

O 18: Solid-liquid Interfaces II

Time: Monday 16:00–19:15

Location: WIL A317

O 18.1 Mon 16:00 WIL A317

Changes in Potential During Pulsed Galvanostatic Deposition of Zinc Oxide on Gold — ●MARTINA STUMPP and DERCK SCHLETTWEIN — Institute of Applied Physics, Justus-Liebig-University Giessen, Germany

Zinc oxide (ZnO) is a promising electrode material for the application in various devices in the fields of chemistry, optics and electronics. Electrochemical deposition is an environmentally-friendly and energy-efficient technique for the deposition of crystalline ZnO . As a solution-based technique, it allows to prepare films on temperature-sensitive substrates and independent on substrate shape leading to a variety of optional device geometries. Electrodeposition of ZnO was carried out under pulsed galvanostatic conditions from aqueous zinc nitrate solutions on Au wires, sheets, microstructured bands or Au -coated polyamide threads. The voltage-time curves attained during these experiments were analyzed and three significant stages were observed for all depositions regardless of the geometry of the substrate despite limitation of the reaction by diffusion processes. The three stages were discussed under variation of the pulsating current density, the deposition time, but also by polarization of only one of two sets of microstructured band electrodes. A correlation between an abrupt drop in the potential and the completed coverage of the Au electrode surface was seen. The detailed characterization of each stage in the potential-time curves allows to prepare thin compact ZnO films without pinholes on a given substrate.

O 18.2 Mon 16:15 WIL A317

Current-time characteristics of the electrochemical deposition of zinc-oxide on microelectrodes and a finite element simulation of the diffusion control — ●CHRISTIAN LUPO and DERCK SCHLETTWEIN — Institute of Applied Physics, Justus-Liebig-University Giessen, Germany

Zinc oxide (ZnO) films were prepared by electrochemical deposition on interdigitated microstructures of gold band electrodes. Electrodeposition was realized at constant electrode potential from an oxygen-saturated aqueous zinc chloride solution in the presence of the xanthene dye *EosinY*. The composition of the solution, the deposition time, the interdigital electrode size, gap width and the number of electrode bands were varied. The current during reduction of O_2 and the subsequent growth of ZnO was measured and correlated with results of scanning electron microscopy and of simulations by the finite element method (FEM). The close match of the observed chronoamperometric curves confirms the diffusion-controlled behavior of the oxygen reduction and of the subsequent deposition of ZnO . Furthermore the FEM simulation can be used to discuss an influence of an increasing surface area during film growth on the diffusion-limited precipitation reaction. Such application of the FEM to electrochemical deposition reactions can provide useful contributions to the further development towards a controlled electrochemical growth on electrodes with different geometric features on the microscale.

O 18.3 Mon 16:30 WIL A317

Understanding the crystal growth inhibition: role of acetate at the calcium oxalate/water interfaces — ●LEILA SALIMI PARVANEH^{1,2}, DAVIDE DONADIO¹, and MARIALORE SULPIZI² — ¹MPI for Polymer Research, Mainz — ²Physics Department, Johannes Gutenberg University, Mainz

Calcium oxalate occurs widely in kidney stones and among a variety of living organisms[1]. The presence of bio-polymers such as polyglutamate during the formation of calcium oxalate crystal has a great impact on the crystalline phase, morphology and growth rate[2]. We have performed DFT-based Born-Oppenheimer Molecular Dynamics (BOMD) simulations to understand the structural and dynamical properties of the interfaces between calcium oxalate dihydrate (COD) (100) and (101) and water. Our study reveals differences in the coordination of calcium ions at the surface with water. We also characterize the interaction between biomolecules and different surfaces of COD. As a first step we consider acetate as a minimal model for glutamate side chain. We estimate the binding free energy on different surfaces and compare it to the binding free energy of calcium and acetate in solution[3]. We also discuss binding structure at different coverage. Preferential binding of carboxylate to the (100) surface is found, providing a rational for

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] J. Kahlen, L. Salimi, M. Sulpizi, C. Peter, D. Donadio, 2013 (submitted).

O 18.4 Mon 16:45 WIL A317

Microscopic characterization of the CaF₂ / water interfaces. — ●RÉMI KHATIB¹, MARIA J. PERREZ-HARO², MISCHA BONN², ELLEN H.G. BACKUS², and MARIALORE SULPIZI¹ — ¹Johannes-Gutenberg University, Mainz, Germany — ²Max Planck Institute for polymer research, Mainz, Germany

From biological membranes to heterogeneous catalysis through atmospheric chemistry, interfaces involving liquid water are common on Earth. Vibrational Sum Frequency Generation (SFG) is a spectroscopic technique which allow a selective characterization of interfacial water. In order to rationalize the experimental results obtained for CaF₂ / water interfaces, a theoretical approach has been used, based on first principles molecular dynamics simulations.

In particular Born-Oppenheimer Molecular Dynamics (BOMD) have been used on different model systems to describe a wide range of pH of the aqueous solution. Different tools, like the Velocity Density of States (VDOS), Radial Distribution Function (RDF), were employed to analyze the data. The preliminary results are promising: a *free OH* peak measured by SFG under basic conditions can certainly be explained by a substitution of F- by HO- at the interface. Moreover a microscopic characterization of the water species and dynamics at low pH is also provided.

O 18.5 Mon 17:00 WIL A317

Nanoconfinement Effects on Hydrated Excess Protons in Layered Materials — ●DANIEL MUÑOZ-SANTIBURCIO, CARSTEN WITTEKINDT, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, 44801 Bochum, Germany

Nanoconfined water has been widely studied in both wire-like and two-dimensional environments. A feature of particular interest in such systems is the behavior of excess protons. While proton transfer in bulk water has been widely studied, almost all efforts in studying excess protons in confined water systems are devoted to water wires due to their importance in biological systems and in view of technological applications such as fuel cells, whereas investigations of hydrated protons at liquid/solid interfaces are scarce. Following our previous work [1] on nanoconfined water between sheets of mackinawite minerals, FeS, which form layer-like superstructures, we address the behavior of hydrated excess protons in this layered material [2]. Even extreme nanoconfinement is shown to not affect the fluxional nature of the topological defect, thus not localizing the excess protons but conserving the efficient structural (Grotthuss) diffusion process known in bulk water. Yet, depending on the width of the slit pore, the defect can bridge the bilayer water structure, thus forcing the excess proton into the water depleted region between the bilayers.

[1] C. Wittekindt and D. Marx, *J. Chem. Phys.* 137, 054710 (2012).[2] D. Muñoz-Santiburcio, C. Wittekindt and D. Marx, *Nat. Commun.* 4:2349 (2013).

O 18.6 Mon 17:15 WIL A317

Wetting Transition in a solid/water/oil system mediated by ion and surfactant -adsorption induced interface interactions — ●BIJOYENDRA BERA, IGOR SÍRETANU, MICHÈL H.G. DUIJS, MARTIEN A. COHEN-STUART, DIRK VAN DEN ENDE, and FRIEDER MUGELE — Physics of Complex Fluids (PCF) Group, TNW, University of Twente, Enschede, The Netherlands

Enhanced oil recovery (EOR) processes rely upon wettability alteration in sandstone rock (silica and clay materials). In this study, by changing the salt (NaCl or CaCl₂), concentration (1 mM to 1000 mM) and pH, we observe wetting transition on mica in an oil (n-Decane) phase. At all pH and concentration of NaCl, contact angles below macroscopic detection limit (around 1.5⁰) are observed, implying complete wetting. For CaCl₂, we observe finite contact angles (up to 10⁰) above a critical concentration of 50 mM. When we add polar amphiphilic molecules (stearic acid) in n-Decane, this wetting transition is more pronounced

since for CaCl_2 solution, contact angles are as high as 70° . In presence of stearic acid, dynamic effects such as autophobing and self-propelling of drops on mica are also observed.

We explain such wetting transition with an ion-adsorption model, causing surface charge reversal at mica/water interface for divalent cations. This proposition is supported with experimental calculations of zeta potential. Based on these values, we calculate surface charge and subsequently, the interaction potential between mica/water and oil/water interfaces. The minimum of this potential corresponds to the film thickness of aqueous phase, which we confirm with ellipsometry.

O 18.7 Mon 17:30 WIL A317

Activation of surfaces with ultrasound (US): from physical effects to chemistry — ●MATTHIEU VIROT¹, SERGUEI I. NIKITENKO¹, THOMAS ZEMB¹, and HELMUTH MÖHWALD² — ¹ICSM Marcoule, Bagnols sur Cèze (France) — ²MPI-KG, Potsdam (Germany)

US propagation in liquid media may lead to acoustic cavitation which is the nucleation, growth, and rapid implosive collapse of vapor filled micro-bubbles. At collapse, these bubbles create extreme transient conditions of several thousand of degrees and hundreds of atm., and possibly light emission (sonoluminescence). At the vicinity of an extended solid surface, these conditions go with the generation of shock waves and micro-jets striking the surface with a high velocity. Non-equilibrium conditions therefore generated at surfaces may offer new alternatives to activate surfaces. Recent investigations carried out at surfaces from the macro- to the nanoscale brought to light new physico-chemical properties and possibilities never reported before: (i) Sonicated (20 kHz, 10-20°C, Ar) silica glass and crystalline Si surfaces were characterized by their unusual physical and chemical transformations. (ii) Spectroscopic investigations performed at the vicinity of a sonicated ($\text{Ce}_0.9\text{Tb}_0.1$)PO₄ pellet surface revealed for the first time that acoustic cavitation can be used as an in-situ source of excitation for photoactive species contained in an extended solid phase via sonoluminescence, while solubilized Ar was found to be excited during the sonication of crystalline Si via mechanoluminescence. (iii) The reductive dissolution of refractory CeO₂ was found to be catalyzed by the sonochemical deposition (20-40°C) of Pt NPs at the surface of ceria.

O 18.8 Mon 17:45 WIL A317

Self-Assembly of Alkyl Phosphonic Acids at $\alpha\text{-Al}_2\text{O}_3$ (0001)-Solvent Interfaces — CHRISTIAN MELTZER, WOLFGANG PEUKERT, and ●BJÖRN BRAUNSCHEWIG — University of Erlangen-Nuremberg; Institute of Particle Technology (LFG), Cauerstrasse 4, 91058 Erlangen
Molecular self-assembly of octadecylphosphonic acids (ODPA) on $\alpha\text{-Al}_2\text{O}_3$ is studied with vibrational sum-frequency generation (SFG) in-situ and in real time. A detailed analysis of SFG spectra shows that both intensity and relative contributions of methylene and methyl bands are excellent indicators for coverage dependent changes in the molecular structure of ODPA self-assembled monolayers (SAMs). Concentrations between 0.1 and 5 mM ODPA in propanol lead to slow adsorption where a SAM is formed over several hours. For concentrations < 1 mM, SAMs with low coverage and possibly flat lying molecules are formed even after prolonged adsorption times. For concentrations > 1mM an equilibrium can be reached, but vibrational spectra still show substantial contributions from gauche defects. Dewetting of these SAMs in N₂ gas leads to an increase in SFG intensity that is accompanied by a substantial decrease in SFG contributions from gauche defects. After re-immersing of dried samples in 2-propanol with 5 mM ODPA, SFG spectra remain unchanged and are representative of well-ordered ODPA SAMs. From these observations we hypothesize that before de-wetting coverage and molecular order are already very high, but final improvements in molecular order are accomplished only at the solid-liquid-gas three phase line.

O 18.9 Mon 18:00 WIL A317

EFFECT OF SONICATION TIME ON THE SELF-ASSEMBLY OF SOLVENT MOLECULE ADSORBED ON HOPG (0001) SUBSTRATE STUDIED BY SCANNING TUNNELING MICROSCOPY AT THE LIQUID-SOLID INTERFACE — ●NGUYEN THI NGOC HA¹, THIRUVANCHERIL G. GOPAKUMAR², and MICHAEL HIETSCHOLD¹ — ¹Institute of Physics, Solid Surfaces Analysis Group, Technische Universität Chemnitz, Germany — ²Indian Institute of Technology, Kanpur, India

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, concentration of dissolved

molecules, 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-assembled molecular pattern formation out of solutions on a crystalline substrate. Sonication treatment of the solutions has been demonstrated to be an efficient method to change these concentrations. The adsorption of TMA (trimesic acid)-undecanol mixture on a HOPG substrate has been investigated. It reveals an adsorption pattern consisting of alternating stripes made of TMA and undecanol solvent molecules which changes in dependence on sonication time. There has been found self-assembled deposition also from pure solvents leading to different patterns which can be controlled by sonication also. These types of studies will give better insight into the adsorption process and may also offer exciting opportunities for nano-patterning.

O 18.10 Mon 18:15 WIL A317

Temperature-controlled 3d self-assembling of benzene-1,3,5-triphosphonic acid observed by scanning tunneling microscopy (STM) at the liquid-solid interface — ●CHAU YEN NGUYEN DOAN¹, NGOC HA NGUYEN THI¹, MICHAEL MEHRING², and MICHAEL HIETSCHOLD¹ — ¹Solid Surfaces Analysis Group, Institute of Physics, TU-Chemnitz, Chemnitz, Germany — ²Institute of Chemistry, TU-Chemnitz, Chemnitz, Germany

Benzene-1,3,5-triphosphonic acid (BTP), which is the phosphonic acid analogue of trimesic acid (TMA), forms a columnar packing in the crystalline solid state that is characterized by strong hydrogen bonds and π -stacking involving the aromatic rings. Therefore, BTP is an interesting intermediate to design both 3D supramolecular hydrogen-bonded architectures and organic-inorganic hybrid frameworks. The 2D or 3D crystal engineering of molecular architectures on surfaces requires controlling various parameters related respectively to the substrate, the chemical structure of the molecules, and the environmental conditions. We investigate here the influence of temperature on the self-assembly of BTP at the undecanol-HOPG interface using ambient STM. The geometry adsorption of the 3D self-assembled BTP can be precisely tuned by adjusting the substrate temperature from 20°C to 60°C. STM images at different substrate temperature reveal the different co-adsorption structures as well as different packing density of BTP and undecanol solvent molecules. Based on these results, temperature-control has been proven to be a versatile tool to adjust the polymorphism of molecular patterns deposited out of solutions.

O 18.11 Mon 18:30 WIL A317

Molecular Dynamics Simulations of the Dissolution of Lactose Crystals — ●BERNA DOGAN, JULIAN SCHNEIDER, and KARSTEN REUTER — Technische Universität München, Germany

Apart from its widespread use in food industry, Lactose is commonly applied in the pharmaceutical industry as an excipient for drug formulations. This application demands an efficient dissolution of its crystalline alpha lactose monohydrate (alpha-LM) phase to enable a fast uptake of the active pharmaceutical ingredient. Seeking for an understanding of the underlying molecular processes, we aim at complementing the available dissolution experiments with force-field molecular dynamics (MD) simulations of the alpha-LM/water interface at the atomistic level.

At near-equilibrium conditions, dissolution is expected to primarily take place at kink sites within step edges. The dissolution velocity of a step edge can then be derived from the kink free energy, as well as the rate constant of the molecular detachment process [1]. Instead of approximating the defect free energies by potential energy differences of rigid crystal arrangements [1], we aim at a precise calculation, including entropic contributions and explicit solvation. We, therefore, present a modification of binding free energy methods of molecular ligand/receptor complexes towards an application to surface defects. Moreover, we show how the molecular rate constants can be calculated at the same level of precision from accelerated molecular dynamics simulations.

[1] R. C. Snyder and M. F. Doherty: Proc. R. Soc. A, **465**, 1145, (2009)

O 18.12 Mon 18:45 WIL A317

Exploring the formation, lifetime and dissociation statistics of acid-amine bonds — ●SANGEETHA RAMAN and MARKUS VALTNER — Department of Interface Chemistry and Surface Engineering, Max-Planck-Institut für Eisenforschung GmbH, D-40237, Düsseldorf, Germany

Understanding the scaling of single molecular interaction forces to

wards an integral interaction between extended surfaces interacting simultaneously through a large number of molecular bonds is a key objective in order to model or predict interactions in realistic situations. Here we study the scaling of interaction forces arising from acid-base bond at both, the single molecular level using force spectroscopy with atomic force microscopy (AFM) and the macroscopic level using surface forces apparatus experiments (SFA). The single molecule experiments reveal two distinct regimes of interaction forces as a function of the bond-loading rate - the equilibrium desorption regime and the force-dependent bond dissociation regime. SFA measurements revealed, that the forces measured in the equilibrium regime using AFM, scale linear with the number density of acid base bonds at the interface. We show that a combined approach of AFM and SFA allows for a detailed understanding of both kinetic aspects of the bond forming and breaking as well as equilibrium scaling of the interaction forces. AFM allows to directly measuring lifetimes of bonds, while SFA allows to directly studying the equilibrium interactions between specific bonds. Our results provide complementary information to predict and model realistic situations of bond forming and breaking.

O 18.13 Mon 19:00 WIL A317

The Theoretical and Experimental Study on the Dynamic Ice-making system Using Supercooling Water Based on the

Nano-fluorocarbon Coating Material — •HONG WANG — School of civil engineering, Henan Institute of Engineering, Zhengzhou city, China

Supercooling water is used as a superior method to generate ice slurry for its high efficiency and energy conservation. However, the ice blockage occurred in the supercooling heat exchanger is a prominent problem that reduces the efficiency of the ice generation system. In order to avoid or retard ice blockage, a fluorocarbon coating with superhydrophobicity was applied onto the surface of the supercooling heat exchanger to continuously make ice slurry without any additive. The characteristics of the coated surface with fluorocarbon coating was determined and analyzed relatively. The results showed that the nano-fluorocarbon film in the average thickness was only 9.7nm. It was the very thin film made the solid surface superhydrophobicity with the contact angle of 163.01° . This film not only has a good property in anti-icing but also anti-scale. Compared with the uncoated surface, the process of water freezing on the coated surface with nano-fluorocarbon was slower which demonstrated that the icing on the coated surface was restrained in the experiment. It was also found that the supercooling degree in the coated supercooling heat exchanger was higher, the supercooling state was longer, and the time of ice blockage was delayed. Thus, more ice production can be obtained accordingly and the efficiency of the whole ice-making system was enhanced.