

## BP 38: Electrolytes at Interfaces - Stern Layer (focus session, joint CPP/BP/O)

Time: Wednesday 15:00–18:00

Location: C 130

**Invited Talk**

BP 38.1 Wed 15:00 C 130

**Ultraslow dynamics of hydrated metal ions at the water-solid interface observed by atomic force microscopy** — ●KISLON VOITCHOVSKY — Durham University, Durham, UK

The lateral organisation and dynamics of ions in the Stern layer of immersed solids is central to many electrochemical and biological processes. However, measuring the lateral organisation and dynamics of single adsorbed ions remains challenging experimentally. Recently we showed that atomic force microscopy could be used to image single metal ions at the surface of various solids in water [1, 2]. Our results indicate that, depending on the hydration landscape of the solid, adsorbed ions can form ordered structures within the Stern layer, through correlation effects that are driven purely by the interfacial water [2]. The dynamics of the adsorbed ions appears surprisingly slow, typically exhibiting residence times above the millisecond. This suggests that water can also dramatically alter the ions dynamics and play a key role in stabilizing adsorbed ions at a given location of the interface. The existence of long-lived ionic structures at interfaces could have important implications for charge transfer and at biointerfaces.

[1] M. Ricci, P. Spijker, F. Stellacci, J.-F. Molinari, K. Voitchovsky, Langmuir, 29, 2207 (2013) [2] M. Ricci, P. Spijker, K. Voitchovsky, Nature Commun., 5, 4400 (2014)

BP 38.2 Wed 15:30 C 130

**Direct observation of ionic structure at solid-liquid interfaces: A deep look into the Stern Layer** — ●IGOR SIRETANU, DANIEL EBELING, MARTIN P. ANDERSSON, CUNLU ZHAO, DIRK VAN DEN ENDE, and FRIEDER MUGELE — Physics of Complex Fluids and MESA+ Institute for Nanotechnology, Department of Science and Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

The distribution of ions and charge at solid-water interfaces plays an essential role in a wide range of processes in biology, geology and technology. While study of the solid-electrolyte interfaces date back to the early 20th century, a detailed picture of the structure of the electric double layer has remained elusive, largely because of experimental techniques have not allowed direct observation of the behaviour of ions, i.e. with subnanometer resolution. Making use of recent advances in Atomic Force Microscopy with atomic level precision, herein, we reveal the local surface charge and the ordered adsorption of the divalent ions, unlikely monovalent ions, to heterogeneous clay surfaces in contact with aqueous electrolytes. Complemented by density functional theory, the experiments produce a detailed picture of the formation of surface phases by templated adsorption of cations, anions and water, stabilized by hydrogen bonding.

BP 38.3 Wed 15:45 C 130

**Probing surface chemistries at mineral surfaces in nanometer-confined electrolytes with atomic force microscopy** — ●CUNLU ZHAO, DANIEL EBELING, IGOR SIRETANU, DIRK VAN DEN ENDE, and FRIEDER MUGELE — Physics of Complex Fluids and MESA+ Institute for Nanotechnology, Department of Science and Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

We adopt atomic force microscopy (AFM) to investigate the chemistries of mineral surfaces in nanometer-confined electrolyte solutions. Firstly, AFM was used to measure interaction forces between tip and solid surfaces with nanometer separation in ambient electrolytes. Then a charge regulation (CR) boundary was formulated for the Poisson-Boltzmann equation to establish a linkage between the AFM measured force curves and the surface chemistries (e.g., pK values of surface (de)protonation and ion adsorption). Finally, we analyzed force vs. distance curves recorded between a silica tip and heterogeneous silica-gibbsite substrates in aqueous solutions of NaCl and KCl within the framework of CR boundary-complemented Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. By fitting experimental force vs. distance curves down to tip-sample separation of 2nm, we determined for both silica and gibbsite surfaces pK values of surface (de)protonation and ion adsorption. The various pK values determined from our AFM experiments are quite consistent with the macroscopic titration measurements tabulated in the literature. This indicates that AFM could be potentially used as a titration tool, but with an unprecedentedly high resolution.

BP 38.4 Wed 16:00 C 130

**Ion adsorption-induced wetting transition in oil-water-mineral systems** — ●FRIEDER MUGELE, BIJOY BERA, ANDREA CAVALLI, IGOR SIRETANU, ARMANDO MAESTRO, DIRK VAN DEN ENDE, MICHEL DUIJS, and MARTIEN COHEN-STUART — University of Twente, MESA+ Institute for Nanotechnology, Physics of Complex Fluids, Enschede, The Netherlands

The relative wettability of oil and water on solid surfaces is crucial to many environmental and technological processes including soil contamination/remediation, oil-water separation, and oil recovery. Good wettability of one fluid generally implies strong retention of that fluid in a porous solid matrix and simultaneously easy displacement of the other one. Here, we demonstrate that the contact angle of aqueous solutions of common chloride salts on mica in ambient oil displays a transition from near zero to finite contact angles up to 10° upon replacing monovalent Na+ and K+ cations in the aqueous phase by divalent Ca2+ and Mg2+ at neutral to elevated pH. This wetting transition is driven by electrostatic forces and originates from charge reversal of the mica-water interface upon adsorption of divalent cations. The ion-induced wettability alteration is synergistically enhanced by small amounts of polar molecules, stearic acid, added to the ambient oil, leading to water contact angles up to 70°.

BP 38.5 Wed 16:15 C 130

**Cardiolipin Monolayers** — ●RENKO KENSBOCK, HEIKO AHRENS, ANDREAS GRÖNING, THOMAS ORTMANN, and CHRISTIANE A. HELM — Physik, Uni Greifswald, 17487 Greifswald, Germany

Cardiolipin-cytochrome c binding in the inner mitochondrial membrane is pertinent to apoptotic processes involving positively charged cytochrome c, motivating a characterization of cardiolipin membranes. Cardiolipins are negatively charged lipids with four alkyl chains. Our approach is to analyse cardiolipin monolayers at the water-air interface, using isotherms and Brewster angle microscopy. The calculation of the in-plane electrostatic pressure consists of an electrostatic contribution using Grahame's equation and a chemical part reflected by the law of mass action. A nonmonotonic ionic strength dependence with a maximum at 0.1 M (NaCl, KCl) is observed for the phase transition surface pressure. This finding is in accordance with the calculations predicting the dominance of charge screening by monovalent counterions only for concentrations above 0.1 M. For lower salt content, its increase causes an elevation of the degree of dissociation and thus electrostatic repulsion within the cardiolipin membrane. The results will be reported, showing pH, concentration, temperature influences on the surface potential, and thus the ability to bind cytochrome c.

**15 min. break****Invited Talk**

BP 38.6 Wed 16:45 C 130

**Water flow along a solid interface affects the Stern layer** — ●MISCHA BONN — Max Planck Institute for polymer research, Mainz, Germany

At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring properties on interfacial water different from bulk water. Owing to its importance for disciplines such as electrochemistry, atmospheric chemistry and membrane biophysics, the structure of interfacial water has received much attention.

We elucidate the structure and structural dynamics of interfacial water using ultrafast surface-specific sum-frequency generation (SFG) vibrational spectroscopy. We make use of the fact that the SFG signal depends critically on the interfacial organization of water molecules.

We attempt to bridge continuum models of laminar flow along interfaces, with molecular-level descriptions of the Stern and diffuse layer, which describe the near-surface distribution of ions. For water at two different mineral interfaces, we report a dramatic effect of water flow along the mineral surface on the organization of water at the interface. Our observations can be explained by considering the coupling between the flow and the dissolution chemistry at the interface. Even for low-soluble quartz at neutral pH, dissolution plays a key role in determining the interfacial water organization through the charge on the surface.

BP 38.7 Wed 17:15 C 130

**Breaking the Symmetry of Ions at the Air-Water Interface** — ●EVA BRANDES<sup>1</sup>, PETER KARAGEORGIEV<sup>1</sup>, PADMANABHAN VISWANATH<sup>2</sup>, and HUBERT MOTSCHMANN<sup>1</sup> — <sup>1</sup>Institute of Physical and Theoretical Chemistry, University of Regensburg, D-93040 Regensburg, Germany — <sup>2</sup>Centre for Nano and Soft Matter Sciences, Jalahalli, Bangalore 560013, India

The air-water interface is a widely discussed system. Controversial opinions exist especially for the arrangement of dissolved ions close to the interface; while the classical picture predicts depletion, more recent investigations suggest a nonmonotonous concentration profile with an enrichment layer followed by a depletion layer. A sophisticated method to investigate the air-water interface is the IR-vis sum frequency generation (SFG) spectroscopy, because this method is intrinsically surface specific for soft media.

In this contribution we investigated the behavior of octahedral metal complex ions close to the air-water interface. No SFG signal is expected for octahedrons unless there is a reduction in symmetry. This distortion can only take place close to the interface because only there is a non-isotropic environment. We got SFG responses from the octahedrons, revealing that they are close to the interface. Furthermore we measured the surface excess via a surface tension isotherm, which turns out to be negative. The combined measurements suggest a non-monotonous concentration profile.

BP 38.8 Wed 17:30 C 130

**Macro- and Microrheology of Heterogeneous Microgel Packings** — FANY DI LORENZO<sup>1,2</sup> and ●SEBASTIAN SEIFFERT<sup>1,2</sup> — <sup>1</sup>Freie Universität Berlin, Germany — <sup>2</sup>Helmholtz-Zentrum Berlin, Germany

Microgels are soft deformable colloids that can be packed by external compression. Such packing transforms a suspension of loose microgel particles into an arrested state with properties similar to that of a macroscopic gel. We follow this idea and prepare microgel packings

that consist of both soft, loosely crosslinked particles and stiff, densely crosslinked particles, considering packing fractions that cover the range from the onset of particle contact to particles that are strongly packed, deformed, and deswollen. With this strategy, we investigate the transition from a particulate suspension to a macrogel-type system with defined, purposely imparted sub-micrometer scale spatial heterogeneity. We study these inhomogeneous composites from macro- and microscopic perspectives by oscillatory shear rheology and by fluorescence recovery after photobleaching to probe their macroscopic mechanics and the microscopic mobility of flexible linear tracer polymers that diffuse through them.

References: F. Di Lorenzo, S. Seiffert, *Macromolecules* 2013, 46, 1962. F. Di Lorenzo, S. Seiffert, *Colloid Polym. Sci.* 2013, 291, 2927.

BP 38.9 Wed 17:45 C 130

**Dielectric Response of the Water Hydration Layer and its Application on the Solvation Energy** — ●CHRISTIAN SCHAAF and STEPHAN GEKLE — University Bayreuth, Bayreuth, Germany

The electric field caused by a charged solute molecule introduced into a dipolar liquid solvent leads to a reorientation of the solvent molecules which is quantified by the solvent's local dielectric constant.

We calculate this dielectric response function using two different methods; linear response for a system with the explicit solute and theoretical calculations using the wave-vector dependent, non-local bulk permittivity. The good agreement leads to our central result: while the water dielectric constant for a radial field in the hydration layer of spherical solutes is strongly different from bulk water, this difference is *not* due to significant restructuring of the hydrogen bond network, but can be traced back almost entirely to bulk properties of pure water.

Finally, integrating our dielectric profiles, we calculate the solvation energies for Na<sup>+</sup>, Cl<sup>-</sup>, I<sup>-</sup>, and Cs<sup>+</sup> and find quantitative agreement with experimental data.