

O 31: Solid-Liquid Interfaces 3: Reactions and Electrochemistry

Time: Tuesday 10:30–12:30

Location: S054

Topical Talk

O 31.1 Tue 10:30 S054

Towards a realistic description of electrified solid-liquid interfaces — ●NICOLAS G. HÖRMANN — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Atomistic modelling of electrified solid-liquid interfaces in the context of electrocatalytic and electrochemical transformations is a challenging task. This is in particular so as the description of many relevant processes involves the consideration of charge transfer, solvent reorganization and the long-range screening of the electrolyte. Many of these processes have been studied in the past using effective model hamiltonians and from a physical chemistry perspective, e.g. based on mean-field kinetic models. However, recent advances in the first-principles-based description have opened up pathways to study the involved phenomena with atomistic resolution and to gain new, fundamental insights.

In this talk, I will give a brief overview of such recent developments, concentrating mainly on the use of and results from DFT calculations in continuum solvation environments[1]. Without doubt, such calculations have had a tremendous impact on the community, as they paved the way to describe the interfacial energetics in a grand-canonical framework, aka at applied potential conditions[2]. In addition to discussing a range of results obtained on model systems, I will as well clarify the evident limitations and inaccuracies of such an approach and discuss briefly possible future pathways to improve upon those.

[1] S. Ringe *et al.*, Chem. Rev. (2021). [2] N.G. Hörmann *et al.*, JCP, **150**, 041730 (2019).

O 31.2 Tue 11:00 S054

Electrostatic potentials in molecular dynamics — ●LUDWIG AHRENS-IWERS¹, GREGOR VONBUN-FELDBAUER¹, and ROBERT MEISSNER² — ¹Institute of Advanced Ceramics, Hamburg University of Technology, Hamburg, Germany — ²Institute of Polymers and Composites, Hamburg University of Technology, Hamburg, Germany

Molecular dynamics (MD) simulations in a constant potential ensemble are an increasingly important tool to investigate charging mechanisms in next-generation energy storage devices. The constant potential method (CPM) can be used in classical MD to model metallic electrodes at an electrostatic potential. In this method, charges of individual electrode atoms are set to meet the applied potential. Unfortunately, existing implementations are either highly specialized or not very performant.

As a new implementation of the CPM, the ELECTRODE package for the MD code LAMMPS is presented. This package integrates a particle-mesh solver to greatly reduce computation times of the long-range Coulomb interactions. Further, a dipole correction that is required for systems with a slab geometry is included. In addition to the CPM, the code features a constant charge method which distributes the charges within each electrode as well as a thermopotentiostat that utilizes the CPM algorithm. Moreover, the integration in LAMMPS allows the use of many tools from the base code and other packages.

O 31.3 Tue 11:15 S054

First-principles molecular dynamics simulations of electrified Pt(111)/H₂O interfaces — ●LANG LI, NICOLAS G. HÖRMANN, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

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 first-principles 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. Additionally, we investigate different methods to determine the reference potential.

We analyze in detail the structure of the interface as well as the obtained capacitance vs. potential curves and compare these with published theoretical and experimental results [1]. Our results highlight the response of interfacial water to an applied potential and its importance for understanding the hump in the capacitance, observed

at high electrolyte concentrations [2].

[1] L. Li, J. -B. Le, J. Cheng, Cell Rep. Phys. Sci., **3**, 100759 (2022).
[2] J.B. Le, Q.Y. Fan, J.Q. Li, J. Cheng, Sci. Adv., **6**, eabb1219 (2020).

O 31.4 Tue 11:30 S054

First step of the oxygen reduction reaction on Au(111): An ab initio molecular dynamics study of the electrified metal/water interface — ●ALEXANDRA M. DUDZINSKI, ELIAS DIESEN, HENDRIK H. HEENEN, VANESSA J. BUKAS, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

The oxygen reduction reaction (ORR) is a key electrocatalytic process for developing sustainable energy technologies. And yet, many aspects of the underlying reaction mechanism are still poorly understood at the molecular level. Especially at weak-binding electrode surfaces such as Au, even the ability to bind aqueous O₂ species as a first mechanistic step remain unclear. Resolving these questions requires going beyond the simplified thermodynamic models of charge-neutral reaction intermediates that have been commonly used in computational electrocatalysis so far. Here, we perform molecular dynamics simulations based on periodic density-functional theory (DFT) to investigate O₂ adsorption at an electrified Au(111)/water interface. We elucidate structural interfacial properties as a function of surface charge, and show that the latter can significantly alter the O₂ binding energy. Adsorption is specifically enhanced under electric fields that are realistic for ORR operation, suggesting this as a very possible first electrochemical, rather than purely chemical step of the mechanism and showing that field effects in corresponding DFT models cannot be neglected. The resulting dependence on (absolute) electrostatic potential may further explain the superior activity measured experimentally for this catalyst in alkaline vs. acidic media.

O 31.5 Tue 11:45 S054

Modeling varying potential conditions in electrochemical simulations: The case of O₂/Au(111) — ●ELIAS DIESEN, ALEXANDRA M. DUDZINSKI, HENDRIK H. HEENEN, VANESSA J. BUKAS, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

While significant insight has been gained in recent years by DFT-based simulations of electrochemical processes, crucial methodological challenges remain, especially for accurate determination of reaction energies under operando conditions. One open question is how to represent the constant electrode potential in simulations of an electrified water/metal interface, where the simulation setup requires a constant charge in the simulation cell throughout the reaction. Here we compare different levels of treatment of the electrochemical interface: explicit ab initio molecular dynamics, an implicit solvent model, and a sawtooth-potential electric field in vacuum, for the case of O₂ adsorption on Au(111). We characterize the dynamics near the surface and identify ways an applied electrode potential influences the adsorption. We find, in all methods, significantly enhanced O₂ adsorption at more reducing conditions. However, we also show that certain aspects of the process can only be captured using a fully explicit treatment of the solvent.

O 31.6 Tue 12:00 S054

Understanding the Interfacial Capacitance of 2D Materials in an Implicit Water Environment — ●HEDDA OSCHINSKI^{1,2}, NICOLAS G. HÖRMANN¹, and KARSTEN REUTER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Technical University of Munich, Germany

The interfacial capacitance (C) is a central quantity in electrochemistry. For metal electrodes, C is dominated by the double layer capacitance that derives from the potential drop in the solvent. However, the finite density of states (DOS) in semiconducting 2D electrodes alters the picture and leads to a vanishing C around the point of zero charge. This entails a challenge in describing the energy-potential relation and the connected field effects when considering adsorbates.

To explore this challenge, we study the interfacial capacitance for 2D metal halides MX₂, using density-functional theory in a continuum solvent environment. We break down C into a DOS-filling-related quantum capacitance and the double layer capacitance. Our analysis demonstrates that such a separation into individual components is not straightforward. Nevertheless, the qualitative behavior of C can be ra-

tionalized, making this study a first step towards better understanding of 2D, in particular semiconducting, electrodes.

O 31.7 Tue 12:15 S054

Two-Dimensional 2D Materials interfacing liquid water : the new frontier from ab initio simulations — BENOIT GROSJEAN¹, FELIX MOUHAT¹, RODOLPHE VUILLEUMIER¹, FRANCOIS-XAVIER COUDERT², and •MARIE-LAURE BOCQUET¹ — ¹Ecole Normale Supérieure, PSL university and CNRS, Paris, France — ²Chimie Paris Tech, PSL university and CNRS, Paris, France

In spite of their computational cost, quantum dynamic insights open unprecedented avenues for the use of 2D materials for nanofluidics. In this talk, I will report on our recent theoretical findings on 2D materials like G (graphene), BN (boron nitride) and GO (graphene

oxide) by means of Ab Initio Molecular Dynamics (AIMD) and their implications to rationalize their peculiar fluid transport and filtration properties. We demonstrate that the charging of pristine ideal 2D materials in aqueous conditions originate from the hydroxide anion and is crucially dependent of the electronic structure of the 2D layers ranging from chemisorption to physisorption. [1] We could pioneer the concept of static versus mobile extrinsic charges on prototypical 2D materials that have a huge impact on electro-kinetic transport.[2] We also predict that the water reactivity is further enhanced on hydrid sheets like planar G-BN heterostructure [3]. Finally, we explore the properties of various GO models in neutral water and we unveil several chemical processes [4].

[1] Nat. Comm. 10, 1656 (2019). [2] J. Chem. Phys. 156, 044703 (2022). [3] Phys. Chem. Chem. Phys. 22, 10710 (2020). [4] Nat. Comm. 11, 1566 (2020).