

O 17: Solid-Liquid Interfaces I: Reactions and Electrochemistry

Time: Monday 15:00–17:45

Location: TRE Phy

O 17.1 Mon 15:00 TRE Phy

Hydration layers at the graphite-water interface: Attraction or confinement? — HAGEN SÖNGEN¹, YGOR MORAIS JAQUES², LIDIJA ZIVANOVIC², SEBASTIAN SEIBERT¹, ●RALF BECHSTEIN¹, PETER SPIJKER², HIROSHI ONISHI³, ADAM S. FOSTER^{2,4}, and ANGELIKA KÜHNLE¹ — ¹Physical Chemistry I, Bielefeld University, Germany — ²COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland — ³Department of Chemistry, Kobe University, Japan — ⁴Division of Electrical Engineering and Computer Science, Kanazawa University, Japan

Water molecules at solid surfaces typically arrange in layers. The physical origin of the hydration layers is usually explained by (1) the attraction between the surface and the water and/or (2) the confinement of water due to the presence of the surface. While attraction is specific for the particular solid-solvent combination, confinement is a general effect at surfaces. A differentiation between the two effects is critical for interpreting hydration structures. At the graphite-water interface, the solid-solvent attraction is often considered to be negligible. Nevertheless, we observe hydration layers using three-dimensional atomic force microscopy at the graphite-water interface. We use Monte Carlo simulations to explain why confinement alone could cause the formation of hydration layers. With molecular dynamics simulations, we show that at ambient conditions, there is a significant graphite-water attraction which is pivotal for the formation of layers at the graphite-water interface.

[1] H. Söngen et al., *Physical Review B*, 100 (2019) 205410

O 17.2 Mon 15:15 TRE Phy

Novel methods to simulate the electrode - electrolyte interface: New approach, old charging methods — ●SUDARSHAN VIJAY¹, GEORG KASTLUNGER¹, HENDRIK HEENEN¹, JOSEPH GAUTHIER², HENRIK KRISTOFFERSEN¹, and KAREN CHAN¹ — ¹CatTheory, Department of Physics, Technical University of Denmark — ²SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering, Stanford University

A major challenge preventing complete mechanistic understanding of reactions at the metal | solution interface is determining ab-initio barriers at constant driving force. Current state of the art methods require calculations to be done at different unit cell sizes and with explicit treatment of the electrolyte. More recently, hybrid continuum charge - explicit solvent models have been developed which account for solvent effects at lower computational expense. Furthermore, it has been suggested that the effective surface charge is the descriptor for activity of reactions occurring at the electrode-electrolyte interface [1]. In this work, we develop methods that can be readily used to simulate electrochemical processes accurately and at minimal computational cost. This novel procedure is applied to two contemporary electrochemical test cases. First, we compute potential dependent kinetics for the electrochemical Hydrogen Evolution Reaction. Second, we explain the experimentally observed [2] change in peak position for hydroxide adsorption with cation size on Platinum stepped surfaces.

1. Gauthier et al. *J. Chem. Theory Comput.* 2019 2. *Angew.Chem.*2017,129,15221-15225

O 17.3 Mon 15:30 TRE Phy

Solvation at metal/liquid interfaces: A benchmark of computational methods — ●HENDRIK H. HEENEN¹, JOSEPH GAUTHIER², THOMAS LUDWIG², HENRIK H. KRISTOFFERSEN¹, and KAREN CHAN¹ — ¹Department of Physics, Technical University of Denmark — ²Department of Chemical Engineering, Stanford University

Recently, the application of continuum solvation methods in DFT simulations has surged in studies of solid/liquid interfaces, specifically when treating electrochemical systems. These continuum solvation models mimic the mean solvent response, effectively relying on parameters derived from solvation energies of molecules in bulk solution. To date, it is unclear how well these methods perform at the solid/liquid interface where directional solvent interactions such as hydrogen bonds may differ from the bulk solution. In this work, we evaluate continuum solvation methods for the metal/liquid interface by benchmarking against *ab-initio* molecular dynamic simulations. This technique presents the most accurate representation for solvation energies at interfaces, which cannot yet be assessed experimentally [1]. Our bench-

mark includes a variety of adsorbates solvated by water on the Pt(111), Au(111), Cu(111), and Cu(211) surface. We find that continuum solvation methods capture solvation energies for weakly solvated adsorbates adequately, but are unable to account for the impact of hydrogen bonding and competitive water adsorption. We quantify these contributions to the resultant binding energies and propose estimations of appropriate corrections.

[1] O.M. Magnussen, A. Groß, *J. Am. Chem. Soc.* **141**, 4777 (2019)

Invited Talk

O 17.4 Mon 15:45 TRE Phy

Tales of 1000 and 1.2 electrons: Grand Canonical Simulations of Electrified Interfaces using Implicit Solvation Models — ●NICOLAS G. HÖRMANN — Chair of Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Germany

In this talk I will present an overview over recent developments in simulation strategies of electrochemical interfaces using hybrid QM/continuum models. In these approaches, grand canonical (GC) interface energies are derived by varying the total number of electrons in the system [1] and by self-consistently including the energy contributions from solvent and electrolyte through an appropriate mean-field (implicit solvation) description. GC calculations allow to determine a wide range of electrochemical observables that are inaccessible by traditional calculations at zero-net-charge – typically referred to as the *Computational Hydrogen Electrode* (CHE) approach. Examples discussed in the talk are non-trivial shifts of electrosorption peaks with pH, non-integer electrosorption valencies or potential-induced surface reconstructions of metallic electrodes. In this context, I will also elaborate on the general limitations of the prevalent CHE method and show how it originates from a low-order Taylor expansion of the GC energetics. Likewise, inherent accuracy limitations of the GC method and of implicit solvation models in general will also be assessed, and possible improvements presented, e.g. using hybrid models with explicitly treated interfacial water [2].

[1] N.G. Hörmann, *et al.*, *J. Chem. Phys.* 150, 041730 (2019). [2] N.G. Hörmann *et al.*, *npj Computational Materials* 5, 100 (2019).

O 17.5 Mon 16:15 TRE Phy

Electrochemical Interfaces Getting Real - Theoretical Modeling of Transition States at Applied Electrode Potential — ●SIMEON D. BEINLICH, NICOLAS G. HÖRMANN, and KARSTEN REUTER — Technische Universität München, Germany

Based on recent improvements in the field of computational modeling of electrochemical interfaces, we present a method that explicitly incorporates the influence of an applied electrode potential on reaction transition states.

Commonly, transition state calculations at electrified solid-liquid-interfaces are performed at zero-net-charge conditions without including electric field and double-layer effects. Under reaction conditions, however, the energetics is influenced by charge-exchange with the electrode which acts as a thermodynamic bath for the electronic degrees of freedom. Using an implicit solvation scheme in combination with a grand canonical description of the system [1], we provide an approach that is able to accurately model processes at electrochemical interfaces with the electrode potential included explicitly in the simulations.

[1] N.G. Hörmann, O. Andreussi, N. Marzari, *J. Chem. Phys.* 150, 041730 (2019)

O 17.6 Mon 16:30 TRE Phy

Electrochemical N₂ reduction: How nature does it & what we can learn from it — ●VANESSA J. BUKAS and JENS K. NØRSKOV — Department of Physics, Technical University of Denmark

Electrochemical conversion of molecular N₂ into ammonia (NH₃) is a key goal in our quest toward global sustainability. Catalyzing this reaction, however, faces the formidable task of breaking the stable N≡N bond, while simultaneously suppressing the parasitic hydrogen evolution reaction (HER). As a result, all attempts to realize such a technology have so far been hindered by invariably large (>1 V) overpotentials and low (~1%) selectivity. Remarkably, the enzyme nitrogenase overcomes these limitations and selectively reduces atmospheric N₂ under ambient conditions to provide NH₃-based fertilizer directly into the soil. Guided by recent experimental evidence of a structurally dynamic cofactor [1], we present here a molecular-level

mechanism of the biologic N_2 fixation from first-principles calculations [2]. The proposed mechanism shows that the enzyme is catalytically activated/deactivated through site-specific ligand exchange in order to drive the most difficult steps of the reaction. In the meantime, rate-limiting electron transfer prevents the reaction from evolving via a series of coherently-coupled proton-electron transfers which, in turn, kinetically suppresses the competing HER. Based on this insight, we propose revised strategies for designing the next generation of solid catalysts for electrochemical NH_3 production.

[1] Sippel *et al.*, Science **359**, 1484-1489 (2018)

[2] Bukas and Nørskov, ChemRxiv (2019)

Invited Talk

O 17.7 Mon 16:45 TRE Phy

Electrochemical microcalorimetry - measuring the entropy of electrochemical reactions — ●ROLF SCHUSTER — Karlsruhe Institute of Technology, Institute of Physical Chemistry, Karlsruhe, Germany

Electrochemical reactions are accompanied by heat transfer between the electrode/electrolyte interface and its surrounding. In electrochemical systems the reversible part of the exchanged heat is directly correlated with the entropy changes in the interface. This gives access to the reaction entropy of the electrochemical processes, including the charge transfer itself as well as non-Faradaic side processes like coadsorption or solvent reordering. The reaction entropy, as a thermodynamic quantity, provides complementary information, e.g., to the charge vs. potential relation, as usually probed by conventional electrochemical methods. We study heat effects during electrochemical surface reactions with minute conversions down to about 1% of a monolayer. This allows for monitoring of the reaction entropy as a function of the electrode potential, for example, during hydrogen adsorption on Pt or underpotential Cu-deposition on Au. After a general introduction, we will present examples for entropy changes upon adsorption processes and double layer charging on Au(111) and discuss the effect of configurational entropy of the adlayer. Time-resolved studies of the heat evolution during Cu-bulk deposition will demonstrate the implications from heat measurements on the reaction steps of this complex reaction.

O 17.8 Mon 17:15 TRE Phy

Microcalorimetric investigation of silver deposition from silver cyanide complexes — ●FRANZISKA KARCHER, MARCO SCHÖNIG, and ROLF SCHUSTER — Institute of Physical Chemistry, Karlsruher Institute of Technology, 76131 Karlsruhe, Germany

Electrochemical silver deposition from cyanide containing solutions is of great technical importance. However, the detailed mechanism of this reaction is still controversially discussed in the literature. Here we study the deposition and dissolution process of silver in 0.01 M $KAg(CN)_2$ electrolyte with different concentrations of KCN by electrochemical microcalorimetry. Measuring the reversibly exchanged heat during an electrochemical reaction enables the determination of the reaction entropy, which, in turn, allows conclusions on the reaction mechanism.

The results show that in solutions with additional KCN the silver deposition takes place by direct reduction of the $[Ag(CN)_2]^-$ -complex after the dissociation of the predominant $[Ag(CN)_3]^{2-}$ -complex. Based on the microcalorimetric measurements the reduction of an adsorbed species seems unlikely. In solutions with low or no additional KCN the formation of a passivating surface layer on the Ag-electrode is detectable. From determination of its formation entropy we conclude that this surface layer consists of solid AgCN.

O 17.9 Mon 17:30 TRE Phy

Entropy change during specific anion adsorption on Au(111) — ●MARCO SCHÖNIG and ROLF SCHUSTER — Karlsruhe Institute of Technology, Germany

The understanding of specific adsorption is of fundamental importance for the description of the electrochemical double-layer (EDL). We used electrochemical microcalorimetry to investigate the specific adsorption of anions (Cl⁻, Br⁻, I⁻) on Au(111) from different electrolytes. Thereby we measure the reversibly exchanged heat during the anion adsorption/desorption process, which is directly correlated with the reaction entropy of the half cell reaction [1]. For all electrolytes we found negative reaction entropy for the adsorption process, with a distinct minimum around half coverage. We provide an interpretation of the data on the basis of a lattice gas model considering adsorbed ions and solvent molecules. [1]K. Bickel, K.D. Etzel, V. Halka and R. Schuster, Electrochim. Acta 2013, 112,801. *