

CPP 25: Focus session: Structure, chemistry, and ion solvation at solid-liquid interfaces II (joint session O, CPP)

Time: Tuesday 14:00–16:00

Location: HE 101

Topical Talk CPP 25.1 Tue 14:00 HE 101
First-Principles Microkinetic Modeling at Solid-Liquid Interfaces: First Steps — ●KARSTEN REUTER — Technische Universität München, Germany

Over the last decade first-principles based microkinetic models have become a common tool to describe solid-gas processes like heterogeneous catalysis or crystal growth. For processes at solid-liquid interfaces such modeling is in its infancy. Challenges arise already in the efficient treatment of solvation effects or in the determination of individual rate constants, where extended time-scale simulations are required to capture the often complex and rough free energy barriers.

In this talk I will review our first steps to address corresponding challenges, focusing on water/aspirin as a showcase application. For corresponding active pharmaceutical ingredients knowledge of their intrinsic dissolution rates is a cornerstone to optimize the pharmacokinetics. We achieve this goal within a spiral-growth microkinetic model that draws on dissolution rate constants obtained within a novel hyperdynamics-metadynamics molecular simulation approach.

Topical Talk CPP 25.2 Tue 14:30 HE 101
Structure of metal electrode-electrolyte interfaces determined from first principles — ●AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany — Helmholtz Institut Ulm - Elektrochemische Energiespeicherung, 89069 Ulm, Germany

The theoretical description of electrode-electrolyte interfaces from first principles is hampered by the complexity of the interface structures and the liquid nature of the electrolyte requiring computationally expensive statistical averaging. Despite these obstacles, significant progress has been made in the modeling in recent years. In this contribution, I will present our attempts to contribute to this progress by systematically increasing the complexity of the considered systems [1, 2]. The electrolyte can be described either as a thermodynamic reservoir or using implicit or explicit solvent models. Using these approaches, the equilibrium coverage of specifically adsorbed anions such as halides as a function of the electrode potential will be addressed. This represents an integral part of the realistic modeling of electrochemical double layers. Additionally, on metal electrodes such as platinum the adsorption of H or OH - depending on the electrode potential - has to be considered in the presence of an aqueous electrolyte. Finally, the structure of organic electrolytes on metal electrodes that is governed by weak dispersion forces will be discussed [2, 3].

[1] Axel Groß *et al.*, *J. Electrochem. Soc.* **161**, E3015 (2014).

[2] Nicolas Hörmann *et al.*, *J. Power Sources* **275**, 531 (2015).

[3] F. Buchner *et al.*, *ACS Nano* **7**, 7773 (2013).

Topical Talk CPP 25.3 Tue 15:00 HE 101
Synchrotron x-ray determination of ion distributions at liquid interfaces — ●JEAN DAILLANT — Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP48, F-91192 Gif sur Yvette Cedex, France

The interfacial behavior of ions is of key importance in a number of phenomena ranging from microfluidics to chemistry in the atmosphere and from protein stability to the transport of pollutants in water.

Beyond Coulombic interaction, the polarisability and hydration of the ions as well as water interfacial structure are important, leading to ion specificity, i.e. possibly dramatically different behavior for ions like Cl^- and I^- . Understanding these effects requires measurements to access the surface composition at the relevant nanometric length-scale.

Investigating the surface composition of alkali-halide aqueous solutions using grazing incidence x-ray fluorescence, differences in concentration over a few angstrom could be resolved, with, for example I^- or $\text{Br}^- > \text{Cl}^-$. These results could be explained by including a short-range potential accounting for short-range solvent mediated couplings.

Polarization of the liquid-Hg aqueous electrolyte induces extremely large decrease in surface energy with strong ion specificity. Using x-ray reflectivity, we could determine the interfacial structure, demonstrating an accumulation of ions at the Hg surface. Our results challenge the long-standing approximation that assimilates the Hg surface to a smooth, chemically inert surface with a uniform surface charge density.

Finally, using the standing wave technique which allows both high spatial and element sensitivity, we have investigated ion distributions in nano-channels, and I will discuss the first results we have obtained.

Topical Talk CPP 25.4 Tue 15:30 HE 101
Modelling of electrical double layers at metal oxide electrodes — ●MICHEL SPRIK¹ and JUN CHENG² — ¹Department of Chemistry, University of Cambridge, Cambridge UK — ²Department of Chemistry, University of Aberdeen, Aberdeen, UK

Oxide surfaces exchange protons with an aqueous electrolyte and can therefore carry a net proton charge. The adsorbed protons at low pH can be partially or fully discharged by conduction electrons or the deprotonated anionic groups at high pH by holes. The "intrinsic" equilibrium constants for this process (acidities, ionization and dehydrogenation free energies) can be computed for charge neutral surfaces. We have developed such a method using Density Functional Theory based Molecular Dynamics (DFTMD, for an application to rutile titania see *Angew Chem Int Ed Engl* (2014) 53, 12046). An electrode with net excess or deficit proton charge can be described in first approximation by a triple layer model consisting of the charged electrode surface, ionic counter charge on the electrolyte side (a Helmholtz layer at high ionic strength) and a space charge layer on the electrode side. After a summary of our DFTMD method, we will outline in this talk how the equilibrium constants computed by the DFTMD simulation can be used in an analytic model for an "electron coupled proton adsorption isotherm". The additional parameter in this model is the capacitance of the Helmholtz layer. Such a parametrized isotherm should enable us to analyse the effect of double layers on the (photo) electrocatalytic properties of metal oxides as will be shown for the example of the oxidation of adsorbed water molecules.