

O 87: Focused Session: Solid-liquid Interfaces III

Time: Friday 10:30–13:00

Location: H31

O 87.1 Fri 10:30 H31

Nonintrusive Optical Visualization of Surface Nanobubbles — ●STEFAN KARPITSCHKA¹, ERIK DIETRICH^{2,3}, JAMES SEDDON², HAROLD ZANDVLIET³, DETLEF LOHSE², and HANS RIEGLER¹ — ¹MPI für Kolloid- und Grenzflächenforschung, Potsdam, Germany — ²Physics of Fluids, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands — ³Physics of Interfaces and Nanomaterials, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Individual surface nanobubbles are visualized with nonintrusive optical interference-enhanced reflection microscopy [1], demonstrating that their formation is not a consequence of the hitherto used intrusive atomic force microscopy technique. We then use this new and fast technique to demonstrate that surface nanobubbles form in less than a few seconds after ethanol-water exchange, which is the standard procedure for their preparation, and examine how they react to temperature variations [2,3].

[1] R. Köhler, P. Lazar, and H. Riegler, *Appl. Phys. Lett.* **89**, 241906 (2006).

[2] S. Karpitschka, E. Dietrich, J.R.T. Seddon, H.J.W. Zandvliet, D. Lohse, and H. Riegler, *PRL* **109**, 066102 (2012).

[3] *Nature Nanotechnology (Research Highlights)* **7**, 549 (2012).

O 87.2 Fri 10:45 H31

Studying confined liquids by using the thermal fluctuations of cantilevers — ●FEI LIU, SISSI DE BEER, DIRK VAN DE ENDE, and FRIEDER MUGELE — MESA+, University of Twente

By analyzing the thermal fluctuations of atomic force microscopy (AFM) cantilevers, we characterize the distance-dependent interaction stiffness and dissipation in bulk/confined octamethylcyclotetrasiloxane (OMCTS), which exhibits short-range ordering (and hence forces) on confinement. In the measurement, the thermal fluctuations of the tip are recorded and parsed into segments as the tip approaches the surface. Each section is transformed to a power spectrum, which we fit to a simple harmonic model. From the fitted resonance frequency and quality factor, we extract the interaction stiffness and damping coefficient. The technique is validated by measuring the bulk viscosity with a blunt tip. Then the experiment is done with sharp tips. It is observed that the interaction stiffness matches well with theory prediction- exponentially decaying oscillatory cosine function w.r.t tip-surface distance. The damping displays non-monotonic behavior and thus deviates from continuum hydrodynamics.

O 87.3 Fri 11:00 H31

Structure and Dynamics of Ionic Liquid-Electrode Interfaces — ●PETER REICHERT¹, JANNIS OCHSMANN¹, KASPER SKOV KJAER², TIM BRANDT VAN DRIEL², MARTIN MEEDOM NIELSEN², HARALD REICHERT³, DIEGO PONTONI³, and MARKUS MEZGER¹ — ¹Max-Planck-Institut für Polymerforschung, Mainz — ²Technical University of Denmark and Riso National Lab, Roskilde — ³European Synchrotron Radiation Facility, Grenoble

Ionic liquids (ILs) are promising electrolytes for electrochemical double-layer capacitors with high energy storage densities. To understand and optimize their capacitance as well as charging and discharging processes, detailed information of the IL molecular scale structure and dynamics at interfaces, i.e. the spatial density profiles of the ions near an electrode, is highly desirable. Analysis of our in-situ high-energy x-ray reflectivity (XRR) experiments on IL-electrode interfaces under potential control revealed oscillatory profiles comprised of alternating anion and cation enriched regions. The relaxation dynamics of the interfacial structure upon potential variation was studied by time resolved XRR experiments on a sub-millisecond timescale. The molecular scale structure and its dynamics are set in relation to differential capacitance curves measured by impedance spectroscopy.

O 87.4 Fri 11:15 H31

Surface patterning by molecular polygons and stars: Designed 2D nanoarchitectures at the solid/liquid interface imaged by STM — ●STEFAN-S. JESTER, EVA SIGMUND, NINA SCHÖNFELDER, LISA M. RÖCK, and SIGURD HÖGER — Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany

The self-assembly of shape-persistent organic molecules at the solution/solid interface is an efficient bottom-up approach towards predictable 2D architectures. Scanning tunneling microscopy yields a submolecularly resolved insight into the monolayer structures. How do the nanoscale patterns - here: supported on graphite - depend on the shapes, sizes, and substituents of the adlayer building blocks? We recently focused on *molecular polygons* (triangles, squares, pentagons, and hexagons) with dithiophene corners and phenylene-alkynylene sides, as well as on *molecular stars*, polycyclic heteroaromatic hydrocarbons for which frustrated self-assembly leads to hierarchically organized superstructures with unit cells of up to 20 molecules. In my talk I will give insight into the relation between discrete geometry and supramolecular adlayers, show cocrystals of triangles and hexagons, and explain how large periodicities beyond 10 nm become accessible.

[1] S.-S. Jester, N. Shabelina, S. M. Le Blanc, S. Höger, *Angew. Chem. Int. Ed.* **2010**, *49*, 6101. [2] S.-S. Jester, E. Sigmund, S. Höger, *J. Am. Chem. Soc.* **2011**, *133*, 11062. [3] S.-S. Jester, E. Sigmund, L. M. Röck, S. Höger, *Angew. Chem. Int. Ed.* **2012**, *51*, 8555.

O 87.5 Fri 11:30 H31

Self-assembly of block copolymers at the air/water interface. — ●IRYNA PEREPICHKA, KATERYNA BOROZENKO, ANTONELLA BADIA, and GERALDINE BAZUIN — Department of Chemistry, University of Montreal, Montreal (QC), Canada

By investigation of a wide range of poly(styrene)-poly(4-vinyl pyridine) (PS-PVP) diblock copolymers and their supramolecular complexes with 3-n-pentadecylphenol (PDP), we have established the molecular parameters and experimental conditions that control the self-assembly of planar, strand and dot morphologies at the air/water interface. This has led to an extensive discussion concerning the mechanisms of nanopattern formation, including kinetic, molecular association, and dewetting contributions. We have shown that the use of high-boiling solvents (not usually used for Langmuir-Blodgett film preparation) can improve the nanostrand order.[1] In addition, we have provided a new interpretation of the phase transition plateau on surface pressure area isotherms of block copolymer Langmuir films with dot morphologies.[2] The ability to produce well-controlled nanopatterned films on various substrates has been demonstrated, and film stability has been verified. Removal of small molecules from the nanostructures has revealed the appearance of new substructure. Our studies form the basis for the use of ultrathin films as templates for nanolithography.

References: [1] Perepichka I.I., Badia, A., Bazuin, C.G. *ACS Nano* **2010**, *4*, 6825. [2] Perepichka I.I., Borozenko E., Badia, A., Bazuin, C.G. *J. Am. Chem. Soc.* **2011**, *133*, 19702.

O 87.6 Fri 11:45 H31

Molecular dynamics simulation of interfaces of gold nanorods — ●SANTOSH MEENA and MARIALORE SULPIZI — Condensed Matter Theory, Institute of Physics, Johannes Gutenberg University, Staudingerweg 7, 55128 Mainz, Germany

Nanorods are widely used in many areas such as drug delivery, photothermal cancer therapy, biochemical sensing and medical imaging. Growth of nanorods starts from small reasonably uniform gold seeds in a widely employed experimental technique, seed-mediated growth. In this technique ascorbic acid (a mild reducing agent), is added to aqueous cetyltrimethylammonium bromide (CTAB) solution of HAuCl₄ for selective reduction of Au(III) to Au(I), followed by the addition of the seed solution which catalyze the reduction of Au(I) on their surface. Isotropic morphology breaking of the seeds results into anisotropic growth and thus formation of nanorods. However, the microscopic mechanism of symmetry breaking and anisotropic growth is still unknown. Therefore, we studied the adsorption mechanism of CTAB surfactant on different facets of gold, namely 110, 100 and 111 using molecular dynamics (MD) simulation. Atomistic models for different gold surfaces with CTAB surfactant in water were built using GRO-MOS 53A6 force-field parameters. Properties like, number densities of species and electrostatic potential were calculated across the gold-CTAB and CTAB-water interfaces in order to understand the adsorption of CTAB on the different gold surfaces. Higher density of adsorbed species were found on 110 and 100 facets than 111, this possibly results growth of the nanorod more in the direction of 111 facet.

O 87.7 Fri 12:00 H31

Calcium oxalate/water interfaces using ab initio Molecular Dynamics — ●LEILA SALIMI PARVANEH^{1,2}, DAVIDE DONADIO¹, and MARIALORE SULPIZI² — ¹MPI for Polymer Research, Mainz — ²Physics Department, Johannes Gutenberg University, Mainz

Calcium oxalate is the main component of kidney stones [1]. The presence of peptides such as poly-glutamate has a great impact on the crystalline phase, morphology and growth rate of calcium oxalate [2]. Understanding the biomineralization process and its inhibition requires a detailed microscopic characterization of the water/mineral and water/polymer/mineral interfaces. We performed Density Functional Theory (DFT) based Molecular dynamics simulations [3] to study the structure of the interfaces between Calcium Oxalate Dihydrate (COD) (100) and (101) / water. Our study reveals differences in the coordination of Calcium ions at the surface with water, which could be responsible for a different interaction with biopolymers. We also characterize the interaction between different surfaces of COD and biomolecules. As a first step we consider acetate as a model system containing a carboxylic group and we estimate its binding structure and free energies on different COD surfaces and for different concentration. Preferential binding of carboxylate to the 100 surface is found, therefore explaining recent experimental results on anisotropic growth of COD crystals in the presence of biopolymers [2]. [1] E. L. Prein and C. Frondel, *J. Urol.* 57, 949, 1947. [2] V. Fischer, K. Landfester and R. Munoz-Espi, *Cryst. Growth Des.* 11, 1880, 2011. [3] CP2K/QUICKSTEP, <http://cp2k.berlios.de/>

O 87.8 Fri 12:15 H31

Probing the interaction of ice nucleating proteins with water molecules using SFG spectroscopy — ●RAVINDRA PANDEY¹, MICHAEL SCHLEEGER¹, JANINE FRÖHLICH², ULRICH PÖSCHL², MISCHA BONN¹, and TOBIAS WEIDNER¹ — ¹Max Planck Institute of Polymer Research, Mainz, Germany — ²Max Planck Institute for Chemistry, Mainz, Germany

Specific Bacteria can cause crop frost damage by using ice-nucleating (IN) proteins anchored to their outer cell surfaces. IN proteins mimic the structure of ice surfaces and, thus, promote the growth of ice crystals by acting as efficient templates for ice nucleation. Frost damage caused by ice crystals facilitates bacterial invasion of affected plants. IN proteins not only play an important role for agriculture - airborne proteins can also promote ice formation in the atmosphere and may change precipitations patterns. The molecular mechanisms by which IN proteins interact with water molecules have not yet been resolved. We have investigated the interaction of IN proteins with water molecules using sum frequency generation (SFG) vibrational spectroscopy. When cooling the sample from room temperature to freezing, we found that the order of water molecules in contact with IN proteins is suddenly increased for temperatures near freezing (4-5°C). This effect was not observed for liquid water surfaces without the protein. The data also indicates a change of protein structure near the nucleation temperature.

O 87.9 Fri 12:30 H31

Quantitative Dissolution Rates of Active Pharmaceutical Molecules at the Crystal-Water-Interface from Molecular Dynamics Simulations — ●JULIAN SCHNEIDER¹, MAXIMILIAN GREINER², BERNA DOGAN¹, HEIKO BRIESEN², and KARSTEN REUTER¹ — ¹Department Chemie, Technical University Munich, Germany — ²Chair for Process Systems Engineering, Technical University Munich, Germany

The dissolution of active pharmaceutical ingredients (API) plays a significant role in the pharmacokinetics of orally administered drugs. For the development of a fully-integrated in-silico multiscale approach to predict the dissolution rate of an API compound, detailed knowledge about the deintegration process of single molecules out of the crystal surface is required. Since a lot of prototypical API molecules, such as aspirin, do not exhibit spontaneous dissolution in the accessible time of atomistic molecular dynamics simulations, gathering such information turns out to be a difficult task. Employing advanced simulation techniques, we propose methods which allow for the accelerated simulation of molecular deintegration processes and the calculation of the associated rate constants. In a subsequent step these values can be used to couple the atomistic representation of the API-water-interface to a kinetic Monte Carlo (kMC) model in order to bridge the scale towards large simulation times and systems.

O 87.10 Fri 12:45 H31

Electrochemical infrared spectroscopy to induce and detect neurotransmitter exchange across a solid-liquid interface — ●NEELIMA PAUL^{1,3}, KENICHI ATAKA², JOACHIM HEBERLE², PETER MÜLLER-BUSCHBAUM³, and MARTHA CH. LUX-STEINER¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — ²Freie Universität Berlin, Department of Physics, Experimental Molecular Biophysics, 14195 Berlin, Germany — ³TU München, Physik-Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85747 Garching, Germany

We present in-situ electrochemical-infrared spectroscopy data on voltage induced vibrational changes of neurotransmitter molecule, monosodium glutamate at a solid/liquid interface. For the polarised glutamate molecule, containing two deprotonated carboxylate groups and one protonated amine group at physiological pH, structural changes on application of different magnitudes of voltages at the solid electrode surface as well as molecular transfer events are resolved by surface-enhanced IR difference absorption spectroscopy (SEIDAS). Angular changes of bonds versus the surface normal have been determined because SEIDAS monitors only those vibrations whose dipole moment are oriented perpendicular to the solid surface. The application of positive and negative surface potentials (0.7 V) leads to the release of the glutamate molecules, which were initially adsorbed at the gold solid surface. This adsorption/release process is completely reversible. A possible application could be retinal implants.