O 45: Solid / liquid interfaces I

Time: Wednesday 10:30–12:30 Location: A 060

O 45.1 Wed 10:30 A 060

Structure of water layers on hydrogen-covered Pt electrodes — •Tanglaw Roman and Axel Gross — Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm

Recently, we have seen a growing number of theoretical studies addressing structures and processes at electrochemical solid/liquid interfaces from first principles. Still it is fair to say that up to now little attention has been paid to the fact that as a function of the electrochemical conditions (electrode potential, pH, electrolyte) in equilibrium electrochemical electrodes are typically covered by adsorbed species such as hydrogen. It is very likely that the presence of these adsorbed species has a severe influence on the structure of the electrochemical electrode-electrolyte interfaces and on the processes occurring at these interfaces. In this light, we have examined the structure of water layers at hydrogen-covered Pt(111) surfaces at room temperature by ab initio molecular dynamics simulations based on periodic density functional theory calculations. The resulting structures have been analyzed in detail as a function of hydrogen coverage. In particular, the thermal disorder in the water layer is examined in terms of deviations from the ice lattice, orientational inhomogeneity within the bilayers, as well as the onset of water dissociation.

O 45.2 Wed 10:45 A 060

Ab-initio derived force-field parameters for molecular dynamics simulations of deprotonated amorphous-SiO_2/water interfaces — •Anke Butenuth[1], Gianpietro Moras[1], and Lucio Colombi Ciacchi[2,3] — [1]Fraunhofer Institute for Mechanics of Materials IWM, Freiburg — [2]Hybrid Materials Interfaces Group, BCCMS, Bremen — [3]Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM, Bremen

Due to its importance for many technologically relevant materials, a large research effort has been devoted to the SiO_2/water interface, where work on the theoretical side is based on both quantum-mechanical and classical atomistic methods. However, most of theses studies consider neutral silica surfaces and are, due to the low isoelectric point of silica, only valid under strong acidic conditions.

We present a force field for molecular dynamics simulations of interfaces between natively deprotonated amorphous SiO_2 surfaces and liquid water, to be used in combination with standard biomolecular force fields. The extent of negative charge delocalisation in the solid that follows the deprotonation of terminal silanol groups is revealed by extensive Bader analysis of electronic densities computed by Density Functional Theory (DFT). The absolute charge values in our force field are determined from best-fitting to the electrostatic potential computed ab-initio (ESP charges).

Our proposed parameter set is found to reproduce the energy landscape of single water molecules over neutral and deprotonated amorphous SiO_2 surfaces.

O 45.3 Wed 11:00 A 060

Atomistic simulations of the ZnO(1-210)/water interface: A comparison between first-principles, tight-binding and empirical methods — •Svea Sauer[1], Susan Köppen[2], Thomas Frauenheim[1], and Lucio Colombi Ciacchi[2] — [1]University of Bremen, Faculty of Physics, Computational Material Science and BCCMS — [2]University if Bremen, Faculty of Production Engineering, Hybrid Materials Interfaces and BCCMS

Owing to the prevalent role of zinc oxide in processing reactions involving water, the zinc oxide water interface is an ongoing field of research. Our study focuses on the (1-210) surface of zinc oxide. Thereby the adsorption starting from a single water molecule up to a full monolayer is investigated. Calculations are performed using ab initio DFT, the DFTB+ code and a reactive forcefield. A comparison of the results obtained by these three methods yields differences especially regarding the number of dissociated water. To study how the monolayer configurations change under the influence of bulk water and how well this is described by the three methods, the vacuum region of the systems is filled up with water. Three different initial monolayer configurations were taken into account: One fully dissociated, one half dissociated and one with a monolayer of molecular adsorbed water. Different trends, already observed for the monolayer could be observed for DFT, DFTB and the reactive forcefield regarding the fraction of dissolved water.

O 45.4 Wed 11:15 A 060

First-principles study of the water structure on flat and stepped gold surfaces — •Xiaohang Lin and Axel Gross — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

The geometric structure and electronic properties of a water layer on flat and stepped gold surfaces have been addressed by periodic density functional theory (DFT) calculations. This work was motivated by a recent electron energy loss spectroscopy study [H. Ibach, Surf. Sci. 604 (2010) 377] indicating that the structure of a water layer on stepped Au(511) differs significantly from the one on Au(100). Based on ab initio molecular dynamics simulations, the measured spectra of H_2O/Au(511) have been reproduced and linked to the geometric arrangement of the water molecules. Furthermore, the electronic structure has been analyzed yielding a strong polarization of the water layers.

O 45.5 Wed 11:30 A 060

On the accuracy of ion hydration energies - an ab-initio study — •Mira Todorova and Jörg Neugebauer — Department for Computational Materials Design, Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

An accurate prediction of hydration free energies of ions and molecules is crucial for modelling chemical, electrochemical and biochemical reactions in water and at water/material interfaces. Experimental measurements are performed on neutral solutions and the extraction of individual ion solvation free energies relies on assumptions, such as the tetraphenylarsonium tetraphenylborate (TATB) extrathermodynamic assumption [1]. This severely hinders the assessment of theoretical approaches to compute such data.

Extending an approach originally derived to describe charged defects and their concentration in semiconductors [2], revealed that the TATB extrathermodynamic assumption employed to obtain experimental free energies is incorrect, and provided criteria to judge the accuracy of calculated ion-hydration energies. Focusing on the hydration energy of H^+(aq) and OH^-(aq) individual free energy contributions to calculated ion hydration energies will be discussed.

[1] Y. Marcus, J. Chem. Soc., Faraday Trans. 1, **83**, 339 (1987).

[2] C.G. Van de Walle and J. Neugebauer, J. Appl. Phys. **95**, 3851 (2004).

O 45.6 Wed 11:45 A 060

Self-assembly of solvent molecules adsorbed on HOPG (0001) controlled by sonication time of the liquid — •Nguyen Thi Ngoc Ha[1], Thiruvancheril G. Gopakumar[2], and Michael Hietschold[1] — [1]Institute of Physics, Solid Surfaces Analysis Group, Chemnitz University of Technology, D-09107 Chemnitz, Germany. — [2]Institut für Experimentelle und Angewandte Physik der Universität Kiel, Olshausenstr.40, D-24098 Kiel, Germany

Self-assembly at the liquid-solid interface depends on several experimental parameters such as temperature, chemical nature of the solvent, functional groups of the solute molecule, etc. which can influence on the interactions between adsorbate, substrate and solvent. The molecular concentration in a solvent has been shown to be a useful control parameter for self-asssembled molecular pattern formation out of these solutions on a crystalline substrate[1,2]. Sonication treatment of the solutions has been demonstrated to be an efficient method to change these concentrations. The adsorption of TMA-alcohol mixture on a HOPG substrate has been investigated which reveals an adsorption pattern consisting of alternating stripes made of of TMA and alcohol solvent molecules which changes in dependence on sonication time[3]. Sonication of the pure alcohol solvent without any other molecules solved within also changes the assembled pattern of the solvent molecules in dependenc of sonication time as we have observed.[1]N.T.N.Ha,etal.J.Phys.Chem.C, 2010,114,3531-3536.[2]N.T.N.Ha,etal.J.Phys.Chem.C,2011,115(44),21743-21749.[3]N.T.N.Ha,e of TMA-alcohol controlled by concentration going to be submitted.

O 45.7 Wed 12:00 A 060

***dI*/*dV* imaging and spectroscopy of single molecules at solid-liquid interfaces** — •Jose D. Cojal[1], Carlos A. Palma[2], Klaus Müllen[3], and Jürgen P. Rabe[1] — [1]Institute of Physics, Humboldt-Universität zu Berlin, Berlin — [2]Physik Department E20, Technische

Universität München, Garching — [3]Max Planck Institute for Polymer Research, Mainz

Scanning tunneling spectroscopy (STS), i.e. superimposing a small high-frequency modulation voltage on the bias and recording the AC current component using a phase sensitive detector (PSD) to obtain the differential of the tunneling current, dI/dV, allows to measure the local density of states (LDOS) at surfaces. This has been widely used at low temperatures and under UHV conditions for metals, semiconductors, organic molecules, carbon nanotubes and graphene. In order to measure both topography and differential tunneling images at solid-liquid interfaces we have modified our home-built STM, and obtained dI/dV maps of single molecules of a monolayer of a hexa-peri-hexabenzocoronene (HBC) derivative, self-assembled at the interface between highly oriented pyrolytic graphite (HOPG) and a molecular solution. This allowed us to better localize HOMO and LUMO of the molecules than previously reported direct measurements of current voltage characteristics [1].

[1] K. Müllen, J. P. Rabe, Acc. Chem. Res. 41 (2008) 511

O 45.8 Wed 12:15 A 060

Adsorption of P123 at the solid-liquid Interface — •Stefan Gerth[1], Michael Klimczak[1], Andrew Nelson[2], Hans-Georg Steinrück[1], and Andreas Magerl[1] — [1]Chair of Crystallography and Structural Physics, Staudtstraße 3, Erlangen — [2]The Australian Nuclear Science and Technology Organization, Australia

Aqueous solutions of tri-block copolymers offer an excellent model system for the study of crystallization in soft matter. Further, these surfactants are well-known for the reduction of surface tension and to reduce friction at the interface. We investigate, as sample, the tri-block copolymer Pluronic P123 consisting of a central part of 70 propylene oxide (PO) units terminated by two end groups of 20 ethylene oxide (EO) units (EO_{20}–PO_{70}–EO_{20}).

Our interest is in the near surface crystallization of a diluted Pluronic P123 system, below the temperature and concentration for crystallization in the bulk. In particular we are interested in the effect of shear for these agglomerated polymers.

The recovery of an adsorbed micellar layer was observed in dependence of the previously applied shear rate and polymer concentration. It has to be stressed that in this concentration and temperature regime no bulk crystallization occurs as investigated in small angle X-ray scattering measurements and rheometry data. Therefore, the ordering is only induced from the interface.