

DY 25: Interfaces and Thin Films II (joint session CPP/O/DY)

Time: Tuesday 9:30–13:00

Location: ZEU 260

Invited Talk

DY 25.1 Tue 9:30 ZEU 260

Phospholipid membranes as model systems for fundamental soft matter research — ●SEBASTIAN JAKSCH — Forschungszentrum Jülich GmbH Jülich Centre for Neutron Science, Garching, Germany

Phospholipid membranes play an important role as interfaces in virtually all biological systems. By their interplay between structure and dynamics they provide the basic functions necessary to support living organisms, such as stability for the cells and trans-membrane transport for nutrients and drugs. Using SoyPC as an example, this presentation will give an overview of grazing incidence neutron techniques for structure and dynamics measurements of phospholipid membranes.[1] We investigated the structure with grazing incidence small-angle neutron scattering (GISANS) at extremely low background conditions [2] and correlated that data with grazing incidence neutron spin-echo spectroscopy [3] (GINSSES). These investigations revealed thermally excited modes in the plane of the membrane and its corresponding structures. This modes could be frozen in at temperatures below room temperature and reappeared after reheating to physiological temperatures.

[1] Jaksch, S., Gutberlet, T., Müller-Buschbaum, P. (2019). Grazing Incidence Scattering - Status and Perspectives in Soft Matter and Biophysics. *Current Opinion in Colloid & Interface Science*.

[2] Jaksch, S., et al. (2019). Long-range excitations in phospholipid membranes. *Chemistry and physics of lipids*, 225, 104788.

[3] Jaksch, S., et al. (2017). Nanoscale rheology at solid-complex fluid interfaces. *Scientific reports*, 7(1), 4417.

DY 25.2 Tue 10:00 ZEU 260

Brownian motion in near-surface pressure driven flows with 3D-nanometric spatial resolution — ●JOSHUA MCGRAW¹, ALEXANDRE VILQUIN^{1,2}, PIERRE SOULARD¹, VINCENT BERTIN¹, GABRIEL GUYARD^{1,2}, DAVID LACOSTE¹, ELIE RAPHAEL¹, FREDERIC RESTAGNO², and THOMAS SALEZ³ — ¹ESPCI Paris — ²Université Paris Sud — ³Université de Bordeaux

In near-surface flows, interfaces play a major role by imposing (typically) no-slip boundary conditions, greatly reducing the fluid velocity compared to the central part of a channel. With total internal reflection fluorescence (TIRF), a flow is illuminated with an evanescent field decaying over a few hundred nanometers into the channel; this decay allowing a determination of nanoparticle altitudes. Combined with particle tracking, experimental determination of the velocity profile and local velocity distributions in three dimensions are possible. Here we present a detailed look at the statistics of near-surface particle motions in pressure-driven water for which diffusion is important compared to advection. The distribution of displacements in the invariant flow direction is Gaussian as for normal diffusion. Significant anomalies are however observed for both of the other spatial dimensions. Combining experiments and simulations, we disentangle contributions from so-called Taylor-Aris dispersion, nanoparticle polydispersity and the optical measurement system. This description of TIRF allows for the study of many Brownian motion problems, such as near-surface polymer solution dynamics or particle motion near soft boundaries.

DY 25.3 Tue 10:15 ZEU 260

Relation between stability and interfacial structure of polyelectrolyte containing foam films — ●LARISSA BRAUN and REGINE VON KLITZING — TU Darmstadt, Darmstadt, Germany

For many industrial applications foams of oppositely charged polyelectrolyte/surfactant-mixtures are of high impact, as they form surface active complexes.

Extensive research on such mixtures was already performed^[1,2] but the influence of the ionic strength is still unclear.

This work focuses on the influence of added LiBr on foam films of mixtures of the anionic polyelectrolyte sPSO₂-220 (similar to PSS but stiffer) with the cationic surfactant C₁₄TAB. Therefore, disjoining pressure isotherms were measured with a fixed C₁₄TAB concentration and a variable polyelectrolyte concentration.

Different stability regimes were identified. Already a low salt concentration of 10⁻⁴ M leads to a considerably less stable foam films regarding the maximum disjoining pressure. An unexpected formation of an unstable Newton Black Film was found at this low salt concentration. Higher salt concentrations will also be considered. These findings will be correlated with the surface excesses of both compounds which can

be separated from each other by neutron reflectometry measurements.

[1] N. Kristen, A. Vüllings, A. Laschewsky, R. Miller, R. v. Klitzing, *Langmuir*, 2010, 12, 9321-9327. [2] M. Uhlig, R. Miller, R. v. Klitzing, *Phys. Chem. Chem. Phys.*, 2016, 18, 18414-18423

DY 25.4 Tue 10:30 ZEU 260

Near-surface dynamics of semidilute polymer solutions: diffusion, nonlinear rheology, and the hydrodynamic boundary condition — ●GABRIEL GUYARD^{1,2}, ALEXANDRE VILQUIN^{1,2}, FREDERIC RESTAGNO², and JOSHUA MCGRAW¹ — ¹ESPCI Paris — ²Université Paris Sud

The near-surface dynamics of polymer solutions challenge both experimental and theoretical efforts – especially in the case of semi-dilute solutions for which chains overlap – yet evanescent wave microscopy allows for the characterization of such interfacial flows. Here we report molecular-size-resolution particle motions in microfluidic channels for pressure-driven flows of semidilute polymer solutions. The results using polymer-free water are in good agreement with Stokes-flow hydrodynamic and diffusive theory. Experiments using polyacrylamide at different volume fractions close to and above the overlap concentration are done in the same chips as for the water experiments. In contrast to Newtonian fluid behaviour, the shear-rate/pressure drop relation is non-linear for the polymer solution flows, suggesting nanometrically-resolved, shear-thinning effects, accompanied with a non-trivial hydrodynamic boundary condition. The diffusive motion of the tracer particles is also distinguished from that of the water experiments, and such motions detailed here. These results set the basis for a study of near-wall hydrodynamic flow and diffusion in complex fluids, notably including semidilute polymer solutions.

DY 25.5 Tue 10:45 ZEU 260

AFM Force-Distance-Curves on Different Lubricants — ●SEBASTIAN FRIEDRICH and BRUNERO CAPPELLA — Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, D-12205 Berlin

AFM force-distance-curves have been recorded on thin films of nine different lubricant liquids. Those lubricants wet the AFM-tip, which causes a capillary force. This force depends on the tip shape, as well as on liquid properties like surface tension, contact angle, and viscosity. Those liquid properties have been measured independently with other methods, so their influence on the shape of the force-distance-curves can be discussed. This study provides a tool for the characterization of thin lubricant films and contributes to the understanding of tribology on the nanoscale.

DY 25.6 Tue 11:00 ZEU 260

Revealing the formation of sputter deposited copper nanolayers on functional polymer thin films for lithium-ion batteries — ●SIMON J. SCHAPER¹, FRANZISKA C. LÖHRER¹, SENLIN XIA¹, MATTHIAS SCHWARTZKOPF², PALLAVI PANDIT², ALEXANDER HINZ³, OLEKSANDR POLONSKY³, THOMAS STRUNSKUS³, FRANZ FAUPEL³, STEPHAN V. ROTH^{2,4}, and PETER MÜLLER-BUSCHBAUM¹ — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — ²DESY, Photon Science, 22607 Hamburg — ³CAU zu Kiel, Institut für Materialwissenschaft, LS Materialverbunde, 24143 Kiel — ⁴KTH, Department of Fibre and Polymer Technology, 100 44 Stockholm, Sweden

Understanding the interface between metals, commonly used as current collectors, and ion-conducting polymers used in polymer lithium-ion batteries (LIBs) is crucial to develop highly reproducible, low-cost and reliable devices. To address these issues, sputter deposition is the technique of choice to fabricate scalable, reproducible and controllable nanometer and sub-nanometer metal layers on polymer thin films. The sputter deposition process, being well understood and controlled, offers advantages over chemical methods to tailor metal thin-film morphologies on the nanoscale and offers a superior adhesion of the deposited material. We use in-situ grazing incidence small angle X-ray scattering (GISAXS) to investigate the formation, growth and, self-assembled structuring of copper on polymer thin films and composites used in LIBs. The growth of copper on polymer thin films is described based on a model approach.

15 min. break

DY 25.7 Tue 11:30 ZEU 260

Insight into ion transport across polypyrrole-electrolyte interfaces by in situ X-ray reflectivity and electrochemistry — ●PIRMIN H. LAKNER^{1,2}, MANUEL BRINKER³, CHRISTOPH SEITZ¹, SERGEY VOLKOV¹, PATRICK HUBER³, and THOMAS F. KELLER^{1,2} — ¹Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Physics Department, Universität Hamburg, Germany — ³Institute of Materials Physics and Technology, Technische Universität Hamburg-Harburg, Germany

Polypyrrole (PPy) is a conducting polymer with actuatoric and pseudocapacitive properties due to potential-induced ion incorporation/expulsion. Electrical potentials were applied to a perchlorate-doped PPy thin film (~ 30 nm) in an aqueous perchloric acid electrolyte and the associated changes in thickness and electron density were recorded by X-ray reflectivity (XRR). Assuming a sole perchlorate anion transfer carrying 50 electrons, a ratio of 50:1 is expected between electrons crossing the PPy-substrate interface and electrons crossing the electrolyte-PPy interface. By correlating the XRR data and the electrochemical data, a ratio of 10:1 was obtained, which indicates that water movement takes place as an anion counter-flow. The recorded low strain-charge coefficient supports this assumption. One explanation is the high stability and the low porosity of the PPy film due to its fast potentiodynamic deposition method. The properties of the analyzed PPy film make it a suitable choice for supercapacitor applications.

DY 25.8 Tue 11:45 ZEU 260

Revealing Lithium Transport Processes in Lithium-Ion Battery Anodes Using Neutron Depth Profiling — ●MARKUS TRUNK^{1,2}, FABIAN LINSSE³, PHILIP RAPP³, JAMIE WEAVER⁴, LUKAS WERNER¹, ROMAN GERNHÄUSER¹, RALPH GILLES², BASTIAN MÄRKISCH¹, ZSOLT REVAY², and HUBERT GASTEIGER³ — ¹TUM, Physik-Department, Garching — ²TUM, Heinz Maier-Leibnitz Zentrum, Garching — ³TUM, Lehrstuhl für Technische Elektrochemie, Chemie Department, Garching — ⁴Material Measurement Laboratory, NIST, Gaithersburg, Maryland

Neutron Depth Profiling (NDP) is a non-destructive, isotope-specific, high-resolution nuclear analytical technique, which is often used to probe lithium or boron concentration profiles in different thin substrates. NDP provides depth sensitivities up to a few ten nanometers and the maximum viewing depth is limited to tens of micrometers. The non-destructive nature of the measurement is of special interest for lithium-ion batteries, where the lithium transport processes can be studied during operation. However, due to the limited viewing depth a special battery cell design is required, which is transparent for the charged particles while ensuring an undisturbed battery performance even at low ambient pressures. We present NDP measurements on lithium-ion batteries performed using a newly developed cell design and discuss insights into the lithium transport processes occurring in the anode material during battery operation.

DY 25.9 Tue 12:00 ZEU 260

Comparison of the effects of solvent additives on the morphology development of printed PPDT2FBT:PC71BM films — ●DAN YANG¹, SEBASTIAN GROTT¹, XINYU JIANG¹, KERSTIN S. WIENHOLD¹, MATTHIAS SCHWARTZKOPF², STEPHAN V. ROTH², and PETER MÜLLER-BUSCHBAUM^{1,3} — ¹TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching — ²Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany — ³Heinz Maier-Leibnitz Zentrum (MLZ), TU München, Lichtenbergstr. 1, 85748 Garching, Germany

The morphology and crystallinity of bulk heterojunction (BHJ) films have profound effects on the performance of organic photovoltaics. Currently, most morphological studies on BHJ films are based on spin-coating as deposition technique. However, to commercialize organic photovoltaic products, large-scale fabrication processes such as printing must be taken into consideration. In the present study, the effects of solvent additives on the morphology formation and polymer crystallinity growth of printed BHJ films are investigated by in-situ grazing incidence small/wide-angle X-ray scattering (GISAXS/GIWAXS). The results show that the solvent additives with different boiling points lead to different film drying behaviors, and the phase demixing is changing in the forming BHJ film along with solvent evaporation. These findings

provide valuable insights into the film morphology and crystallinity developments of printed BHJ films, which determines the future design of BHJ film printing for large-scale fabrication.

DY 25.10 Tue 12:15 ZEU 260

Functionalization of Metalloids surfaces with Porphyrins — ●KLAUS GÖTZ^{1,2}, ANNEMARIE PRIHODA^{1,2}, and TOBIAS UNRUH^{1,2} — ¹Lehrstuhl für Kristallographie und Strukturphysik, Universität Erlangen-Nürnberg, Staudtstr. 3, 91058 — ²Interdisziplinäres Zentrum für Nanostrukturierte Filme, Cauerstr. 3, 91058 Erlangen

Porphyrins are widely studied for their use as catalysts and in dye sensitized solar cells. In these systems the porphyrins are bound to metal oxide surfaces as a functionalizing layer.

We study the binding mechanism in the porphyrin - metal oxide interface on TiO₂ and Co₃O₄. Special emphasis of our work is focused on the exchange process of organic stabilizing molecules with porphyrins. This process is studied using a variation of different scattering techniques. The talk will focus on the characterization of the exchange reaction on the surface of nanoparticles.

Therefore, the combination of small angle x-ray and neutron scattering (SAXS and SANS) experiments will be a key element. These measurements are well suited to study core/shell systems. X-rays interact mainly with electrons and therefore SAXS yields information about the inorganic core of the nanoparticles. Neutrons on the other hand are very sensitive to hydrogen and therefore SANS is well suited to get information about the organic stabilizer shell.

The talk will focus on SAXS/SANS measurements and give an overview over complimentary technique. Furthermore, their usage in the characterization of the morphology of the produced particles and the ligand exchange to porphyrins will be presented.

DY 25.11 Tue 12:30 ZEU 260

Atomistic modelling of confined molecules between atomically flat surfaces — ●JOSE D. COJAL GONZALEZ and JÜRGEN P. RABE — Department of Physics and IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany

The contact interface created between an atomically flat cleavage plane of a layered crystal and a 2D material forms a flexible slit or nano pore which can be occupied by (macro)molecules. This arrangement offers a versatile platform for the study of structural, vibrational, elastic and electrical properties of those highly confined molecules. Using molecular dynamics simulations of a graphene-mica slit pore filled with small solvent molecules such as water and ethanol, we provide an instructive model to establish structure and dynamics, i.e. nature and interactions of the molecular layers, mica and graphene. Furthermore, it provides the first step towards the incorporation of larger molecules, such as Rhodamine 6G and dendronized polymers (denpols) in order to complement and better understand the results obtained from Raman spectroscopy and scanning force microscopy measurements.

DY 25.12 Tue 12:45 ZEU 260

Exploring the Resistive Switching Properties of HfO₂ Nanoparticle Assemblies — ●SONAM MAITI¹, CHEN LIU¹, THORSTEN OHLERTH², ULRICH SIMON², and SILVIA KARTHÄUSER¹ — ¹Peter Grünberg Institut (PGI-7), Forschungszentrum Jülich GmbH, Germany — ²Institute of Inorganic Chemistry (IAC), RWTH Aachen University, Germany

Hafnium oxide nanocrystals (NCs) can be considered as possible candidates for further miniaturization of future resistive random access memories. The switching properties of NC assemblies remain underexplored due to difficulties in fabricating ordered structures. Here, we use a facile, low-cost method to prepare highly ordered assemblies of 6 nm HfO₂ NCs capped with TOPO via evaporation based self-assembly. X-ray photoelectron spectroscopy is applied to investigate the oxidation state of near surface HfOx under various conditions. Electrical transport measurements were performed on devices with micrometer and nanometer sized gaps to determine the resistive switching character of NCs arrays. They enable the observation of cyclic voltammograms with redox reaction peaks when used with micrometer sized gaps. We discuss the electronic properties of these devices in the light of varying contributions of electronic vs ionic transport and highlight the effect on the device stability. We especially focus on the resistive switching behaviour of the NP assemblies which is dependent on the oxygen vacancy formation under the influence of the capping ligand.