O 28: Solid-Liquid Interfaces II: Structure and Spectroscopy

Time: Tuesday 10:30–13:15 Location: H 1012

O 28.1 Tue 10:30 H 1012

Just How Anisotropic is the Air-Water Interface? An SFG/DFG Study — •Martin Thämer[1], Alexander Fellows[1], Álvaro Díaz Duque[1], Vasillios Balos[2], Louis Lehmann[3], Roland Netz[3], and Martin Wolf[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]IMDEA Nanociencia, Madrid, Spain — [3]Freie Universität, Berlin. Germany

The air-water interface belongs to the most abundant interfaces on our planet and its unique properties are at the heart of numerous chemical processes in both nature and industrial applications. However, despite decades of research, some of the most fundamental aspects of the air-water interface still remain controversial, particularly the thickness of the interfacial region.

Here we directly address this question by employing our recently developed depth-resolved vibrational spectroscopy, which is based on the simultaneous measurement of phase-resolved sum- and difference-frequency signals and allows for precise depth-profiling on the sub-nm scale. Through isotopic exchange experiments the second-order spectra are separated into their resonant and non-resonant contributions, allowing the origins of each to be determined along with the length-scales of their decaying contributions. These results provide the first direct experimental measurement of the anisotropic layer thickness and yield important insight into the different signal contributions in second-order spectroscopy on water.

O 28.2 Tue 10:45 H 1012

Surface stratification determines the interfacial water structure of simple electrolyte solutions — •Yair Litman[1,2], Kuo-Yang Chiang[2], Takakazu Seki[2], Yuki Nagata[2], and Mischa Bonn[2] — [1]Yusuf Hamied Department of Chemistry, University of Cambridge, U. K. — [2]MPI for Polymer Research, Mainz, Germany.

For the past twenty years, the electrical-double layer (EDL) model has been the primary framework for analyzing how ions behave at the interface between water and air and interpreting various types of surface-selective experimental measurements. In this talk [1], I will present a combination of surface-sensitive heterodyne-detected vibrational sum frequency generation (VSFG) and *ab initio* based molecular dynamics simulations to study the liquid/air interface of several aqueous electrolyte solutions. Our VSFG measurements highlight the shortcomings of the EDL model for a range of electrolytes, including but not restricted to NaCl, NaBr NaI, NaOH, and CsF aqueous solutions. We rationalize our findings by proposing a new microscopic picture in which the surface of simple electrolyte solutions is stratified and consists of an ion-depleted outer surface and an ion-enriched subsurface layer, jointly determining the water interfacial structure.

[1] Y. Litman, K-Y. Chang, T. Seki, Y. Nagata, M. Bonn, submitted.

O 28.3 Tue 11:00 H 1012

Depth-Resolved SFG/DFG Spectroscopy of Charged Aqueous Interfaces — •Álvaro Díaz Duque, Alexander Fellows, Martin Wolf, and Martin Thämer — Fritz Haber Institut der MPG, Berlin, Germany

Charged aqueous interfaces are omnipresent in our world, being a crucial ingredient on both natural systems and technical devices. The charges at such interfaces generate electric fields which interact with the electrolyte and can extend over relatively large length scales. The evolution of the potential in such systems is typically described by the Gouy-Chapman-Stern (GCS) theory. However, much less in known about the depth-dependent structural properties of the main constituent of the electrolyte, the water.

Vibrational Sum-frequency generation spectroscopy is commonly used to study aqueous interfaces. The particular strength of this technique is its sensitivity to structural anisotropy and its ability to report on the molecular orientation and intermolecular environment of water. Here, we utilize our recent development that combines phase-resolved SFG and DFG which additionally yields depth resolution on the nm scale. We study the details of the depth-dependent water structure within the electric double layer and correlate these to the defining thermodynamic and electrostatic quantities in the investigated electrolyte. Based on the results we demonstrate that the continuum solvent model that is typically assumed within the GCS theory is clearly insufficient to accurately describe water in such systems.

O 28.4 Tue 11:15 H 1012

Exploring Dynamic Solvation Effects at the Electrochemical IrO_2/Water Interface — •Nikhil Bapat, Hendrik H. Heenen, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Upon electrification, solid-liquid interfaces are known to undergo significant alterations, not least due to the potential-induced adsorption of surface species. Computational studies conveniently explore this phenomenon via an *ab initio* thermodynamics based Pourbaix analysis, which compares the potential-dependent stability of multiple structural and compositional configurations. To render the computational cost tractable, solvation effects are thereby presently if at all mostly only implicitly treated.

Here, we assess this approximation for the highly hydrophilic IrO_2(110) oxide catalyst surface by comparing to results from extensive molecular dynamics simulations including explicit water. This approach is computationally enabled at first-principles predictive-quality level by the use of efficient and accurate machine-learning potentials that are trained to density functional-theory data via an active learning approach. The detailed comparison to the analog Pourbaix diagram obtained with implicit solvation sheds light on the effect of dynamic H-bonding networks at the complex, corrugated oxide surface, while the analysis of the potential-dependent interfacial water structure and mobility gives insight to which degree these networks may be mimicked by static ice overlayers.

O 28.5 Tue 11:30 H 1012

Molecular Dynamics Modeling of Pulsed Laser Fragmentation of Solid and Porous Si Nanoparticles in Liquid Media — •Dmitry Ivanov and Martin Garcia — University of Kassel, Kassel, Germany

The production of non-toxic and homogeneous colloidal solutions of nanoparticles (NPs) for biomedical applications is of extreme importance nowadays. Among the various methods for generation of NPs, pulsed laser ablation in liquids (PLAL) has proven itself as a powerful and efficient tool in biomedical fields, allowing chemically pure silicon nanoparticles to be obtained. Due to a number of complex and interrelated processes involved in the laser ablation phenomenon, however, the final characteristics of the resulting particles are difficult to control, and the obtained colloidal solutions frequently have broad and multimodal size distribution. Therefore, the subsequent fragmentation of the obtained NPs in the colloidal solutions due to pulsed laser irradiation can be utilized. The resulting NPs characteristics, however, depend on the parameters of laser irradiation as well as. Thus, reliable knowledge of the mechanism of NP fragmentation is necessary for generation of a colloidal solution with NPs of predesigned properties. To investigate the mechanism of a laser-assisted NP fragmentation process, in this work, we perform a large-scale molecular dynamics (MD) modeling of FS laser interaction with colloidal solution of Si NPs. The corresponding conclusion about the relative input of the properties of different laser-induced processes and materials to the mechanism of NP generation is drawn.

O 28.6 Tue 11:45 H 1012

Visualizing solvent structures at electrified solid-liquid interfaces by electrochemical atomic force microscopy — •Andrea Auer[1,2], Thorben Eggert[3], Nicolas G. Hörmann[3], Karsten Reuter[3], and Franz J. Giessibl[1] — [1]Institute of Experimental and Applied Physics, University of Regensburg, Germany — [2]Institute of Physical Chemistry, University of Innsbruck, Austria — [3]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

To design efficient electrochemical interfaces for sustainable energy conversion, it is crucial to resolve the molecular structures of the electric double layer, where inevitably all electrocatalytic reactions take place. Here, we employ electrochemical atomic force microscopy (AFM) with stiff qPlus sensors[1,2], which allows us to probe the potential-dependent, vertical solvent layering at well-defined electrified solid-liquid interfaces with high spatial resolution. Investigations of a Au(111) electrode in various aqueous electrolytes reveal distinct oscillatory frequency shift modulations in z-direction. Depending on the applied potential, the charge of the electrode and the type of ions, we attribute these oscillations to water and/or ion layering close to the electrode, which we can correlate with atomistic molecular dynamics simulations.

[1] F.J. Giessibl, Rev. Sci. Instrum. 90, 011101 (2019). [2] A. Auer, B. Eder and F.J. Giessibl, J. Chem. Phys. 159, 174201 (2023).

O 28.7 Tue 12:00 H 1012

A Comparative Study of Classical Force Fields and the MB-Pol Water Model in Understanding Water/Metal Interfaces — •Saeyeon Lee, Yevhen Horbatenko, Seungchang Han, and Stefan Ringe — Department of Chemistry, Korea University

Metal/water interfaces hold profound significance in the material or energy science fields. They form pivotal junctures where the behavior of metals and their interactions with aqueous environments give reference to various industrial, technological, and environmental applications. At these interfaces, water-water interactions are expected to be very distinctive compared to the bulk, raising a question about the validity of classical force fields. In this study, we attempt to follow this question and compare classical force fields for the description of interfacial water with a high-level reference, the MB-Pol water model. This model is based on the many-body expansion of the water interaction energy based on coupled-cluster calculations. We use this model and a simplified description of water-metal interactions to study the impact of the water force field on water-metal interactions and present a detailed analysis and justification for using many-body force fields.

O 28.8 Tue 12:15 H 1012

Atomistic modeling of the electric double layer at water/Ag(111) interfaces — •Sung Sakong and Axel Gross — Institut für Theoretische Chemie, Universität Ulm, 89081 Ulm, Germany

The structures and processes at the electrode/electrolyte interface are crucial components of electrochemical cells play a critical role in energy conversion and storage. Recently, the subject has attracted significant interest from a first-principles perspective. Despite their significance, no conclusive consensus exists on how to include the electrochemical environment in atomistic simulations. Here, we address the structure and properties of electrochemical interfaces from an atomistic perspective based on ab initio molecular dynamics simulations in the presence of ionic species. We use the water/Ag(111) interface as an example and explore how to take the electrode potential into account properly in first-principles simulations. In particular, we discuss whether local charges, e.g., surface charges, can correspond to physical observables. Finally, we address the driving force for forming electric double layers at electrochemical interfaces.

[1] A. Groß and S. Sakong, Chem. Rev. **122** , 10746 (2022).

[2] A. Groß and S. Sakong, Curr. Opinion Electrochem. **14**, 1 (2019).

O 28.9 Tue 12:30 H 1012

Unraveling electrocatalysts and electrochemical interfaces in situ at the nanoscale — •Christopher Kley — Helmholtz Young Investigator Group Nanoscale Operando CO2 Photo-Electrocatalysis, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 14109 Berlin, Germany — Department of Interface Science, Fritz Haber Institute of the Max Planck Society, 14195 Berlin, Germany

Recent advances in electrochemical atomic force microscopy will be presented, with a focus on deciphering the local properties of electrocatalysts under liquid phase reaction conditions. Reactions include the electroreduction of CO2 (CO2RR) and CO (COR), as well as the oxygen evolution reaction (OER). Selected results provide insights into (i) the complex surface structures of Cu electrodes during CO2RR and COR in distinct electrolytes, (ii) the electrical conductivity, chemical-frictional, and morphological properties of electrocatalysts, and (iii) the in situ surface structure and catalytic activity of OER catalysts. Complementary spectroscopic approaches and findings will be discussed and a perspective given on the potential of scanning probe microscopy for nanoscale catalysis and rational innovation of energy conversion materials.

O 28.10 Tue 12:45 H 1012

Electrokinetic Measurement: A Tool for Characterization of Piezoelectric Materials in liquid media — •Mohsen Sadeqi-Moqadam and Julia Glaum — Department of Materials Science and Engineering, Norwegian University of Science and Technology

Piezoelectric materials have pervasive applications across industries like telecommunications, automotive, electronics, and aerospace. Recently, their use in liquid environments for biomedical engineering, electrochemistry, and electromechanical systems has surged, prompting inquiries into their behavior and performance in such conditions. To probe this, an innovative experimental setup was devised, employing electrokinetic measurements to characterize polarized piezoelectric materials like lead zirconate titanate under mechanical stress (up to 150 MPa) in liquid media. This setup revealed a direct link between applied stress and the piezoelectric sample's electrokinetic response. Dynamic stress variations closely mirrored changes in the sample's electrokinetic behavior and affected the flow cell's resistance. Conversely, the non-piezoelectric alumina sample showed negligible alterations in both electrokinetics and resistance during stress application. Finite element modeling further supported these experimental findings, showcasing consistent outcomes for the electrical processes induced by mechanical stress variations on piezoelectric samples. This exploration sheds light on understanding and predicting piezoelectric material responses within liquid environments, impacting diverse fields reliant on their functionality.

O 28.11 Tue 13:00 H 1012

Efficient and Accurate Description of Solid-Liquid Interface Dynamics Using High-Dimensional Neural Network Potentials — •Knut Nikolas Lausch[1,2], Marco Eckhoff[3], Peter Blöchl[4], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany — [3]Theoretische Chemie, Eidgenössische Technische Hochschule Zürich, Switzerland — [4]Institut für Theoretische Physik, Technische Universität Clausthal, Germany

Solid-liquid interfaces play a central role in many processes that are of utmost importance for a sustainable energy future. From energy storage solutions to heterogeneous catalysis, understanding interface dynamics and reactivity plays a key role in developing new materials. Molecular dynamics simulations of such interfaces rely on an accurate description of solid-liquid interactions, and density functional theory (DFT) can in principle provide reliable results. However, due to the high computational costs, time and length scales of ab initio simulations are severely limited. This can be overcome by employing machine learning potentials, which yield energies and forces several orders of magnitude faster while retaining chemical accuracy. Here, we present a high-dimensional neural network potential for lithium manganese oxide (LMO) in water as a model system for the electrocatalytic oxygen evolution reaction.