion, coating and nanocomposites. Mechanical and permeability properties of polymers are strongly connected to the free volume cavity size and fractions, which might be different at the boundary

layer. Positron annihilation lifetime spectroscopy is a widely accepted experimental technique to study the free volume in polymers. The ortho-positronium lifetime is directly connected to the mean free volume size. A tunable low-energy positron beam allows us to measure the free volume as a function of the depth on a nm scale. For the first time we investigated several Teflon AF2400/silicon interfaces at different positron beam energies which corresponds to various depths from surface to interface. By this we obtain information about free volume, the thickness of the interphase region and changes in the free volume in this area. First evaluation shows a decrease in free volume fraction at the interface while the size of the cavities stays constant. We acknowledge the financial support by the DFG within the priority program (SPP) 1369 (Ra 796/5-1).

CPP 5.8 Mon 12:15 ZEU 160

Tuning of surface properties by self assembled mixed monolayers — •DAVID POLSTER, HARALD GRAAF, and CHRISTIAN VON BORCZYKOWSKI — Center of Nanostructured Materials and Analytics, University of Technology Chemnitz, 09107 Chemnitz, Germany

Self assembled monolayers covalently bond on silicon surfaces were prepared from different mixture ratios of 1-decene (DEC) and methyl-10-undecenoate (UND). A two step radical reaction induced by heat treatment was used to prepare the monolayers. The prepared films have been studied with contact angle measurements, using water as polar liquid and diiodomethane as dispersive liquid as well as atomic force microscopy (AFM). For the mixed monolayers a decrease in the water contact angle, 110° to 75° , was found with increasing ratio of UND in the monolayer. Smaller contact angles could be explained by increasing polarity of the surface induced by the increasing amount of ester groups containing beside dispersive also polar character. Furthermore work of adhesion increases by higher polarity of the mixed monolayers and thereby the process of wetting happens easier and liquids spreads wider. In addition angle hysteresis and mole free energy of

dewetting were constant. Beside contact angle investigations scanning probe measurements showed that all surfaces were extremely smooth. By AFM force spectroscopy it could be shown that with increasing polarity of the surface also a slight increase of adhesive force between AFM tip and surface was found.

CPP 5.9 Mon 12:30 ZEU 160

Direct measurement of normal and shear forces between grafted-from polyelectrolyte layers — •IAIN DUNLOP^{1,4}, WUGE BRISCOE¹, SIMON TITMUS¹, ROBERT JACOBS¹, VICKY OSBORNE², STEVE EDMONDSON², WILHELM HUCK², and JACOB KLEIN^{1,3} — ¹Dept. Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QZ, U.K. — ²Melville Laboratory for Polymer Synthesis, University Chemistry Laboratory, Lensfield Road, Cambridge, CB2 1EW, U.K. — ³Dept. Materials and Interfaces, Weizmann Institute of Science, PO Box 26, Rehovot 76100, Israel — ⁴Present address: Dept. New Materials and Biosystems, Max-Planck-Institute for Metals Research, Heisenbergstraße 3, 70569 Stuttgart, Germany, and University of Heidelberg, Biophysical Chemistry, INF 253, D-69120 Heidelberg.

We present direct measurements, using the surface force balance (SFB), of the normal and shear forces in aqueous solutions between grafted-from polyelectrolyte layers that were grown by surface-initiated atom transfer radical polymerization on mica substrates. The successful formation of the grafted-from polyelectrolyte layers was confirmed using X-ray reflectometry. Normal force measurements in water showed a long-range force due to an electrical double layer that extended beyond the swollen polyelectrolyte layers, as well as a stronger repulsion when the layers were in contact. Upon addition of 1:1 electrolyte, the long-range force became undetectably small, due to screening effects. Shear force measurements in pure water showed a measurable friction that may arise from the bridging of polymer chains between the surfaces.