

CPP 61: Interfaces and Thin Films I (joint session CPP/DY, organized by CPP)

Time: Thursday 16:15–18:15

Location: H51

Invited Talk

CPP 61.1 Thu 16:15 H51
Tuning of ordering in colloidal suspensions confined in thin films — SEBASTIAN SCHÖN¹, YAN ZENG¹, SABINE KLAPP², and ●REGINE VON KLITZING¹ — ¹TU Berlin, Institut für Chemie, Strasse des 17. Juni 124, 10623 Berlin — ²TU Berlin, Institut für Theoretische Physik, Hardenbergstraße 36, 10623 Berlin

Characteristic lengths of the structuring of silica nanoparticle suspensions confined between two silica surfaces were extracted from the oscillatory force profile of colloidal-probe atomic force microscopy (CP-AFM) measurements and compared with the bulk counterparts as obtained from structural peak of small angle X-ray scattering (SAXS). The wavelength λ extracted from CP-AFM correlates well with the mean particle distance $2\pi/q_{\max}$ as obtained from SAXS structural peak. This observation suggests that there is no confinement effect on characteristic lengths themselves that represent the structuring, even though the confinement indeed induces a layered structure of the particles. A more quantitative study shows a relation of oscillatory wavelength of silica nanoparticle suspensions with the particle number density as $\lambda = \rho^{-1/3}$, irrespective of particle size, surface charge of the particles and ionic strength of the solution. CP-AFM measurements on modified and deformable confining surfaces show an increase in amplitude with increasing surface potential and decreasing surface roughness and deformability. However, the corresponding wavelength remains unaffected. Current studies address the ordering of soft particles like thermosensitive nanogels in the confinement of thin films, where the inter particle interactions can be switched on and off.

CPP 61.2 Thu 16:45 H51

Highways for ions in polymers - 3D-imaging of electrochemical interphase formation — ●KARL-MICHAEL WEITZEL¹, VERONIKA WESP¹, JULIA ZAKEL¹, MARTIN SCHÄFER¹, ILKA PAULUS², and ANDREAS GREINER² — ¹Fachbereich Chemie, Philipps-Universität Marburg — ²Makromolekulare Chemie II, Universität Bayreuth

The formation of a cesium interphase in-between a polymer film and a platinum electrode has been initiated by low energy bombardment induced ion transport [1]. To this end two different samples of a poly(p-xylylene)(PPX) film, deposited on a platinum electrode have been bombarded by a low energy cesium ion beam. Ions are transported through the film according to the laws of electro-diffusion. They are neutralized at the interface between the PPX film and the metal electrode. Consequently, a cesium interphase is formed. 3D imaging of the interphase by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS) reveals a correlation between structural characteristics of the interphase and conduction properties of the PPX film. The bombardment of PPX films consisting of a homogenous network leads to the formation of a uniform interphase. The bombardment of PPX films with nonintermittent pathways (NIPs) for the transport of ions leads to the formation of cesium islands which ultimately spread out laterally leading to a non-uniform interphase behind the PPX film. This picture is supported by measurements of the ionic conductivity which differs characteristically for the two kinds of PPX films.

[1] Wesp et al., *Electrochimica Acta*, 170 (2015) 122-130

CPP 61.3 Thu 17:00 H51

Evidence of a three-Layered structure in ultra-thin PVME and PVME/PS blend Films by nano-sized relaxation spectroscopy — ●SHERIF MADKOUR¹, PAULINA SZYMONIAK¹, MOJDEH HEIDARI², REGINE VON KLITZING², and ANDREAS SCHÖNHALS¹ — ¹BAM Bundesanstalt für Materialforschung und -prüfung, Unter den Eichen 87, 12205 Berlin (Germany) — ²Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin (Germany)

Despite the many controversial discussions about the nanometric confinement effect on the properties of ultrathin films, many details remain not understood and/or experimentally unproven. Here, a combination of Broadband Dielectric Spectroscopy (BDS), Specific Heat Spectroscopy (SHS), and ellipsometry was utilized to investigate the glassy dynamics of ultra-thin films of Poly (vinyl methyl ether) (PVME) and PVME/Polystyrene (PS) 50:50 wt-% miscible blend (thicknesses: 8nm - 200nm). For BDS measurements, a recently developed nano-structured sample arrangement; where ultra-thin films are spin-coated on an ultra-flat highly conductive silicon wafer and sandwiched be-

tween a wafer with nanostructured SiO₂ nano-spacers, was used. For PVME films, two processes were observed and interpreted to be the α -processes of a bulk-like layer and an adsorbed layer to the substrate. BDS and SHS showed that glassy dynamics are bulk-like. However, for films lower than 15nm, BDS showed weakly slowed dynamics. For PVME/PS blend, by measuring the dynamic Tg in dependence on the film thickness, both BDS and SHS, showed that the Tg of the whole film was strongly influenced by a nanometer thick surface layer.

CPP 61.4 Thu 17:15 H51

Molecular Structure of Polyelectrolyte/Surfactant Mixtures with Tunable Electrostatic Interactions at Air-Water Interfaces — ●FELIX SCHULZE-ZACHAU and BJÖRN BRAUNSCHEWIG — Institute of Particle Technology (LFG), Friedrich-Alexander University of Erlangen-Nürnberg (FAU), Cauerstrasse 4, 91058 Erlangen, Germany

Mixtures of poly(sodium 4-styrenesulfonate) (NaPSS) polyelectrolytes and cetyltrimethylammonium bromide (CTAB) surfactants were studied at the air/water interface with tensiometry, ellipsometry and vibrational SFG spectroscopy. Additionally, macroscopic foams from these mixtures were studied in order to relate information on the interfacial molecular structure and charging state to foam stability and foamability. At low NaPSS concentrations, hydrophobic PSS⁻/CTA⁺ complexes adsorb at air/water interfaces with co-adsorbed free CTA⁺ ions. The latter leads to relatively stable foams. For mixtures with equimolar concentrations, there is a significant rise in surface tension to values close to the tension of neat water that is accompanied by negligible foamabilities. However, SFG spectroscopy and ellipsometry provide evidence that PSS⁻/CTA⁺ complexes are at the interface with high coverage. Obviously, at these concentrations PSS⁻/CTA⁺ complexes are highly solvated at the interface but in a subsurface configuration with a covering water layer with free OH groups that give a clear signature in our SFG spectra. For excess NaPSS concentrations, surface adsorption is mainly determined by the molecular properties of PSS⁻ interfacial layers which provide good foamability and stability.

CPP 61.5 Thu 17:30 H51

Structure of films prepared from block copolymer mixtures: computer simulations and GISAXS experiments — ●ANATOLY V. BEREZKIN¹, JUSTUS OBERHAUSEN¹, FLORIAN JUNG¹, DORTHE POSSELT², and CHRISTINE M. PAPADAKIS¹ — ¹Technische Universität München, Physik Department — ²Roskilde University, Department of Science, Systems and Models, Denmark

Block copolymer films are promising as nano-structured templates, e.g. for lithography. Mixtures of block copolymers provide a robust route towards the preparation of non-trivial morphologies with an easily controlled domain size. We investigated a mixture of short and long symmetric diblock copolymers experimentally using GISAXS and in simulations (dissipative particle dynamics). We addressed the case, when macrophase separation of the mixture is expected along with the microphase separation in each of two phases. Simulations, in accordance with the experiment, show that the phase rich in short chains is usually located near the film surfaces, while long chains concentrate in the film core. Thick lamellae in the film core are usually perpendicular to the substrate, while thin lamellae in the interfacial layers can be parallel or perpendicular, depending on polymer/surface interactions. Selective adsorption of one block stabilizes lying lamellae. In very thin films confined between two selective surfaces, the conflict between orientations of thick standing lamellae and thin lying lamellae leads to unusual lens-like non-orthogonal structures.

CPP 61.6 Thu 17:45 H51

Adsorption Behavior of a rigid Polyelectrolyte/Surfactant Mixture at the Air/Liquid Interface and its Influence on Foam Film Stability — ●MARTIN UHLIG¹, ANDREAS WOHLFARTH², KLAUS-DIETER KREUER², and REGINE V. KLITZING¹ — ¹Technische Universität Berlin — ²Max-Planck-Institut für Festkörperforschung, Stuttgart

The properties of foams are of interest for many industrial applications such as enhanced oil recovery and in personal care products and are therefore the subject of many studies. To control and manipulate the properties of a foam, it is essential to understand the behavior of

the single building blocks, the so-called foam films. A way to produce stable foam films is to mix surfactants with oppositely charged polyelectrolytes, as highly surface-active complexes can be formed with the two compounds. Extensive research on such mixtures was already performed with the focus on very flexible Polyelectrolytes, as PSS and PAMPS. However, it is still unclear what the influence of the backbone rigidity of the polyelectrolyte on the resulting foam film properties is. In this work a mixture of a newly synthesized polyelectrolyte (S220) with a stiffer backbone is used and mixed with the cationic surfactant C14TAB. The system has been investigated by means of surface tension measurements, surface elasticity, foam film stability measurements and neutron reflectometry. Those measurements have shown a much higher surface activity and foam stability for the S220/C14TAB mixture than for mixtures with more flexible polyelectrolytes.

CPP 61.7 Thu 18:00 H51

Excluded Volume Effects in Polymer Brushes at Moderate Chain Stretching — ●DIRK ROMEIS and MICHAEL LANG — Leibniz Institut für Polymerforschung Dresden e.V.

We develop a strong stretching approximation for a polymer brush made of self-avoiding polymer chains [1]. The density profile of the brush and the distribution of the end monomer positions in stretching direction are computed and compared with simulation data. We find that our approach leads to a clearly better approximation as compared to previous approaches based upon Gaussian elasticity at low grafting densities (moderate chain stretching), for which corrections due to finite extensibility can be ignored. In addition, we test our predictions for the obtained scaling form of the distribution of free chain ends. In contrast to the previous approaches our scaling form is confirmed by simulation data.

[1] Romeis, D.; Lang, M.; Journal of Chemical Physics **141** (10) 104902 (2014)