

CPP 12: Polymer Physics III: Interfaces

Time: Tuesday 10:00–12:30

Location: H40

CPP 12.1 Tue 10:00 H40

Monte Carlo simulations of tethered chains in contact with an adsorbing surface — ●RADU DESCAS¹, JENS-UWE SOMMER², and ALEXANDER BLUMEN¹ — ¹Albert-Ludwigs-University, Theoretical Polymer Physics, Freiburg — ²Technical University of Dresden, Institute for Theoretical Physics, Dresden

We use MC simulations combined with scaling arguments to study the adsorption of tethered polymer chains at flat surfaces [1]. In the two-dimensional semi-dilute surface regime we analyze the average extension of single chains in the direction parallel and perpendicular to the surface. Our simulation results agree well with previous scaling predictions [2], especially for the parallel extension of the chains and much below the saturation concentration of the adsorbed layer. Increasing the surface concentration, saturation effects influence the adsorption free energy. The investigation of the free energy function leads us to propose a new scaling parameter which controls the saturation behavior in polymer layers. The strong decrease of the fraction of adsorbed monomers per chain with increasing concentration confirms our assumptions. Based on our model we infer the existence of a crossover-scaling region between the semi-dilute and the saturated state. Our results for the chains' extension give further support to our scaling model. Furthermore, we investigate the over-saturated surface regime which can be understood as the coexistence of a brush-like layer formed on top of a saturated adsorption layer.

[1] R. Descas, J.-U Sommer, and A. Blumen, *J. Chem. Phys.* in press.

[2] E. Bouchaud and M. Daoud, *J. Physique* 48, 1991 (1987).

CPP 12.2 Tue 10:15 H40

Polymer rings on structured surfaces — ●PETRA GUTJAHR, REINHARD LIPOWSKY, and JAN KIERFELD — Max Planck Institute of Colloids and Interfaces, Science Park Golm, 14424 Potsdam, Germany

Semiflexible polymer rings such as circular DNA which are adsorbed onto chemically or topographically structured substrate surfaces, exhibit a variety of morphologies. A simple but instructive example is provided by a striped surface domain. Upon increasing the adhesive strength of the striped domain, we find a morphological transition from a round toroidal conformation dominated by bending energy to an elongated configuration, in which the polymer ring is confined to the adhesive stripe. We determine the complete bifurcation diagram of the polymer shapes as a function of their contour length and the ratio of adhesion contrast to bending rigidity. This diagram exhibits several metastable configurations of the semiflexible polymer rings. In addition, these rings can undergo an adhesion transition, at which they bind to the striped domain.

CPP 12.3 Tue 10:30 H40

Submonolayer coverage of long chain alkanes at SiO₂/air interfaces: Nucleation, and phase behaviour - Molecular transportation, and structure formation — ●RALF KÖHLER and HANS RIEGLER — MPI of Colloids and Interfaces, Dept. Interfaces, 14424 Potsdam-Golm, Germany

The ordering behavior of submonolayers of long chain alkanes at SiO₂/air interfaces is a surprisingly complex phenomenon with two-dimensional nucleation, surface flow and structure formation. On-line optical microscopy observations (1) show three growth scenarios depending on the overall alkane coverage. The observed fractal crystallites (2,3) can be related to a process analogous to diffusion-limited aggregation (4). At least two qualitatively and quantitatively different domain shapes can be distinguished which could also be reproduced by computer simulations. 2d-nucleation theory reveals reasonable values for line tension and activation energies. The 2d-geometry also allows the identification of active nucleation sites in comparison to quasi-homogenous nucleated domains. The system also shows the equilibrium coexistence of the solid domains and a fluid alkane film in between whose thickness depends on the temperature. The observed confinement-induced melting temperature shift is in agreement with thermodynamical calculations assuming an effective interface potential. (1) R.Köhler et al., *Appl.Phys.Lett.* 89, 241906 (2006); (2) A.Holzwarth et al., *Europhys.Lett.* 52, 653 (2000); (3) H.Schollmeyer et al., *Langmuir* 19, 5042 (2003); (4) L.Knüfing et al., *Langmuir* 21, 992 (2005)

15 min. break

CPP 12.4 Tue 11:00 H40

Amphiphilic Block Copolymers at the Liquid-Fluid Interface: Dynamics in Different Regimes — ●ANTONIO STOCOC¹, STERGIOS PISPAS², and REINHARD SIGEL¹ — ¹MPI of Colloids and Interfaces, D-14476 Golm — ²Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, Athens, Greece

Structure and dynamics of a block copolymer at the water-air (WA) and the water-dodecan (WD) interface are investigated. Because of its amphiphilic property, polyisoprene-block-polyethyleneoxide (PI-PEO) is attracted to such interfaces. By changes of the interface concentration, the overlap and the stretching of the blocks is varied from the mushroom to the brush regime. The extent of the interfacial polymer layer is followed by reflection ellipsometry. Complementary information is obtained from static and dynamic evanescent wave light scattering. For both types of interface, a 2D diffusion process is found which slows down with increasing interface concentration. The significantly slower diffusion at the WD interface compared to the WA interface is discussed.

CPP 12.5 Tue 11:15 H40

Smectic Layering at Surfactant-laden Isotropic Liquid Crystal/Water Interfaces — ●CHRISTIAN BAHR — Max Planck Institute for Dynamics and Self-Organization, D-37073 Göttingen

Thermotropic liquid crystals exhibit surface-induced order at temperatures where the bulk phase is disordered. Many smectic compounds show in their isotropic phase the formation of a smectic layer at interfaces to air or solid substrates; when the isotropic – smectic-A bulk transition is approached, the ordered surface phase grows in thickness via a series of individual layering transitions. Theoretical models [1] predict complex surface phase diagrams in which the individual layer transition lines end at critical points or collapse at triple points to multiple-layer transitions.

We present here the first study of smectic layering at surfactant-laden liquid crystal/water interfaces. Variation of the surfactant concentration c_s offers an easy way to tune the strength of the ordering surface field [2]. Whereas at higher c_s -values the usual series of single-layer transitions occurs, we observe at low c_s -values layering transitions at which the thickness of the surface phase jumps by a multiple number of single smectic layers. The multiple-layer transition lines split off at triple points into single-layer transition lines. This is the first experimental observation of this type of surface triple points.

[1] Z. Pawłowska, T. J. Sluckin, and G. F. Kventsel, *Phys. Rev. A* **38**, 5342 (1988); A. M. Somoza, L. Mederos, and D. E. Sullivan, *Phys. Rev. E* **52**, 5017 (1995).

[2] Ch. Bahr, *Phys. Rev. E* **73**, 030702(R) (2006).

CPP 12.6 Tue 11:30 H40

Preferred orientations and stability of medium length *n*-alkanes solidified in mesoporous silicon — ●ANKE HENSCHEL, TOMMY HOFMANN, PATRICK HUBER, and KLAUS KNORR — Saarland University, Saarbruecken, Germany

The *n*-alkanes C₁₇H₃₆, C₁₉H₄₀, and C₂₅H₅₂ have been imbibed and solidified in mesoporous, crystalline silicon with a mean pore diameter of 10nm. The structures and phase sequences have been determined by x-ray diffractometry. Apart from a reduction and the hysteresis of the melting/freezing transition, we find a set of six discrete orientation states ("domains") of the confined alkane crystals with respect to the lattice of the silicon host. The growth process responsible for the domain selection is interpreted as a nano-version of the Bridgman technique known from single crystal growth. Oxidation of the pore walls leads to extrusion of the hydrocarbons upon crystallization, whereas the solidified *n*-alkanes investigated in non-oxidized, porous silicon are thermodynamically stable.

CPP 12.7 Tue 11:45 H40

C60 modified PPO Polymer Membranes: Free Volume by Positron Annihilation Lifetime Spectroscopy — ●JAN KRUSE¹, KLAUS RÄTZKE¹, FRANZ FAUPEL¹, DANA STERESCU², DIMITRIOS STAMATIADIS², and MATTHIAS WESSLING² — ¹Universität

Kiel, Lehrstuhl für Materialverbunde, Kaiserstr. 2, 24143 Kiel —
 2University of Twente, Membrane Technology Group, P.O. Box 217,
 7500 AE, Enschede

PPO (poly(2,6-dimethyl-1,4-phenylene oxide)) is a well known membrane material showing good gas separation properties. Addition of nanoparticles can greatly enhance the performance of composite membranes. We have modified PPO polymer with C60 buckyballs up to a content of 2wt%. Permeability experiments show a strong dependence on whether the C60 is dispersed in the polymer or chemically bonded to the polymer chains. Free volume studies performed by positron annihilation lifetime spectroscopy (PALS) were performed on samples with different C60 concentrations. Spectra of all samples containing C60 exhibit an additional large positronium lifetime, indicating large local free volume elements. The orthopositronium intensity decreases with increasing C60 content, stronger for chemically bonded than for dispersed C60. As the inhibition of positronium formation can be attributed to the C60 molecules, this will be discussed with respect to the homogeneity of distribution.

CPP 12.8 Tue 12:00 H40

New observations during onset and final stages of capillary-breakup experiments on semidilute polymer solutions —
 •RAINER SATTLER and CHRISTIAN WAGNER — Universität des Saarlandes, Geb. E2 6 3.OG, Postfach 151150, 66041 Saarbrücken

We investigate the droplet-pinching and capillary-breakup of polymer solutions using high speed video microscopy. Recent experiments on semidilute solutions of Polyethylene Oxide were performed to examine the nature and prerequisites for the supposedly iterative formation of

beads on the thinning filament, which form as the extension of the polymers saturates.

There are clear indications for concentration enhancement during the formation of the different generations of beads not taken into consideration in existing models. Special emphasis is put on the discussion which mechanisms control the onset of the instability. We found indirect evidence showing that besides inertial effects modes of capillary waves at amplitudes below the resolution of optical microscopy cause dramatic deviations from expectations assuming a simple extensional flow during the thinning of the capillary bridge.

The presented experimental results can contribute to a better understanding of the growth of these instabilities and the behaviour of polymers in extensional flow relevant for technical and biological processes as well as giving reason for enhancements in theoretical description.

CPP 12.9 Tue 12:15 H40

Oscillating Phase Separation in Polymer Solutions — DORIS VOLLMER and •GÜNTER AUERNHAMMER — MPI für Polymerforschung, Ackermannweg 10, 55128 Mainz

The kinetics of phase separation of polymer solutions under slow cooling is discussed. For a broad range of compositions (about 1g/L until 20g/L) and cooling rates (cooling rates below about 5K/h) the mixtures show pronounced oscillations in the heat capacity and the turbidity. Whereas the oscillations in the heat capacity seem to be due to the gel phase, the oscillations in the turbidity are due to the sol phase. The period of the oscillation does not depend on composition within the investigated temperature interval. The oscillations are of thermodynamic origin.