

CPP 25: Interfaces and Thin Films II

Time: Tuesday 9:30–13:00

Location: PC 203

Invited Talk

CPP 25.1 Tue 9:30 PC 203

Understanding self-assembly in gyroid terpolymer films — ●ILJA GUNKEL — Adolphe Merkle Institute, Fribourg, Switzerland

Block copolymer (BCP) self-assembly is an effective tool for generating various nanostructured morphologies. Over the past decades, tremendous progress has been made in both understanding and controlling the self-assembly of BCP thin films. However, this has been mostly seen in diblocks, the simplest BCP architecture, enabling the generation of well-ordered two-dimensional patterns with applications, for example, as nanolithography masks. Simply extending a diblock by a third chemically distinct block, thereby creating a so-called triblock terpolymer, provides access to more complex morphologies, *e.g.* the gyroid. The unique geometry of the gyroid - a bicontinuous and triply periodic cubic morphology with inherent chirality - holds promise for enabling new applications like optical metamaterials. Creating the desired functionality in these plasmonic materials requires precise structural control of the polymer template used for their fabrication. However, this level of control and detailed understanding of triblock terpolymer self-assembly have yet to be achieved. In this talk, I will present recent results showing that gyroid terpolymer films with long-range order can be generated by controlled solvent vapor annealing. I will further show that terpolymer self-assembly in films during annealing can be tracked by *in situ* grazing-incidence small-angle x-ray scattering (GISAXS). These experiments provide detailed structural information, which is key to generating well-ordered gyroid terpolymer films that can serve as templates for the fabrication of optical metamaterials.

CPP 25.2 Tue 10:00 PC 203

Solvothermal Annealing of a Diblock Copolymer Film in Solvent Vapor Mixtures — ANATOLY V. BEREZKIN¹, FLORIAN JUNG¹, DORTHE POSSELT², DETLEF-M. SMILGIES³, and ●CHRISTINE M. PAPADAKIS¹ — ¹TU München, Physik-Department, Garching, Germany — ²Roskilde University, Department of Science and Environment, Denmark — ³Cornell University, Cornell High Energy Synchrotron Source, Ithaca NY, U.S.A.

Solvent vapor annealing is often used to control the structure of block copolymer thin films [1]. Solvothermal vapor annealing (STVA) combined with variable mixing of solvent vapors allows one to produce a number of morphologies. We carried out STVA on a thin film from polystyrene-*b*-polydimethylsiloxane (PS-*b*-PDMS) using vapors from *n*-heptane and toluene at elevated temperature, varying the vapor composition step by step. Cylindrical and lamellar morphologies are detected using *in-situ*, real-time grazing-incidence small-angle X-ray scattering. To corroborate these morphologies, they are generated by molecular simulations, and the corresponding 2D GISAXS maps are calculated. The solvent distribution in the two types of nanodomains is estimated from the intensity of the Bragg reflections along with the swelling ratio of the film. The combination of these methods opens up for the efficient preparation of block copolymer thin films having the desired morphology and orientation and furthers the understanding of the underlying mechanisms.

[1] Posselt et al., *Prog. Polym. Sci.* **66**, 80 (2017).

CPP 25.3 Tue 10:15 PC 203

Self-propulsion of Janus Particles near a brush Surface: Impact of the Brush Chain Length — ●MOJDEH HEIDARI¹, SANTIAGO MUINOS LANDIN², FRANK CICHOS², and REGINE VON KLITZING¹ — ¹Smart Matter at Interfaces, Department of Physics, Technical University of Darmstadt, Alarich-weiß-straße 10, 64287 Darmstadt, Germany — ²Molecular Nanophotonics Group, Peter Debye Institute for Soft Matter Physics, Faculty of Physics and Earth Sciences, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany

GoldAu-polystyrene Janus particles demonstrate a thermophoretic induced motion under laser illumination ($\lambda=532$ nm). The plasmons in the gold cap of the particle get excited and cause the particle to create a local temperature gradient. Such out-of-equilibrium condition at the surface of the particle leads to its self-propulsion.

In this study we explore the 2D self-propulsion of Janus particles between two glass substrates. The substrate is functionalized with PNIPAM brushes. Our former experiments have proved that particles express an enhanced self-propulsion close to PNIPAM-brush. Here we alter the brush thickness and subsequently investigate its impact on the

self-propulsion of the particle. Trajectories of particles are represented under different laser intensities.

CPP 25.4 Tue 10:30 PC 203

Near surface dynamics of PEG and PNIPAM based polymer brushes — ●JUDITH WITTE¹, TETYANA KYREY^{1,2}, REGINE VON KLITZING³, OLAF HOLDERER², and STEFAN WELLERT¹ — ¹TU Berlin, Institute for Chemistry, Berlin, Germany — ²Heinz Maier Leibniz Zentrum, JCNS, Garching, Germany — ³TU Darmstadt, Institute for Condensed Matter Physics, Darmstadt, Germany

The physical properties of stimuli-responsive polymer brushes still receive vast interest in basic research. Polymer brushes undergoing a temperature induced phase transition are of major interest for technical applications such as (bio)functional coatings. Polymer brushes are polymers end-tethered to a solid surface. A variation of the chemical composition, brush height or grafting density allows for a wide range of different polymer coatings with distinct properties. Among them, thermoresponsive polymer brushes based on P(MEO₂MA-co-OEGMA) are, due to their biocompatibility, promising candidates for smart biocoatings. PNIPAM based polymer brushes serve as a prominent model system for thermoresponsive polymer coatings. Here we focus on recent grazing incidence neutron spin echo spectroscopy experiments probing the dynamics inside these polymer brush layers on the nanometer length and nanosecond time scale. At two neutron penetration depths we explored the segmental dynamics well below the LCST. The data suggest an influence of the nonuniform blob size on the relaxation time inside the brushes which is discussed in the talk.

CPP 25.5 Tue 10:45 PC 203

3D Depth Profiles of the Tip-Sample Interaction on Polystyrene Swollen in Chloroform Vapor using Atomic Force Microscopy — ●MARTIN DEHNERT and ROBERT MAGERLE — Fakultät für Naturwissenschaften, Technische Universität Chemnitz, Germany

In atomic force microscopy (AFM) on soft polymers and liquids, the tip-sample interaction is dominated by long range van der Waals and capillary forces and the tip can indent several tens of nanometers into the surface. Therefore, measuring the unperturbed shape of the soft surface can be challenging. Here, we examine polystyrene droplets swollen in chloroform vapor, where we can adjust the specimens' mechanical properties via the solvent vapor concentration from a stiff solid to a fluid film. With the same AFM tip, we measure three-dimensional (3D) depth profiles of the tip-sample interaction with two different AFM force spectroscopy methods: force-distance (FD) curves and amplitude-phase-distance (APD) curves. The 3D depth profiles reconstructed from FD and APD measurements provide a detailed insight into the tip-sample interaction mechanism with a fluid PS droplet. Furthermore, we discuss how the unperturbed shape of a fluid droplet can be determined from FD and APD depth profiles. We expect that this versatile methodology can also be used for investigating other fluid and gel-like objects on the nanometer scale.

15 min. break**Invited Talk**

CPP 25.6 Tue 11:15 PC 203

Soft Interfaces Studied with the Quartz Crystal Microbalance — ●DIETHELM JOHANNSMANN and ARNE LANGHOFF — Institute of Physical Chemistry, TU Clausthal

The response of soft interfaces to acoustic shear waves gives clues to their structure, dynamics, and functionality. This response is conveniently probed with the quartz crystal microbalance (QCM). In recent years, the quartz crystal microbalance has turned into a surface-analytical tool with capabilities much beyond gravimetry.

Among the recent novel application of the QCM is high-frequency contact mechanics. Exploiting the amplitude dependence of the shifts in resonance frequencies and the resonance bandwidths on the different overtones, one can follow the transition from stick to (oscillatory) slip. A second field with recent progress are fast measurements (10 ms) combined with a modulation of the electrical potential. For repetitive processes, accumulation drives the precision down the level of a few mHz. Combination of the QCM with potential modulation amounts to a novel sensing dimension even outside electrochemistry.

CPP 25.7 Tue 11:45 PC 203

Interaction-dependent structure of biomimetic soft interfaces : a new method for neutron reflectometry studies — ●SAMANTHA MICCIULLA^{1,2}, YURI GERELLI², and EMANUEL SCHNECK¹ — ¹Max-Planck-Institut für Kolloid und Grenzflächenforschung, Potsdam, Germany — ²Institut Laue-Langevin, Grenoble, France

The structural investigation of biological interfaces encounters significant methodological restrictions, due to the limited number of techniques able to probe buried interfaces with high resolution and in a perturbation-free manner. Neutron reflectometry meets these fundamental requirements and it owes the unique capability of selecting individual parts of molecular assemblies by isotopic labelling. In our group, we exploit this technique to study biomimetic interfaces under controlled interaction conditions. In this contribution, a new method to study the structure of soft interacting surfaces at varying separation distances by neutron reflectometry is presented. The method exploits a fine control of the interfacial distance by moving a lipid monolayer at the oil/water interface against a functionalized solid surface. Its applicability to study interacting soft interfaces is demonstrated by the results of recent experiments on systems showing very diverse interaction behavior, from full adhesion to strong repulsion. Finally, morphological features and dynamics of the fluid interface at different distances from the solid substrate are deduced by fluorescence microscopy.

CPP 25.8 Tue 12:00 PC 203

In situ growth study during spray deposition of bio-based materials — ●CALVIN BRETT^{1,2,3}, NITESH MITTAL^{1,2}, WIEBKE OHM³, BJÖRN FRICKE³, DANIEL SÖDERBERG¹, and STEPHAN V. ROTH^{3,4} — ¹Department of Mechanics, Royal Institute of Technology (KTH), Stockholm, Sweden — ²Wallenberg Wood Science Center (WWSC), Stockholm, Sweden — ³Photon Science, Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — ⁴Department of Fibre and Polymer Technology, Royal Institute of Technology (KTH), Stockholm, Sweden

Assemblies of high aspect-ratio nanoparticles are used in large-scale processes to create high-performance materials. We transferred these concepts to self-assembled thin films with tunable properties. Airbrush spray deposition - a scalable and rapid film fabrication process - is used to fabricate cellulose nanofibril (CNF) thin films. CNF as produced from wood presents a renewable and sustainable bio-material which draws increasing attention as template material for flexible, yet disposable electronics. By combining airbrush spray deposition with bio-based materials as CNFs we thus aim for scalable, industrially applicable, sustainable templates. In order to fully understand the fabrication kinetics during film growth, we took the advantage of surface sensitive X-ray scattering techniques in combination with in situ surface differential reflectance spectroscopy. Our study reveals very homogeneous CNF thin films with an unprecedented roughness below 2 nm in combination with a tunable wettability.

CPP 25.9 Tue 12:15 PC 203

Thin films of perfluorinated sexithiophene and blends with sexithiophene — ●BERTHOLD REISZ¹, SIMON WEIMER¹, RUPAK BANERJEE², CLEMENS ZEISER¹, CHRISTOPHER LORCH¹, GIULIANO DUVA¹, JOHANNES DIETERLE¹, KEIICHIROU YONEZAWA³, JIN-PENG YANG³, NOBUO UENO³, SATOSHI KERA^{3,4}, ALEXANDER HINDERHOFER¹, ALEXANDER GERLACH¹, and FRANK SCHREIBER¹ — ¹Universität, Tübingen, Deutschland — ²IIT, Gandhinagar, India — ³Chiba University, Chiba, Japan — ⁴Institute for Molecular Science, Okazaki, Japan

This is the first study of thin films containing perfluorinated sexithiophene (PF6T), a molecule which was firstly synthesized in 2001 [1]. We found a new thin film polymorph and a coexistence of lying-down and standing-up molecules depending on the substrate temperature dur-

ing organic molecular beam deposition [2]. Furthermore, we prepared blended thin films by co-evaporation of PF6T and its non-fluorinated counterpart 6T at different mixing ratios and examined their morphology, as well as their electronic and optical properties [2]. Atomic force microscopy shows a continuous transition from terraced islands to tall columnar features with increasing amount of PF6T. Grazing incidence X-ray diffraction patterns indicate that an excess of 6T-molecules is segregated from a statistically mixed phase. Finally, UPS data and optical absorption measurements suggest that 6T-PF6T blends could serve as a donor-acceptor system for optoelectronic applications.

[1] Y. Sakamoto et al., *J. Am. Chem. Soc.* **123** (2001)[2] B. Reisz et al., *J. Mater. Res.* **32** (2017)

CPP 25.10 Tue 12:30 PC 203

Real-Time Study on Growth and Packing Behavior of PDIs Thin Films Influenced by Side-Chains Modification — ●VALENTINA BELOVA¹, BENJAMIN WAGNER¹, BERTHOLD REISZ¹, CLEMENS ZEISER¹, GIULIANO DUVA¹, JAKUB ROZBOŘIL², JIŘÍ NOVÁK², ALEXANDER GERLACH¹, ALEXANDER HINDERHOFER¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Tübingen, Germany — ²Masaryk University, Brno, Czech Republic

We study the growth of two highly performing small molecule organic semiconductors from the perylene diimide family (PDIs) interesting for photovoltaic application due to their good electron-accepting properties [1]: PDIR-CN2 and PDIF-CN2 whose chemical structures differ only in the imide substituents: branched alkyl chains and linear fluoroalkyl chains, respectively. Both types of substituents introduce some degree of steric hindrance for intermolecular interaction affecting solid state packing during vacuum deposition and thus induce specific structure-dependent optoelectronic properties in thin films. The phase transition from an amorphous structure to crystalline domains was followed in situ and in real-time by X-ray diffraction as a function of substrate temperature. We examined the relationship between structural properties and optical signatures probed via differential reflectance spectroscopy in real-time, ellipsometry and photoluminescence. A new crystalline polymorph for PDIR-CN2 at high temperatures was found. We observed that the fluorinated chains contribute to crystallization inhibition and surface roughening due to their high electron density. [1] V. Belova et al., *JACS*, **139**, 8474 (2017).

CPP 25.11 Tue 12:45 PC 203

Grazing Incidence Small Angle X-ray Scattering Study on Nucleation Processes during Electrodeposition — ●GILLES MOEHL and ANDREW HECTOR — Chemistry, University of Southampton, Southampton, SO17 1BJ, UK

Developing the next generation of electronic devices requires the deposition of high-quality functional materials in a controlled fashion in complex structures in order to unleash the true potential of devices such as thermoelectrics, phase change memory (PCM) and infra-red detectors. Within EPSRC programme grant ADEPT *Advanced Devices by ElectroPlating* (EP/N035437/1), new techniques and materials are to be developed for that matter. Previously, it has been shown that the electrodeposition of materials from weakly-coordinating solvents is capable of producing such complex structures (1). Nucleation, being the earliest stage of any deposition process is a key feature which has to be understood in order to achieve fully controlled and reproducibly fabricated materials. This requires techniques capable of monitoring the formation of deposited material on a substrate at various stages in time on very short length scales. Grazing incidence small angle scattering (GISAXS) allows for this, giving insight into the structural properties of the investigated layer and thus possibly enables the derivation of a growth model. In this work, the nucleation of the thermoelectric bismuth telluride Bi₂Te₃ and gold during electrodeposition from dichloromethane and an aqueous electrolyte, respectively, onto titanium nitride (TiN) is investigated through GISAXS. (1). Bartlett, Philip N., et al. *Materials Horizons* **2.4** (2015): 420-426.