O 60: Solid-Liquid Interfaces III: Reactions and Electrochemistry

Time: Wednesday 15:00–17:45 Location: MA 042

O 60.1 Wed 15:00 MA 042

An from insightful ab-initio view molecular on free dynamics energies at metal-water interfaces — •Fabiola Dominguez Flores, Sung Sakong, and Gross Axel — Institute of Theoretical Chemistry, Ulm University

Solid-liquid interfaces are a key element of all technological processes and devices in interfacial electrochemistry, where atomistic modeling encounter major challenges in measuring accurately thermodynamic properties comparable to experiments. Ab initio molecular dynamics (AIMD) simulations have been used to sample the statistical properties of the electrochemical interfaces. However, there is no feasible method to treat the entropy, only the structural properties of the simulations can be safely analyzed. Using the two-phase thermodynamic (2PT) model, which estimates the entropy from the vibrational density of states of liquids, we obtained the free energy of the electrochemical interfaces of ion-free water on several metal surfaces. Based on the grand canonical thermodynamic scheme, we will discuss the free energy of solvation on metal surfaces and their respective energetics at the interfaces. The information is essential to understand the energetics at the electrochemical interfaces as well as for further development of effective solvent modeling and parametrization of solvent models.

O 60.2 Wed 15:15 MA 042

Oxidation of functionalized monolayers on gold in classical molecular dynamics (MD) — •Ludwig Ahrens-Iwers, Gregor Vonbun-Feldbauer, and Robert Meissner — Hamburg University of Technology, Hamburg, Germany

Monolayers of thiols can self-assemble on gold surfaces. If they are functionalized with ferrocene, this functional group can oxidize and transfer an electron to the gold surface in the process. In order to allow an electron transfer in classical MD, partial charges of gold atoms are modeled using the constant potential method (CPM) which distributes charges on metal electrodes. The charge transfer from the ferrocene to the gold surface is modeled using free energy perturbation methods giving access to the reduction potential.

As an implementation of the CPM, the ELECTRODE package for the MD code LAMMPS is presented[1]. This package features a particle-mesh solver to greatly reduce computation times of the long-range Coulomb interactions[2].

[1] L. Ahrens-Iwers et al., J. Chem. Phys. 157, 084801 (2022)

[2] L. Ahrens-Iwers, R. Meißner, J. Chem. Phys. 155, 104104 (2021)

O 60.3 Wed 15:30 MA 042

SiO2-water interface with long-range Charge Equilibration (Qeq) — •Kamila Savvidi[1], Ludwig Ahrens-Iwers[1], and Robert Meissner[1,2] — [1]Hamburg University of Technology, Hamburg, Germany — [2]Helmholtz-Zentrum Hereon, Geesthacht, Germany

Charge equilibration (Qeq) methods enables the accurate calculation of partial charges in molecular dynamics. The charges are predicted based on the minimization of the electrostatic potential energy, which is in principle calculated up to a cut-off radius. Long-range contributions improve the accuracy of the Coulomb interactions in a system with periodic images, that can advance the prediction of the atomic charges. To this end, we implemented a long-range Qeq scheme in a similar way to the original Qeq method [1] by adding terms with the electronegativity and atomic hardness to the electrostatic energy. The long-range contributions to the Coulomb energy are calculated using Ewald summation and gaussian charges. This method is part of the ELECTRODE package in LAMMPS [2] and shows agreement with the constant potential method when an electric potential is applied. SiO2 and Si electrodes with aqueous electrolytes are studied using the method and compared to results with other Qeq models.

[1] A. Rappe, W. Goddard, Phys. Chem., 95, 3358-3363 (1991) [2] L. Ahrens-Iwers, M. Janssen, S. Tee, R. Meißner, J. Chem. Phys. 157, 084801 (2022)

O 60.4 Wed 15:45 MA 042

Understanding Competitive Adsorption at Metal-Water Interfaces via Cavity Formation — •Thorben Eggert[1,2], Nicolas G. Hörmann[1,2], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Technische Universität München

Adsorption energies from the gas phase differ significantly from their respective values in aqueous environments, e.g. the reduced adsorption energy of phenol on Pt(111) in water [1]. While computationally costly, explicit solvation models can partially capture this reduction, adsorption energies of phenol are not changed in implicit solvation models [2]. The latter deficiency arises from the common approximation to base the cavity formation cost, i.e. the exclusion of solvent by the adsorbate, solely on bulk liquid energetics.

To measure the missing energetic contribution from the competitive binding of adsorbate *and* solvent, we study the free energy of cavity formation with classical molecular dynamics simulations and free energy perturbation via the Multistate Bennett Acceptance Ratio. We demonstrate that cavity formation at interfaces depends on the interaction strength between the substrate and the solvent, which can be rationalized by the respective adsorption energy [3]. These results allow for a quantification of the competitive nature of adsorption processes at solid-liquid interfaces, which is a prerequisite for a parametrized substrate-specificity in improved solvation models.

[1] N. Singh and C.T. Campbell, ACS Catal. **9**, 8116 (2019).

[2] P. Clabaut *et al.*, J. Chem. Theory Comput. **16**, 6539 (2020).

[3] T. Eggert *et al.*, J. Chem. Phys. **159**, 194702 (2023).

Topical Talk O 60.5 Wed 16:00 MA 042

Ab initio insights into atomistic processes at electrified solid/liquid interfaces — •Mira Todorova[1], Jing Yang[1], Sudarsan Surendralal[1], Florian Deissenbeck[1], Stefan Wippermann[1,2], and Jörg Neugebauer[1] — [1]Max-Planck-Insitut für Eisenforschung GmbH, Düsseldorf, Germany — [2]Phillips-Universität Marburg, Germany

Many of the challenges we face today towards achieving a greener economy focus on processes occurring at electrified solid/liquid interfaces. Understanding how the interactions between the solid, the liquid and dissolved species are affected by the applied potential will aid our ability to achieve rational design and targeted optimization of relevant processes. Ab initio molecular dynamic simulations have proven an indispensable tool to gain insights at the scale of atoms and electrons. The talk will present insights into reactions at electrified solid/liquid interfaces enabled by our recent developments of a thermopotentiostat [1,2], and the coupling of DFT calculations with thermodynamic models. The power of these approaches will be demonstrated for two examples: H adsorption on the Pt electrode [3] and Mg surface stability and dissolution.

[1] S. Surendralal, M. Todorova, M. Finnis, and J. Neugebauer, Phys. Rev. Lett. 120, 246801 (2018)

[2] F. Deißenbeck, C. Freysoldt, M. Todorova, J. Neugebauer, and S. Wippermann, Phys. Rev. Lett. 126, 136803 (2021)

[3] S. Surendralal, M. Todorova, and J. Neugebauer, Phys. Rev. Lett. 126,166802 (2021)

O 60.6 Wed 16:30 MA 042

Response Properties of Water at the Electrified Pt(111) Surface — •Lang Li, Nicolas G. Hörmann, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Metal-water interfaces play a fundamental role in electrochemistry. An accurate understanding of their properties is required in any attempt to describe electrochemical phenomena such as electrocatalytic reactions or charge transfer processes. In this work, we benchmark the description of electrified Pt(111)/water interfaces based on *ab initio* molecular dynamics simulations at applied potential conditions using density functional theory. We apply the potential by introducing excess electrons that are counterbalanced by partially charged hydrogen atoms. This method is tested with a variety of slab setups and cell sizes. We analyze in detail the structure of the interface as well as the obtained capacitance vs. potential curves and compare with published theoretical and experimental results [1,2]. In addition, we decompose the interfacial water response on Pt(111) into dipolar and chemisorption-related contributions as a function of the introduced electronic excess charge, and introduce a nuanced four-state model of interfacial water with one chemisorbed and three physisorbed states. Our results highlight the response of interfacial water to an applied potential and its importance for understanding overall capacitance, in particular at high electrolyte concentrations [3]. [1] A. Bouzid and A. Pasquarello, J. Phys. Chem. Lett. **9**, 1880 (2018). [2] J.B. Le, Q.Y. Fan, J.Q. Li, and J. Cheng, Sci.Adv. **6**, eabb1219 (2020). [3] L. Li, Y.P. Liu, J.B.

Le, and J. Cheng, Cell Rep. Phys. Sci. **3**, 100759 (2022).

O 60.7 Wed 16:45 MA 042

Oxygen Adsorption at the Electrochemical Metal/Water Interface: Au(111) vs. Pt(111) — •Alexandra M. Dudzinski, Elias Diesen, Karsten Reuter, and Vanessa J. Bukas — Fritz-Haber-Institut der MPG, Berlin

Due to its key role in fuel cell technologies, the oxygen reduction reaction (ORR) has been the subject of extensive studies over the last decades. Dedicated experiments on model single-crystal electrodes have specifically served to establish fundamental trends across transition metal catalysts, e.g., in terms of product selectivity and the effect of applied potential. Such studies revealed that in contrast to Pt-based electrodes, Au shows a distinct preference towards forming hydrogen peroxide (rather than water) with activity that depends strongly on the (absolute) electrode potential. The microscopic origins of this difference are still not well understood and likely lie in details of key elementary reaction steps. Using *ab initio* molecular dynamics, we recently predicted O_2 adsorption as a critical, potential-dependent step of the ORR on the weak-binding Au(111) surface [1]. In this study, we now draw a direct comparison to the more reactive Pt(111) surface and (i) systematically analyze structural and dynamical properties of the two electrochemical interfaces, as well as (ii) investigate O_2 adsorption as a function of potential. Prominently, we find the more reactive Pt(111) to be predominantly covered by specifically adsorbed solvent species under operating ORR conditions, while chemisorbed O_2 shows an almost negligible response to potential.
[1] Dudzinski *et al.*, ACS Catal. **13**, 12074 (2023).

O 60.8 Wed 17:00 MA 042

Interfacial properties of non-planar Platinum slab in contact with water via Deep Potential Molecular Dynamics (DP-MD) — •Muhammad Saleh[1], Alexander Lozovoi[2], Riccardo Martina[1], Clotilde S. Cucinotta[2], and Marialore Sulpizi[1] — [1]Theoretical Physics of electrified liquid-solid interface, Ruhr-University Bochum, Germany — [2]Department of Chemistry, Imperial College London, UK

One of the crucial aspects that determines the reaction of the metal-liquid is its surface properties, for instance, the dynamics of interfacial interactions between metal-liquid and liquid-liquid species or surface charge distribution. Knowing these mechanisms gives us an insight into the development of catalysts, batteries, or electrochemical reactions in general. However, obtaining the atomistic resolution is experimentally challenging, while most atomistic modeling only focuses on the clean planar surface, which is somewhat inaccurate given that the surface is primarily rough under actual conditions. On the other hand, an adequate representation of a model system requires a sizable number of atoms (i.e., more than 1000 atoms), which increases the computational cost, particularly when employing high-quality approaches. In this work, we adopt the deep neural networks (DNNs) model named deep potential molecular dynamics (DPMD) to reproduce the potential energy surface (PES) of ab initio molecular dynamics (AIMD), enabling an extensive simulation trajectory. As a result, a thorough analysis of the surface characteristics of platinum metal in contact with water is possible.

O 60.9 Wed 17:15 MA 042

Extracting free energy charge transfer paths of solvated ions from molecular dynamic simulations — •Zhenyu Wang, Mira Todorova, Christoph Freysoldt, and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str.-1, D-40237, Düsseldorf, Germany

The Marcus theory is indispensable for understanding and predicting electron transfer reactions, which are fundamental in various chemical and biological systems. While solvation shells play a key role in stabilizing ions in solution, a quantitative approach to assess charge transfer intricacies is currently absent. This study introduces a quantitative model to elucidate solvation shell formation precisely. In our model, ions' charges (q_{core}) serve as generalized coordinates, and we derive free energy profiles as functions of q_{core}. We present a systematic workflow for generating solvation configurations around ions with varying charges. Thermodynamic integration aligns the free energy of ions in different charge states. Our approach successfully reproduces Marcus parabolas, revealing a pivotal transition in the solvation mode at $q_{core} \approx 0.5$ e. This model significantly enhances our ability to quantitatively analyze charge transfer complexities, providing fresh insights into solvation shell dynamics. The outcomes of this work holds promise for advancing the understanding of electron transfer reactions in chemical and biological contexts.

O 60.10 Wed 17:30 MA 042

Power of the interface: Understanding (electro-)valorization of biomass-derived chemicals — •Sihang Liu[1], Nitish Govindarajan[2], and Georg Kastlunger[1] — [1]Catalysis Theory Center, Department of Physics, Technical University of Denmark (DTU), 2800 Kgs. Lyngby, Denmark — [2]Materials Science Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, California 94550, United States

In this contribution, we combine grand-canonical density functional theory (GC-DFT) calculations, microkinetic modeling, ab initio molecular dynamics (AIMD) and experiments to study aqueous-phase furfural adsorption on various transition metal surfaces and understand trends in reactivity of copper for furfural electroreduction. Using AIMD simulations of the metal-water interfaces, we find furfural binding strength in aqueous phase is reduced due to water replacement and reorganization. We then identify the binding energy of OH in vacuum to be a good descriptor to estimate the solvation energy of furfural(Ref1). In the latter study on Cu electrodes, we combine GC-DFT based microkinetic modeling and pH dependent experiments to highlight the predominant role of proton-coupled electron transfer-based pathways and elucidate the possible rate-determining steps towards furfuryl alcohol and 2-methyl furan, respectively(Ref2). Our work improves understandings of interfacial catalysis and chemistry to upgrade furfural and other biomass-derived chemicals. 1. Liu et al. J. Chem. Phys. 2023, 159, 084702 2. Liu et al. EES. Catal., 2023, 1, 539-551