

CPP 4: Interfaces and Thin Films

Time: Monday 9:30–12:45

Location: H 0111

CPP 4.1 Mon 9:30 H 0111

Structure and dynamics in functional polymer hydrogel films — ●LUCAS KREUZER¹, CALVIN BRETT², JACQUES OLLIVIER³, STEPHAN ROTH², ANDRÉ LASCHEWSKY⁴, CHRISTINE M. PAPADAKIS⁵, and PETER MÜLLER-BUSCHBAUM⁵ — ¹Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II) — ²Deutsches Elektronen Synchrotron (DESY) — ³Institut Laue-Langevin (ILL) — ⁴Universität Potsdam, Institut für Chemie — ⁵TUM School of Natural Sciences, Technische Universität München

Hydrogel films made from responsive polymers are able to switch between a swollen and a contracted film state in response to slight changes in their surroundings. This behavior can be used to generate highly functional hydrogel thin films e.g., from a multi-responsive diblock copolymer model system containing a zwitterionic poly(sulfobetaine) and a nonionic poly(N-isopropyl acrylamide) block. With neutron scattering techniques, we identified discrete thin-film states, regarding their thickness and film morphology, which can be precisely tuned upon changing external stimuli such as temperature or the composition of the surrounding solvent vapor. Using this knowledge, we now focus on a nanocomposite film from cellulose nanofibrils (CNF) and the electrically conductive polymer poly(3,4-ethylenedioxythiophene):poly styrene sulfonate (PEDOT:PSS). Upon cyclic swelling and drying processes, we investigated the film morphology and internal dynamics. Moreover, the influence of temperature was studied. A first analysis already indicates a correlation between the structural properties, dynamics of water inside the film, and electrical conductivity.

CPP 4.2 Mon 9:45 H 0111

Interfacial Jetting of Microgel Dispersions Induced by Surface Acoustic Wave — ●ATIEH RAZAVI¹, REGINE VON KLITZING¹, AMIN RAHIMZADEH¹, MEHRZAD ROUDINI², and ANDREAS WINKLER² — ¹TU Darmstadt, Hochschulstraße 8, 64289 Darmstadt, Germany — ²SAWLab Saxony, Leibniz Institute for Solid State and Materials Research, Dresden

This study investigates Surface Acoustic Wave (SAW)-induced jetting, focusing on microgel dispersions in acoustofluidics. While SAWs have been used by others to create jets from pure liquids, this research explores the jetting of liquids with microgels as surface active polymer networks at interfaces. The work explores how microgel softness influences interfacial stability during rapid jetting induced by SAWs. Soft microgels demonstrate superior adaptability, preventing interface disintegration and sustaining longer jets compared to stiffer particles. Furthermore, higher dispersion concentrations lead to more stable jets. At 1 wt% concentration, MG1 (microgels including 1 mol% cross-linker) creates a very long jet having normalized jet length $L/R = 8.47 \pm 0.18$, compared to pure water which has an L/R of about 6.5. These findings provide critical insights into the role of microgel softness in stabilizing interfaces during millisecond-order extensions. They highlight the potential for soft microgels to significantly impact dynamic interfacial engineering in high-speed phenomena, particularly in acoustofluidics. Understanding this interplay between microgel properties and interfacial stability holds promise for advancements in rapid droplet manipulation and diverse technological applications reliant on dynamic interface control.

CPP 4.3 Mon 10:00 H 0111

Are refractive index and relative permittivity of an interphase connected to the interfacial adhesion? — ●DOROTHEE SILBERNAGL¹ and HEINZ STURM^{1,2} — ¹BAM, Berlin, Germany — ²TU Berlin, IWF, Germany

Polymer interphases usually form between bulk polymer and more rigid materials. These interphases have distinct physical properties, which can differ significantly from the polymer's bulk properties. Since the dimension of those interphases are usually in the nanometer-scale we chose atomic force microscopy (AFM) force distance curves (FDC) as technique. As sample geometry we chose thin films of poly-n-butylmethacrylate (PnBMA) with different film thicknesses between 30 and 120 nm. This allows for measuring perpendicular to the film-substrate surface with a defined distance to the interface. Additionally, substrates (Si wafers) were etched locally to change the surface' polarity (Si-O versus Si-H-termination), thus tuning the interfacial adhesion of film and substrate from weak to strong. Measuring Young's moduli

of such samples we were able to show the influence of interfacial adhesion. The stronger the interfacial adhesion, the higher the substrate's contribution to the overall mechanical properties. Analysis of FDCs' attractive regime revealed that also the measured Hamaker constant correlates with interfacial adhesion, showing higher contribution from the substrate with stronger adhesion. Since the Hamaker constant is derived from refractive index n and relative permittivity ϵ we hypothesize that - depending on the polymer-substrate adhesion - the polymer interphase inherits the electrodynamic properties of the substrate.

CPP 4.4 Mon 10:15 H 0111

Growth Kinetics and Molecular Mobility of the Adsorbed Layer of Poly(bisphenol-A Carbonate) (PBAC), Polysulfone (PSU), and Poly(2-Vinyl Pyridine) (P2VP) — ●HASSAN OMAR, PAULINA SZYMONIAK, ANDREAS HERTWIG, and ANDREAS SCHÖNHALS — Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany

Interactions between a polymer and a substrate interface play a vital role in understanding the improvement in thin film material properties as well as serving as a model for nanocomposites. For any non-repulsive polymer-substrate interactions, polymer segments form an irreversibly adsorbed layer and show a slowdown in the glassy dynamics and thus an increase in the thermal glass transition temperature compared to the bulk-like values. The growth kinetics of the adsorbed layer showed a deviation for both poly(bisphenol-A carbonate) (PBAC) and polysulfone (PSU), two bulky polymers containing a functional group (phenyl ring) in the backbone, compared to conventional polymers previously studied like poly-2-vinyl pyridine (P2VP). This deviation was attributed to the bulkiness of the phenyl rings. Further investigations into the influence of the adsorbed layer on glassy dynamics were conducted. The molecular mobility and glass transition for thin films of PBAC and PSU were compared to bulk samples of each polymer. Broadband dielectric spectroscopy, atomic force microscopy, and ellipsometry were primarily used and additionally supported by sum frequency generation spectroscopy.

CPP 4.5 Mon 10:30 H 0111

Investigating the Ag growth on PET foil with dcMS and HiPIMS — ●YUSUF BULUT^{1,2}, BENEDIKT SOCHOR¹, KRISTIAN RECK³, SUZHE LIANG², ZHUIJUN XU², ALEXANDER MEINHARDT^{4,5}, ARNO JEROMIN⁴, THOMAS F. KELLER^{4,5}, ANDREAS STIERLE^{4,5}, THOMAS STRUNSKUS³, FRANZ FAUPEL³, PETER MÜLLER-BUSCHBAUM^{2,6}, and STEPHAN V. ROTH^{1,7} — ¹DESY, 22607 Hamburg — ²TUM School of Natural Sciences, Chair for Functional Materials, 85748 Garching — ³CAU Kiel, Chair for Multicomponent Materials, Faculty of Engineering, 24143 Kiel — ⁴CXNS, 22607 Hamburg — ⁵UHH Hamburg, Department of Physics, 22607 Hamburg — ⁶MLZ, TUM, 85748 Garching — ⁷KTH, SE-100 44 Stockholm

High Power impulse magnetron sputtering (HIPIMS) is a novel industrially-relevant deposition technique enabling increased adhesion and denser film formation of thin deposited metal layers on polymers. No pre- and post-treatment is required to achieve these properties. So far, no report has discussed the nucleation and growth process during HiPIMS deposition. In this new study, polyethyleneterephthalate (PET) foil is studied under various deposition conditions. Results of simultaneous in situ grazing-incidence small angle X-ray scattering (GISAXS), grazing incidence wide-angle X-ray scattering (GIWAXS) and field emission scanning electron microscopy (FESEM) are presented.

CPP 4.6 Mon 10:45 H 0111

Controllable Capillary Assembly of Magnetic Janus Particles at Fluid-Fluid Interfaces — ●QINGGUANG XIE¹ and JENS HARTING^{1,2} — ¹Helmholtz-Institut Erlangen-Nürnberg for Renewable Energy (IEK-11), Forschungszentrum Jülich GmbH, Erlangen, Germany — ²Friedrich-Alexander-Universität Erlangen-Nürnberg, Nürnberg, Germany

Self-assembly of particles at fluid-fluid interfaces is a promising route to fabricate functional materials from the bottom-up. However, directing and controlling particles into highly tunable and predictable structures, while essential, is a challenge. Here, we apply a hybrid approach combining the lattice Boltzmann, and the discrete element

methods to investigate the behaviour of magnetic Janus particles adsorbed at a fluid-fluid interface interacting with an external magnetic field. Depending on their tilt angle and shape (e.g. sphere, ellipsoid), the anisotropic particles deform the interface and generate capillary dipoles or hexapoles. Driven by capillary interactions, multiple particles thus arrange into reconfigurable chain-, hexagonal-lattice-, and ring-like structures, which can be actively controlled by varying the external magnetic field. We develop interface energy models to reveal the underlying mechanism and find good qualitative agreement with simulation results. Our results have implications for the fabrication of varied microstructures for use in microdevices, organic electronics, or advanced display applications.

CPP 4.7 Mon 11:00 H 0111

Elastic Capsules in Contact — ●FELIX KRATZ and JAN KIERFELD — TU Dortmund

Contact phenomena between soft or elastic bodies are ubiquitous in nature. They are encountered in problems across the scales and include important biological processes, such as cell interactions, as well as medical applications e.g. angioplasty and drug delivery. An important hallmark in the understanding of contact mechanics is the Hertz-problem, studied and solved by Heinrich Hertz in 1881. It predicts the contact properties of bulk elastic bodies without adhesion or friction. While the contact between two bulk elastic objects is well understood by this theory, the understanding of thin-walled and pressurised elastic objects is still evolving. In this work we want to explore the contact mechanics of two thin walled, pressurised adhesive elastic capsules – with and without bending stiffness – suspended from two opposing capillaries and pressed against each other by an external force. The theoretical investigation is performed in terms of variational calculus of the appropriate free energy. We differentiate between free-slip and no-slip contact boundary conditions and derive the full set of shape and contact equations independent of the elastic constitutive law. Finally, we integrate the resulting shape equations numerically and analyse the parameter-shape-space and the force-contact-length relationship.

15 min. break

CPP 4.8 Mon 11:30 H 0111

Making stable thin nanoporous polymer films — ●HSIAO-PING HSU and KURT KREMER — Max-Planck-Institut für Polymerforschung, Mainz, Germany

Thin polymer films have attracted much attention due to their usefulness as supporting media in tissue engineering or as membranes in the separation processes. Thus a simulation guides processing is highly desirable. Starting from a fully equilibrated free-standing thick film of highly entangled polymer melts based on a weakly semiflexible bead-spring model [1], we apply a simple “biaxial expansion” deformation mechanism to stretch the film. For the present study the film is of thickness of several radii of gyration of the chains and the glass transition temperature T_g is the same as in the bulk case [2]. We analyze the local morphology, the void formation and its stabilization upon cooling after expansion all the way well below T_g . Motivated by these simulations a similar process is applied experimentally on films of highly entangled polystyrene and compared to simulations. Our results show an excellent qualitative and even semi-quantitative agreement [3].

[1] H.-P. Hsu, K. Kremer, *J. Chem. Phys.* 150, 091101 (2019); 153, 144902 (2020).

[2] H.-P. Hsu, K. Kremer, *J. Chem. Phys.* 159, 071104 (2023).

[3] H.-P. Hsu, M. K. Singh, Y. Cang, H. Thérien-Aubin, M. Mezger, R. Berger, I. Lieberwirth, G. Fytas and K. Kremer, *Adv. Sci.* 10, 2207472 (2023).

CPP 4.9 Mon 11:45 H 0111

Neutron Reflectivity of Superspreading and Non-Superspreading Trisiloxane Surfactants — ●JOSHUA REED¹, SÉFORAH CAROLINA MARQUES SILVA^{1,2}, JOACHIM VENZMER², TATIANA GAMBARYAN-ROISMAN¹, and EMANUEL SCHNECK¹ — ¹TU Darmstadt, Darmstadt, Germany — ²Evonik Operations GmbH, Essen, Germany

Some trisiloxane surfactants have the remarkable property of being able to superspread: Small volumes of water rapidly wet large areas of hydrophobic surfaces. The molecular properties which govern this technologically relevant effect are still under debate. To gain a deeper understanding, the surfactant behaviour during the spreading process needs to be studied at molecular length scales. Here, we

present neutron reflectivity analyses of two trisiloxane surfactants of similar structure, of which only one exhibits superspreading properties. We present an approach to determining the composition of the adsorbed surfactant layer in droplets at the solid-liquid and at the liquid-air interface, and accounting for neutron attenuation of back-reflections in thin layers. Subtle differences between superspreading and non-superspreading surfactants in the volume fractions of the self-consistent analysis might be able to explain the difference in spreading behaviour.

CPP 4.10 Mon 12:00 H 0111

Spiralling Hierarchical Structures in Chiral Lipid Monolayers Mapped with SFG Microscopy — ●ALEXANDER FELLOWS, BEN JOHN, MARTIN WOLF, and MARTIN THÄMER — Fritz-Haber-Institut der MPG, Berlin, Germany

The importance of phospholipids cannot be overstated. Their amphiphilic nature promotes self-assembly into two-dimensional membranes in which the hydrophobic tails tightly pack and point away from the membrane interface. Beyond this well-defined out-of-plane structure, the specific in-plane molecular arrangement also has profound implications in a vast range of physiological processes. Studies of model systems have shown condensed lipid islands (rafts) to form with a wide range of sizes and morphologies. Whilst there has been some suggestion that these domains possess in-plane molecular anisotropy and mesoscopic structural chirality, the details of their in-plane molecular orientations nevertheless remain largely unknown.

Here, we employ a newly developed SFG microscope with a novel imaging system to investigate the condensed lipid domains within monolayers with mixed chirality. We find that the domains possess curved in-plane molecular directionality within a spiralling mesoscopic hierarchical packing structure. By comparing different enantiomeric mixtures, both the molecular and spiral turning directions are shown to depend on the chirality, but with a clear deviation from mirror symmetry in the formed structures. This demonstrates strong enantioselectivity in the domain growth process, with potential connections to the evolution of homochirality in all living organisms.

CPP 4.11 Mon 12:15 H 0111

Adaptive Air-Water Interfaces with Spiropyran and Arylazopyrazole Photoswitches — ●MICHAEL HARDT and BJÖRN BRAUNSCHWEIG — University of Münster, Center for Soft Nanoscience, 48149 Münster, Germany

Interfaces that can be tuned in their properties by external stimuli such as light or temperature are of great interest to drive macroscopic properties of interface-controlled soft matter materials and offer the possibility to integrate adaptive functions. Using molecular switches that respond to orthogonal triggers, the properties of fluid interfaces can be preconditioned, resulting in a low level of adaptivity that extends the possibilities of soft matter interfaces beyond being purely responsive. In this contribution, we report on air-water interfaces decorated by spiropyran (SP) and arylazopyrazole (AAP) photo-responsive surfactants. The SP surfactants increase their surface activity when irradiated with UV light, which causes a ring-closure reaction. E/Z photo-isomerization of the AAP surfactants causes a substantial decrease in surface activity and, thus, desorption from the interface. At low pH, the short thermal lifetimes of the surfactant isomers offer the use of a thermal dissipative pathway as an alternative trigger to regain the initial properties. The combination of SP and AAP surfactants allows to precondition the interface with UV light and to gain adaptive interfacial properties. This is characterized by surface tensiometry and vibrational sum-frequency generation (SFG) that provide information on interfacial composition as well as on interfacial kinetics.

CPP 4.12 Mon 12:30 H 0111

From X-ray reflectometry to surfactant surface coverage with the help of MD simulations — ●KAY-ROBERT DORMANN¹, JOSHUA REED¹, MATEJ KANDUČ², BENNO LIEBCHEN¹, and EMANUEL SCHNECK¹ — ¹Institut für Physik kondensierter Materie, Technische Universität Darmstadt, Hochschulstr. 8, 64289 Darmstadt, Germany — ²Department of Theoretical Physics, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Adsorption of surfactants to fluid interfaces occurs in numerous technological and daily-life contexts. The surfactant surface coverage Γ governs important interface characteristics like tension, viscoelastic properties, or the stability of thin foam films. Direct measurements of Γ are therefore highly desirable but have remained challenging, especially for non-ionic surfactants without easily detectable (e.g., elemental) labels

[1]. Here, we utilize atomistic MD simulations of surfactant-loaded air/water interfaces with defined Γ to obtain the associated interfacial electron density profiles. From these profiles, we compute theoretical X-ray reflectivity curves, which are then compared to experimental curves recorded with a conventional laboratory instrument. An important aspect in this procedure is the apparent interfacial roughness in

experiments and simulations. For two non-ionic surfactants with previously verified force-fields [2,3] we demonstrate the suitability of this combination of experiments and simulations to deduce Γ as a function of the surfactant bulk concentration. [1] Kovalchuk et al., *Langmuir* 39, 3537 (2023). [2] Kanduč et al., *J. Chem. Theory Comput.* (2023). [3] Kanduč et al., *J. Colloid Interf. Sci.* 586, 588 (2021).