

CPP 49: Poster: Surfaces, Interfaces, Thin Films, Nanostructures

Time: Wednesday 18:30–21:00

Location: P2-OG1

CPP 49.1 Wed 18:30 P2-OG1

3D Depth Profiles of the Tip-Sample Interaction on Compliant Polymers — ●MARTIN DEHNERT and ROBERT MAGERLE — Fakultät für Naturwissenschaften, Technische Universität Chemnitz, Germany

Attractive forces between the tip of an atomic force microscope and a polymer melt or a swollen polymer act over several tens of nanometers. The tip indentation into these compliant materials is of similar size. Both effects cause a large uncertainty in height measurements. Here we compare 3D depth profiles of the tip-sample interaction measured with force-distance (FD) and amplitude-phase-distance (APD) measurements. In particular, we compare the height profiles reconstructed from different characteristic points on FD and APD curves that might characterize the unperturbed surface position: (a) the onset of attractive forces, (b) the contact point where attractive and repulsive forces balance each other, and (c) the position of the maximal attractive force in FD measurements. All three geometrical quantities do not require assumptions about material properties or a specific contact model. As examples, we study polystyrene melts with low molecular weight and polystyrene droplets swollen in solvent vapor. A solid Si wafer serves as substrate and height reference. Our approach allows for accurate height and 3D shape measurements of compliant polymeric nanostructures.

CPP 49.2 Wed 18:30 P2-OG1

Annealing of Diblock Copolymer Thin Films using Solvent Vapor Mixtures — ●FLORIAN JUNG¹, ANATOLY V. BEREZKIN¹, DETLEF-M. SMILGIES², DORTHE POSSELT³, and CHRISTINE M. PAPADAKIS¹ — ¹Technical University of Munich, Physics Department, Garching, Germany — ²Cornell University, CHESS Wilson Lab, Ithaca, NY, U.S.A. — ³Roskilde University, Department of Science and Environment, Denmark

Block copolymers self-assemble into nanostructures. Solvent vapor annealing (SVA) is an efficient method to improve the long-range order or to alter the morphology in block copolymer thin films.

In the present work, SVA is carried out on thin films from a polystyrene-*b*-poly(dimethyl siloxane) (PS-*b*-PDMS) diblock copolymer. For annealing, vapor mixtures of toluene and *n*-heptane were used, which are weakly selective for PS and highly selective for PDMS, respectively. The morphological changes were investigated by in-situ, real-time grazing-incidence small-angle X-ray scattering (GISAXS). Varying the vapor composition during the annealing cycle results in a lamellar morphology and cylinders with different orientations. Using the scattering contrast, the distribution of the two solvents in the microphase separated thin film can be determined. This information can be transferred to a phase diagram and be related to the observed morphologies during annealing.

The results show that solvent exchange during SVA gives control over the morphology, and that GISAXS can be used to track the trajectory through the phase diagram experimentally.

CPP 49.3 Wed 18:30 P2-OG1

NPT Kinetic Monte Carlo Simulations of Photo-Switchable Molecules on a Surface — ●FREDERICO BRÜCKELMANN, MATTHEW DENNISON, and HOLGER STARK — Institut für Theoretische Physik, Technische Universität Berlin, Hardenberg Str. 36, 10623 Berlin, Germany

Photo-switchable molecules can undergo a light-induced trans-cis isomerization. Used as a functional group in polymers, one can fabricate porous media with light-switchable surface area, diffusivity, and permeability (e.g. for CO₂ and O₂ [1]). This promises new functional materials with reversible light-controlled macroscopic properties.

We use a molecular model for the porous medium, which builds on previous work in [2,3], where the trans and cis isomers are modeled as straight and bent hard-core needles, respectively. We develop a kinetic Monte Carlo simulation in the isothermal-isobaric ensemble that allows for moves in the system volume, which are coupled to the system's response time through the Frank elastic constants. We investigate the system's response as the molecules undergo trans-cis isomerization and monitor changes in volume and the distribution of pore sizes.

[1] D. Becker, N. Konnertz, M. Böhning, J. Schmidt, and A. Thomas,

Chem. Mater. (2016), DOI:10.1021/acs.chemmater.6b02619.

[2] R. Tavarone, P. Charbonneau, and H. Stark, J. Chem. Phys. **143**, 114505 (2015).

[3] R. Tavarone, P. Charbonneau, and H. Stark, J. Chem. Phys. **144**, 104703 (2016).

CPP 49.4 Wed 18:30 P2-OG1

Adsorption Simulations of Plasma Proteins on Silica Surfaces — ●TIMO SCHÄFER^{1,2}, GIOVANNI SETTANNI^{1,3}, and FRIEDERIKE SCHMID¹ — ¹Johannes Gutenberg-University Mainz — ²Graduate School Materials Science in Mainz — ³Max Planck Graduate Center with the Johannes Gutenberg-University Mainz

Nanoparticle based therapeutics are a topic of ongoing research, promising effective use as drug delivery systems that shield aggressive and/or fragile drugs while transporting them to a target location inside the body. One of the major challenges in their application is the formation of a layer of adsorbed plasma proteins as soon as the nanoparticle enters the blood stream. This so-called protein corona can significantly impair the nanoparticle's functionality such as active targeting or enhancement of blood circulation times. While the corona formation can be limited, existing techniques cannot completely prevent it, and molecular details of the underlying mechanism are largely unknown. Here, we study the early adsorption of plasma proteins onto the surface of a silica nanoparticle using classical atomistic molecular dynamics simulations. Using a sophisticated silica surface model, adsorption dynamics, interaction patterns and the impact of the adsorption on protein structure and functionality are analyzed.

CPP 49.5 Wed 18:30 P2-OG1

Specific Ion Effects on the Adsorption and Structure of Dodecyl Sulfate Modified Air/Water Interfaces — ERIC WEISSENBORN¹, ●CHRISTIAN SAUERBECK², and BJÖRN BRAUNSCHWEIG¹ — ¹Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany — ²Institute of Particle Technology (LFG), Friedrich-Alexander University of Erlangen-Nürnberg (FAU), Cauerstrasse 4, 91058 Erlangen, Germany

The influence of Li⁺, Na⁺ and Cs⁺ cations on the coverage and structure of dodecyl sulfate (DS) anions at the air/water interface was investigated with a thin film pressure balance (TFPB) and vibrational sum-frequency generation (SFG). Particularly we have addressed the change in amplitude of O-H stretching bands which provides information on the charging state of the interface. That is because the static electric field within the interfacial's double layer can polarize and polarize interfacial H₂O molecules. As a consequence, the amplitude of O-H bands in SFG spectra becomes strongly dependent on the interfacial net charge. In addition, an analysis of the symmetric S-O stretching band at 1070 1/cm as a function of bulk salt and DS concentration provides information on the surface coverage and Gibbs free energies of adsorption when an adsorption isotherm is fitted to the experimental data. Here, we can show that the latter are a function of the bulk salt concentration and are ion specific. The magnitude of this ion specific effect decreases with the size of the alkali cation in the following way Cs⁺ > Na⁺ > Li⁺.

CPP 49.6 Wed 18:30 P2-OG1

Stack of ultrathin Gallium layers — ●SEBASTIAN RUNDE, HEIKO AHRENS, and CHRISTIANE A. HELM — Inst. of Physics, Greifswald University, D-17487 Greifswald

Fabrication of ultrathin conductive layers is important for many technological applications. We describe a forced wetting method for the formation of ca. 3 nm thin gallium layers that extend up to 10 cm². Optical and atomic force microscopy image the layers on different length scales. X-ray reflectivity measurements show that the Ga layers immediately form a sub-nm thick oxide coating at the film/air surface under ambient conditions. Different substrates are used successfully (Si wafers, partially oxidized Si wafers, borosilicate glass). Up to five layers can be formed by forced wetting on top of each other. According to X-ray reflectivity, the repeat distance of the Ga layers in the stack is 2.7-2.8 nm.

CPP 49.7 Wed 18:30 P2-OG1

Towards functionally graded latex films: preparation using plasma-electrochemistry during drying — SEBASTIAN HOCHSTÄDT¹, ALEXANDER MÜLLER¹, HEIKE RÖMERMANN¹, OLIVER HÖFFT², FRANK ENDRES², and DIETHELM JOHANNSMANN¹ — ¹Institute of Physical Chemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 4, 38678 Clausthal-Zellerfeld — ²Institute of Electrochemistry, Clausthal University of Technology, Arnold-Sommerfeld-Str. 6, 38678 Clausthal-Zellerfeld

Coatings with functionality varying from top to bottom have widespread applications. One way to achieve such gradients is surface treatment on dry films, for instance with a plasma or a flame. Here, we report on plasma treatment of wet films during drying. Both reductive and oxidative plasmas were used. In the first case, we employed a cold atmospheric argon plasma jet. The latex films contained metal salts, which, upon reduction, formed metal particles (copper and silver) on top of the film, or reduced potassium hexacyanoferrate (III) to change its color. These were studied with optical microscopy, SEM, and CLSM. Such particles can find applications as biocides. In the second case, an oxidative atmospheric DBD plasma was used to create a vertical gradient in the concentration of red potassium hexacyanoferrate (III) across the film. The salt had been introduced into the film in its yellow form and was oxidized to the red form. The gradient was qualitatively analyzed using UV-VIS spectroscopy and optical microscopy.

CPP 49.8 Wed 18:30 P2-OG1

Local dynamics in macromolecules at the interface to inorganic fillers — JANA SCHABER¹, FRANCK FAYON², and ULRICH SCHELER¹ — ¹Leibniz-Institut für Polymerforschung Dresden e.V. — ²CEMHTI CNRS Orleans

Dynamic NMR is well suited for the investigation of polymer chain dynamics. However NMR experiments are usually bulk measurements which yield an ensemble average. Two approaches are demonstrated for the selective excitation of protons from the polymer in the vicinity of the filler. A combination of T2 filter and chemical shift selection permits the selective excitation of the OH protons Hydroxyapatite nanoparticles. A second approach is based on heteronuclear magnetization transfer from the filler (29Si enriched silica) to the protons of the surrounding polymer. Subsequent spin diffusion transfers the magnetization further to the protons in the polymer matrix. A combination with relaxation experiments gives the relaxation time as a function of the distance to the filler particle. In the direct vicinity to the interface a short T2 indicative of restricted motion has been found. The combination with chemical shift resolution allows to attribute the observed relaxation times to functional groups or the water contained in the biomimetic nanoparticles.

CPP 49.9 Wed 18:30 P2-OG1

Direct photo alignment of tetracene via light-directed molecular self-assembly (LDSA) — LINUS PITHAN^{1,3}, PAUL BEYER¹, LAURA BOGULA¹, ANTON ZYKOV¹, PETER SCHÄFER¹, JONATHAN RAWLE², CHRIS NICKLIN², ANDREAS OPITZ¹, and STEFAN KOWARIK¹ — ¹Humboldt-Universität zu Berlin, Institut für Physik — ²Diamond Light Source, Didcot, UK — ³ESRF, Grenoble, France

There is an ongoing quest to tailor molecular thin film growth and thereby enhance the functionality of organic thin film structures. Here, we introduce light-directed molecular self-assembly (LDSA) to align and pattern molecular crystallites on amorphous, isotropic substrate.[1] We grow tetracene ($C_{18}H_{12}$) thin films on amorphous SiO_x surfaces via organic molecular beam deposition (OMBD) and study the direct-photo-alignment of molecular crystallites through 532 nm laser illumination, which matches the absorption band of the lower Davydov component of tetracene.

Based on LDSA we produce thin films that feature patterned, polarised optical emission due to the inherent anisotropic optical properties of aligned polycrystalline tetracene structures. We use grazing incidence X-ray diffraction (GIXD) as well as polarisation sensitive optical spectroscopy to analyse the degree of azimuthal alignment in the film and its dependency on the laser light intensity during growth.

[1] L. Pithan et. al. Adv. Mater. 2016 doi:10.1002/adma.201604382

CPP 49.10 Wed 18:30 P2-OG1

Sublimation enthalpy and vapor pressure of thermally unstable substances from fast scanning calorimetry — AMIR ABDELAZIZ, DZMITRY ZAITSAU, SERGEY VEREVKIN, and CHRISTOPH SCHICK — University of Rostock, Germany

The determination of vapour pressure and corresponding enthalpy of sublimation lay within focus of many scientific fields and industrial applications. These values directly connected to the intermolecular forces in crystal state, provides the lattice energy and change in ordering by going from crystal to gas phase. In the present study the fast scanning calorimetry was successfully applied for determination of vapour pressure and enthalpies of sublimation of low volatile organic substances. In many cases investigation of such systems is accomplished with low thermal stability of them and application of classic techniques often fails by determining the decomposition rate of the system. The technique is based on the determination of the mass loss rate of the sample from the experimental total heat capacity and preliminary determined specific heat capacity of the compound under study. Sublimation of the sample is carried out during repeated isotherms of pre-defined duration and at selected temperatures. Sample is heated to needed temperatures at high heating rates accessible by this technique, what allows reaching the sublimation temperatures without any mass loss during the heating time. From the other side in the proposed technique the sublimation area is so big that sublimation mass loss rate is incomparably higher than decomposition rate. Thus the sample of tenth nano grams sublimates without any thermal degradation.

CPP 49.11 Wed 18:30 P2-OG1

Large-Area Surface Relief Gratings on Thin Films of Azobenzene-Containing Molecular Glasses — STEFAN HARTUNG¹, LOTHAR KADOR¹, ANDREAS SCHEDL², KLAUS KREGER², and HANS-WERNER SCHMIDT² — ¹University of Bayreuth, Institute of Physics and BIMF, 95440 Bayreuth, Germany — ²University of Bayreuth, Macromolecular Chemistry I, 95440 Bayreuth, Germany

Illumination of azobenzene-containing materials with a light intensity grating does not only give rise to a refractive-index modulation in the bulk but, depending on the type of material and the polarization state of the light, also to the formation of a surface relief grating (SRG). SRGs feature high diffraction efficiencies and are, therefore, promising candidates for technical applications such as diffractive optical elements (DOEs). We demonstrate that holographic illumination with two coherent expanded laser beams ($\lambda = 489$ nm) can efficiently produce SRGs with grating constant of 1 micrometer and diameter of more than 1 centimeter on thin films of an azobenzene-containing molecular glass. Due to the non-contact holographic generation, the gratings are virtually defect-free over the whole area. AFM measurements on various spots of the grating demonstrate that for short writing times, the amplitude follows the Gaussian cross section of the writing laser, whereas a more homogeneous amplitude distribution can be achieved with longer inscription. With laser powers of a few hundred milliwatts, typical writing times are on the order of several minutes. Repeated illumination under different rotation angles of the film gives rise to complex two-dimensional SRGs.

CPP 49.12 Wed 18:30 P2-OG1

Morphology improvement of ZnO/P3HT-b-PEO bulk heterojunction films by using a low temperature route — KUN WANG¹, YU TONG², RUI WANG³, STEPHAN V.ROTH⁴, LORENZ BIESSMANN¹, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching — ²LMU, Department für Physik und CeNS, Amalienstraße 54, 80799 München — ³JCNS at MLZ, Lichtenbergstr. 1, 85748 Garching — ⁴DESY, Notkestr. 85, 22607 Hamburg

Hybrid solar cells, a combination of conventional inorganic and organic photovoltaic systems, offer outstanding potential due to their minor investment compared to inorganic solar cells and higher stability compared to organic solar cells. However, so far device efficiencies are significantly lower as compared to the other photovoltaic systems. A possible way to improve the film structure and thereby the device efficiency is to introduce amphiphilic block copolymers into the sol-gel synthesis of the inorganic part such as ZnO. Unlike the traditional diblock copolymer, in the present approach we make use of a new functional block copolymer PEO-b-P3HT. In the PEO block the ZnO phase is synthesized and the P3HT block can be used directly as the hole transporting layer. The nanostructure inside thin films is probed with GISAXS. Moreover, SEM and AFM detect the surface morphology of the composite films. The optical properties are examined with UV/Vis spectroscopy and the thickness is investigated by profilometry measurements.

CPP 49.13 Wed 18:30 P2-OG1

Slip effects on forced dewetting — TAK SHING CHAN, MARTIN

BRINKMANN, and RALF SEEMANN — Experimental Physics, Saarland University, D-66041 Saarbrücken, Germany

Slippage of fluid over a solid surface is known to have a weak (logarithmic) effect in macroscopic dynamic wetting. In this contribution, we study the forced dewetting of a liquid of viscosity η confined in a cylindrical tube of radius r_0 for a wide range of slip length b using the boundary element method. For $b \ll r_0$, the prediction of the critical velocity (U_c) of entrainment $Ca_c \equiv \eta U_c / \gamma \sim 1 / \ln(cr_0/b)$ by classical dynamic wetting models is recovered. Here γ is the surface tension of liquid/air interface and c an undetermined prefactor. When increasing the slip length, we demonstrate a crossover from the logarithmic relation to a regime where Ca_c scales linearly with b for large b . In this regime, the energy input to the system is mainly dissipated by the friction at the solid/ liquid boundary. Our finding connects the dynamical wetting phenomena in macroscopic systems and small-scaled fluidic systems.

CPP 49.14 Wed 18:30 P2-OG1

Pinned and Sliding Drops – Bifurcations and Statistics –

•SEBASTIAN ENGELNKEMPER, MARKUS WILCZEK, SVETLANA GUREVICH, and UWE THIELE — Institut für Theoretische Physik, Westfälische Wilhelms-Universität, Corrensstr. 2, 48149 Münster

The long-wave evolution equation for a liquid film (thin-film equation) describes the dynamics of free surface structures (e.g., drops and ridges) on solid substrates. On homogeneous substrates all structures move for any applied lateral driving force (e.g., inclining the substrate). They change their shape and may at a critical driving force undergo a pearling instability where large drops emit small satellite drops [1]. On heterogeneous substrates (e.g., with a wettability pattern) drops remain pinned at more wettable spots even at small driving force. At a critical driving the drops undergo a depinning transition as analyzed for 2d drops in [2]. Here we implement the thin-film equation in the continuation-toolbox PDE2PATH [3] and analyze shape changes of 3d sliding and pinned drops on homo- and heterogeneous substrates, respectively. Main control parameters are drop volume and substrate inclination. The pearling instability of sliding drops is identified as a global bifurcation of stationary sliding drops [4]. Finally, the single-drop continuation results are related to the drop size statistics obtained in direct simulations of large drop ensembles. [1] T. Podgorski et al., Phys. Rev. Lett. 87, 036102 (2001); [2] U. Thiele, et al., NJP 8, 313 (2006); [3] H. Uecker et al., arXiv:1208.3112v2 (2012); [4] S. Engelnkemper et al., Phys. Rev. Fluids 1, 073901 (2016);

CPP 49.15 Wed 18:30 P2-OG1

Utilizing Confocal Active Interference Scattering Microscopy to directly measure the phase of light scattered by a single nanoparticle – •OTTO HAULER, FRANK WACKENHUT, KAI BRAUN, and ALFRED J. MEIXNER — Institute of Physical and Theoretical

Chemistry, Tübingen, Germany

In the recent years the optical properties of noble metal nanoparticles of different shapes and sizes have been widely studied and exploited by nanotechnology based assays. Especially gold nanoparticles are promising candidates for various applications due to their outstanding optical properties, which are dictated by their particle plasmons [1-4]. A powerful tool to investigate single gold nanoparticles is confocal scattering microscopy combined with higher order laser modes. We extended this established method in a way that allows us to directly measure the phase of the scattered light by introducing an interferometrical detection scheme similar to a Michelson interferometer. This enables us to measure the phase and amplitude of the light scattered by single gold nanoparticles and will enhance the usefulness of this imaging technique. [1] Frank Wackenhut, Antonio Virgilio Failla, Tina Züchner, Mathias Steiner, and Alfred J. Meixner, Applied Physics Letters 100 (26), 263102 (2012). [2] Frank Wackenhut, Antonio Virgilio Failla, and Alfred J. Meixner, The Journal of Physical Chemistry C 117 (34), 17870 (2013). [3] Frank Wackenhut, Antonio Virgilio Failla, and Alfred J. Meixner, Phys. Chem. Chem. Phys. 15 (15), 5407 (2013). [4] Frank Wackenhut, Antonio Virgilio Failla, and Alfred J. Meixner, Anal Bioanal Chem 407 (14), 4029 (2015).

CPP 49.16 Wed 18:30 P2-OG1

Silver iodide nanowires grown in amphiphilic tubular templates – •EGON STEEG, KATIE HERMAN, HOLM KIRMSE, JÜRGEN P RABE, and STEFAN KIRSTEIN — Institut für Physik, Humboldt-Universität zu Berlin

It was shown in previous work [1] that silver nanowires 6 nm in diameter can be grown by reduction of AgNO_3 in the presence of tubular aggregates of cyanine dyes in aqueous solution. Here we present an adaptation of this system for the growth of AgI structures by using additional iodide ions. Wire-like, single crystal structures of AgI that fill the inner space of the tubular aggregates are found. These AgI structures have diameters of 6 to 7 nm and lengths of tens of nanometers. The crystal structure of the AgI wires was investigated by means of high resolution transmission electron microscopy and selected area electron diffraction. The AgI could be clearly identified by its typical wurtzite structure. Small crystallites of pure silver can be found embedded in these AgI wires. The relative orientation of the respective crystal lattices indicates epitaxial growth of AgI on pure Ag or vice versa. It is possible that the negatively charged iodide ions have a higher concentration in the interior of the tubular aggregates than in the surrounding solution. This would favor the growth of AgI crystals within the tubules. These findings may demonstrate a possible route for growing other metal halide structures within the amphiphilic cyanine dye tubules.

[1] E. Steeg et al., Journal of Colloid and Interface Science 472(2016)187