O 13: Solid / liquid interfaces I

Time: Monday 15:00–17:00 Location: WIL B321

O 13.1 Mon 15:00 WIL B321

On the Nature of the Pt(111)/H_2SO_4 Interface: A DFT Study — •Aleix Comas-Vives, Jochen Bandlow, and Timo Jacob — Institut für Elektrochemie, Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm, Deutschland

Anion adlayers such as SO_4^{2-} are influencing the adsorption and desorption processes on electrode surfaces, their properties, and the kinetics of electrochemical reactions.[1] Due to these effects (bi)sulfate-induced changes on the morphology of electrodes under electrochemical conditions have been investigated by surface-sensitive in situ and electrochemical techniques. However, the structure and composition of the adsorbed anion layer as well as the influence of possible co-adsorbates is still not completely understood. Motivated by our studies on the Au(111)/H_2SO_4 interface,[2,3] the aim of this work was to extend these investigations to Pt electrodes. Focusing on the well established $\sqrt{3} \times \sqrt{7}$ R19.1° adlayer periodicity, we performed DFT studies on sulfate/bisulfate co-adsorbed with different amounts of water and/or hydronium molecules. Besides structural and stability information, we used the charge density distribution of the most stable adlayers to propose distance tunneling spectroscopy profiles, providing the basis for upcoming experimental studies.

[1] O. M. Magnussen, *Chem. Rev.*, **102**, 679 (2002).
[2] S. Venkatachalam, T. Jacob, *Z. Phys. Chem.*, **221**, 1393 (2007).
[3] F. C. Simeone, D. M. Kolb, S. Venkatachalam, T. Jacob, *Angew. Chem. Int. Ed.*, **46**, 8903 (2007).

O 13.2 Mon 15:15 WIL B321

Static Dielectric Reponse of Water at Planar Interfaces — •Douwe Jan Bonthuis, Stephan Gekle, and Roland Netz — TU München, Deutschland

The water structure close to an interface strongly influences the interaction between charged solutes. A key factor in these short-ranged interactions is the dielectric response function of the first few water layers, which differs appreciably from the bulk dielectric constant. From molecular dynamics simulations, we calculate the static dielectric tensor of water close to various surfaces, using two different methods: (1) relating the dielectric function to the fluctuations of the polarization density and (2) directly calculating the response to an external electric field. While the components of the tensor parallel to the surface closely follow the water density, the perpendicular component shows a highly non-trivial profile.

O 13.3 Mon 15:30 WIL B321

Ab-initio parameterisation of inter-atomic force fields for the description of solid-solid and liquid-solid interfaces — •Carlos Pinilla[1], Nicola Seriani[1], and Sandro Scandolo[1,2] — [1]Abdus Salam International Centre for Theoretical Physics, Trieste, Italy — [2]Democritos Simulation Center, CNR-IOM, Istituto Officina dei Materiali, 34151, Trieste, Italy

We present a discussion on the generation of classical force field for the description of solid-solid and solid-liquid interfaces. We use the Tangney-Scandolo method [1] based on the use of forces, energies and stresses from ab-initio calculations for the generation of a potential able to provide a fully atomistic representation of the interface, by the inclusion of the most relevant two and three body interactions as well as polarisation. Hence, yielding a potential capable to describe correctly the structural properties of the interface within a wide range of pressures and temperatures. We discuss the application of this method to the generation of a force field for the a-SiO2/water interface and extend our study to the TiO2/a-SiO2 interface. Finally, we look into the generation of potentials that include ionic impurities. We compare our classical results to density functional calculations and show how our procedure leads to potentials that are greatly improved in comparison to the ones currently used to describe interfaces. This work is part of the FP7 project ADGLASS. [1] P. Tangney and S. Scandolo, J. Chem. Phys. 117, 8898 (2002)

O 13.4 Mon 15:45 WIL B321

Understanding the hydrophobic nature of nano-rugged solid surfaces at the molecular scale — •Frédéric Leroy — Eduard-Zintl-Institut für Anorganische und Physikalische Chemie and Center for Smart Interfaces, TU-Darmstadt, Darmstadt, Germany

We aim to contribute to the understanding at a molecular level of the origin of the hydrophobic nature of surfaces exhibiting roughness at the nanometer scale. We present molecular dynamics calculations of the surface free energy of water in contact with graphite-based smooth and model surfaces whose roughness dimension stretches from a few Angstroms to a few nanometers.

Both Cassie and Wenzel wetting states are studied. All the rugged surfaces are observed to yield higher surface free energy than the perfectly smooth one.

The surface free energy of Cassie states is predicted from a Cassie-Baxter like equation. The origin of the hydrophobic nature of surfaces yielding Cassie states is therefore the reduction of the number of interactions between water and the solid surface having atomic defects.

On the contrary, Wenzel's theory fails to predict the variation of the solid-liquid surface free energy with respect to the roughness pattern. While graphite is found to be slightly hydrophilic, Wenzel states are dominated by an unfavorable effect arising from the hydrogen-bonding network perturbation that overcomes the favorable enthalpic effect induced by the surface roughness.

O 13.5 Mon 16:00 WIL B321

What fluorinated water-solid interfaces tell us about the origin of the hydrophobic gap. — •Markus Mezger[1], Felix Sedlmeier[2], Dominik Horinek[2], and Harald Reichert[3] — [1]Max-Planck-Institut für Polymerforschung, Mainz — [2]Physik Department, TU München — [3]European Synchrotron Radiation Facility, Grenoble, France

The density deficit of water at hydrophobic interfaces, frequently called the hydrophobic gap, has been the subject of numerous experimental and theoretical studies. Recent experiments give values for the interfacial depletion that consistently correspond to less than a monolayer of water. However, its origin and the relation to the chemistry and molecular geometry of a particular hydrophobic coating or with macroscopic parameters such as the contact angle are still unclear. To elucidate how the underlying mechanisms affect the extent of the interfacial depletion we carried out a high-energy X-ray reflectivity study of water adjacent to a perfluorinated hydrophobic surface with a spatial resolution on the molecular scale. Comparison of experimental data and MD simulations on perflurinated and hydrocarbon water-solid interfaces revealed the influence of different contributions to the observed interfacial depletion.

Reference: M. Mezger et al., *J. Am. Chem. Soc.* **132**, 6735-6741 (2010).

O 13.6 Mon 16:15 WIL B321

Water lithography: a bottom-up solution — Nicola Berger, •Masoud Amirkhani, Frank Zocholl, Mohamed Abdel Mohsen, and Othmar Marti — Institut für Experimentelle Physik Universität Ulm Albert-Einstein-Allee 11 89081 Ulm, Germany

Porous honeycomb-structured polymer films can be obtained by Breath Figure (BF) technique. Highly ordered honeycomb structures were readily formed by blowing airflow across the solution surface in a moist atmosphere (humidity 80%) after a 2 wt % polystyrene monocarboxy(PSC) terminated in toluene was drop-cast on a glass slide. The results show, solvent (toluene, chloroform and carbon disulfide) does not change bubble diameter and regularity of the pattern within an ordered area, whereas the size of the regular area is significantly larger for chloroform and carbon disulfide.

Silica particles were added to both solutions of PSC and polystyrene (PS) in order to find the effect of particles on the pattern formation. Our study shows silica particles does not have any effect on the pattern formation of PSC solution. However, while linear PS cannot produce a regular pattern through BF technique, mixing of silica particles with PS solution can form a good pattern. The size of a bubble varies around 4% within a regular area, but it changes in the different area from 5 to 7 μm for PSC and from 6 to 9 μm for mixed particles and PS solution.

O 13.7 Mon 16:30 WIL B321

Light induced switching of surfaces: turning superhydrophobic into hydrophilic surfaces — •Jonas Groten and Jürgen

Rühe — University of Freiburg - IMTEK, D-79110 Freiburg, Germany

We report on a method to generate a surface whose wettability can be switched between a superhydrophobic and hydrophilic state by simple, short UV irradiation. The system is based on a silicon surface with a nanoscale roughness (black silicon) to which a polymer monolayer is attached.The polymer contains a fluorinated azobenzene moiety. In these polymers the azobenzene moiety can be switched between the cis and trans states depending on the wavelength of the light used during illumination. In the described system the surface energy of the polymer coating is carefully adjusted to the energy value which separates distinct wetting regimes of the nanorough surface. This coupling of light induced switching to a wetting transition can cause large changes in the surface wetting behavior even when the surface energy is changed only in a rather small range. In one state the surface is superhydrophobic and has a critical tilt angle for roll off of only 3. Upon short illumination, however, the drop completely sticks to the surface and does not roll off upon tilting at any angle. Such strong changes in the wetting behavior offer an interesting potential for applications in microfluidic systems.

O 13.8 Mon 16:45 WIL B321

Probing the intrinsic switching kinetics of thermoresponsive polymer brushes at the water/substrate interface — Crispin Amiri Naini, Steffen Franzka, Sven Frost, Mathias Ulbricht, and •Nils Hartmann — Fakultät für Chemie, CeNIDE, NETZ, Universität Duisburg-Essen, Universitätsstr. 5, 45141 Essen

Stimuli-responsive polymers are widely used as actuators and sensors in a variety of applications including adaptive microoptics, microfluidic chips and smart membranes. A detailed knowledge of the intrinsic switching kinetics of such materials is of key importance. Here we demonstrate a stroboscopic photothermal laser manipulation technique, which allows for real-time observation of the switching behavior of poly-n-isopropylacrylamide brushes at the water/substrate interface. A modulated beam of a microfocused laser is used to intermittently heat the substrate surface and locally trigger swelling and deswelling of the thermoresponsive polymer film. Spatial variations of the swelling ratio are monitored using reflectometric interference video microscopy. This facilitates direct parallel measurement of the temperature-dependent switching kinetics of brush layers with thicknesses below one hundred nanometers. Response times range from the millisecond down to the microsecond range demonstrating the prospects of surface-grafted polymer films in fabrication of nanosized polymeric actuators and sensors with fast responsivities.

[1] M. Mathieu, A. Friebe, S. Franzka, M. Ulbricht, N. Hartmann, Langmuir 25 (2009) 12393.