

# Challenges for ab initio molecular dynamics simulations of electrochemical interfaces

Axel Groß<sup>1,2,\*</sup>

<sup>1</sup>*Institute of Theoretical Chemistry,  
Ulm University, 89069 Ulm, Germany*

<sup>2</sup>*Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, 89081 Ulm, Germany*

## Abstract

The modelling of electrochemical interfaces between a liquid electrolyte and an electrode from a quantum chemical perspective is typically done by performing ab initio molecular dynamics simulations. Thus the statistically nature of the electrolyte structure can be taken into account by performing the proper averages. However, in order to obtain reliable results for such electrochemical interfaces, the simulations should be performed for sufficiently large systems and sufficiently long times under potential control. These requirements lead to significant challenges for running such simulations which will be addressed in this contribution, together with possible approaches to address these challenges.

Keywords: Electrochemistry, interfaces, quantum chemistry, liquid electrolytes, electrode potential

---

\* axel.gross@uni-ulm.de

## I. INTRODUCTION

Processes at electrochemical interfaces play a critical role in electrochemical energy conversion and storage [1]. The study of such processes is thus not only interesting from a fundamental, but also from a technological point of view. However, the complexity of these interfaces causes severe problems as far as the reliable theoretical and numerical modelling of such processes is concerned [2]. Furthermore, the required appropriate consideration of the crucial electrochemical control parameter adds additional difficulties [3–7]. In principle, there is an obvious approach from an atomistic perspective, in particular if also reactions at such electrochemical interfaces should be described: First-principles electronic structure calculations need to be performed under potential control for a sufficiently large system faithfully representing the electrochemical interface, and the statistical nature of the liquid electrolyte should be properly taken into account by performing *ab initio* molecular dynamics (AIMD) simulations [8–17].

However, first of all the still considerable numerical effort associated with performing AIMD simulations prevents their routine systematic application. And second, there is still no generally accepted method in the field of computational electrochemistry to perform first-principles simulations under potential control. This also means that the field of the modelling of electrochemical interfaces has not fully matured yet. It is only fair to say that a thorough understanding of electrochemistry is also hindered by the very complex formulation of the concepts of electrochemistry routed historically in a more phenomenological approach, which for example has resulted in a confusing multitude of different potential definitions [18, 19]. However, this also means that it is still worthwhile to enter this exciting and important research field, as still important contributions can and need to be made.

In this Opinion, I will briefly sketch the challenges associated with performing *ab initio* molecular dynamics simulations of electrochemical interfaces, but also propose possible routes to overcome these challenges. Furthermore, I will also briefly review some important insights already gained from such simulations, but also address challenges in our current understanding of structures and processes in interfacial electrochemistry.

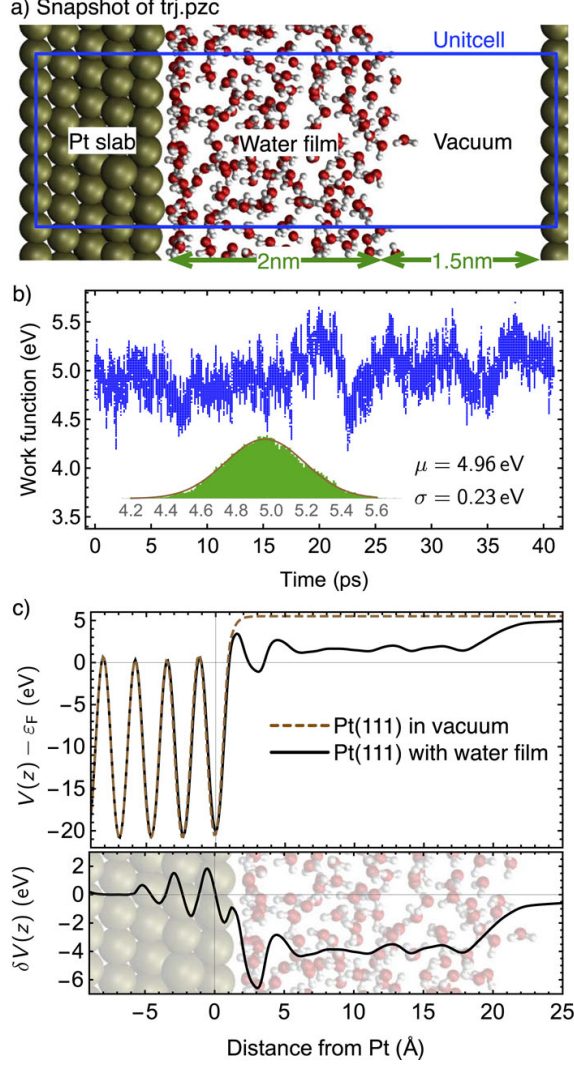


FIG. 1. a) Snapshot of a AIMD simulation of six water layers on Pt(111) within a  $(6 \times 6)$  periodicity with in total 144 water molecules [20]. (b) Time evolution of the work function along the trajectory to determine the potential of zero charge. (c) Electrostatic potential  $V(z)$  of Pt(111) in a vacuum (dashed line), the averaged electrostatic potential and its change  $\delta V(z)$  (lower panel) caused by the presence of the water film. Reprinted from Ref. [20], with the permission of AIP Publishing.

## II. QUANTUM-CHEMICAL ASPECTS OF ELECTROCHEMICAL INTERFACES

Interfacial electrochemistry is concerned with structures and processes at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte [21]. At such an interface, an electric double layer (EDL) evolves [22]. From a continuum point of view, the properties of the EDL are rather similar to those of a p-n junction or a Schot-

tky diode, respectively, in semiconductor physics, depending on whether the electrode is semiconducting or metallic. At such interfaces, there is a charge rearrangement, which in semiconductor physics is driven by the fact that the Fermi energy needs to be uniform throughout the whole system. In principle, the same should also be true in electrochemistry.

It is also important to realize that the whole EDL needs to be charge-neutral because otherwise there would be electric fields acting on the charge carriers in both electrolyte and electrode leading to a charge rearrangement which eventually ensures the charge neutrality. Just recently it has become obvious that the particular structure of the EDL, for example with respect to the concentration of cations close to the electrode, can have a significant influence on electrocatalytic processes at this electrode [23–25].

A critical parameter characterizing electrochemical interfaces is the potential of zero charge (pzc). According to Trasatti [26], the pzc can be derived from the work function of the electrode without any adsorbates covered by an ion-free water film. Figure 1 shows the typical setup of an AIMD simulation used for the modelling of the interface between Pt(111) and an aqueous electrolyte [20]. In order to determine the work function, a vacuum region has been introduced, and the corresponding electrode potential is derived from the average work function, as is now the typical approach used in AIMD simulations of water/metal interfaces [8, 10–12]. The width of the fluctuations in the work function is mainly caused by the finite size of the unit cell used in the periodic calculations and can become significantly smaller for larger surface unit cells [8, 20]. For the sake of completeness note that there are also quantum chemical approaches, in which the electrode potential can be determined from bulk properties of the electrolyte [27].

In panel c of Fig. 1, the averaged electrostatic potential and its change with respect to the Pt(111)/vacuum interface is plotted. It becomes obvious that even under the pzc conditions, there are strong polarization effects at the Pt(111)/water interface which are in fact also associated with a significant charge rearrangement at this interface [13, 28]. The interaction of water with Pt(111) leads to a sizable charge transfer from the first water layers towards the Pt(111) surface. To faithfully capture these important effects requires the explicit consideration of the electronic systems through quantum chemical approaches.

The observation of the strong charge transfer at pzc conditions in principle also calls for a reinterpretation of the potential of zero charge. It is usually defined as the potential at which the electrode has no surface free charge [13]. However, quantum chemically there is

no unique definition of the surface charge. To determine any local charge from a quantum chemical calculation requires to integrate the charge density over a given volume which at the surface needs to correspond to a layer of a certain location and thickness. Yet, there is no criterium that would define such a surface layer. Hence in principle surface charge is an ill-defined quantity. Any quantity should be rather defined based on observables, and the definition of Trasatti [26] of the pzc rests on such an observable, namely the work function, and should therefore be preferred.

The definition of Trasatti also gives a simple recipe to set up a simulation cell for AIMD simulations at the pzc. However, it does not provide a recipe how the electrode potential can be changed. Note that the electrode potential corresponds to an intensive property of the system that needs to be uniform in electrochemical equilibrium. There have been numerous approaches to change the effective electrode potential in a computational setup of electrochemical interfaces. In the materials-oriented electronic structure theory, there has been a focus on rearranging the electron distribution. Electrodes are usually viewed as charged systems whose charge needs to be balanced by counter charges. Following the seminal work by Lozovoi *et al.* [3], several methods to allow for a change of the electrode potential through charging the electrode have been implemented [4–7, 29–31]. In these approaches, the focus was on the change of the charge of the electrode whereas the location of the necessary counter charge was dictated by numerical convenience, either as a homogeneous charge background or by some localized charge inside or outside of the electrolyte layer.

These approaches have certainly advanced the field. However, with respect to the charge distribution in the EDL, these methods almost entirely focused on the electronic distribution and on changing the charge of the electrode, but neglected the specific structure of the EDL in the electrolyte. The counter charge has basically only been introduced in order to guarantee the charge neutrality of the periodic unit cell. However, at real electrochemical interfaces, charge neutrality is guaranteed by the presence of the EDL. Hence a proper representation of the EDL is key to a reliable modelling of electrochemical interfaces. As far as the equilibrium structure of metal electrodes under electrochemical conditions covered by small atoms such as hydrogen or halogens is concerned, the explicit consideration of the EDL does not appear to be crucial in order to obtain agreement with experiment [19, 32]. However, as mentioned above, there are systems in which the explicit presence of ions close to the electrochemical interface does matter [23, 24] so that they need to be explicitly taken into account in a

reliable modeling.

There is an approach to control the electrode potential in quantum chemical simulations which is based on the explicit presence of ions that was originally proposed by Skulason *et al.* [33]. Adding or removing hydrogen atoms or adding alkali or halogen atoms to the explicit water layer leads to the formation of ions in the liquid layer by transferring electrons to or from the Fermi level of the metal electrode [8, 10–12, 20]. The charge transfer alters the dipole moment at the electrolyte/electrode interface and consequently also its work function, thereby changing the electrode potential. In this approach, the charge neutrality of the electrochemical interface is preserved so that there is no need for any compensating charges which makes this approach very suitable for AIMD simulations [8, 10–12, 20]. The question remains whether the rather high ion concentrations in the electric double layer are realistic, but it is fair to say that there is still a limited knowledge of ion concentrations close to the electrode surface, as will also be discussed below.

### III. TAKING THE LIQUID NATURE OF ELECTROLYTES APPROPRIATELY INTO ACCOUNT

As mentioned in the introduction, the presence of a liquid electrolyte poses severe challenges in the description of electrochemical interfaces as a proper modeling of liquids requires a statistical sampling over many different structures. In principle, there are two ways to perform these averages: either one first averages and then performs the simulations, or one first performs the simulations and then averages. The first approach is usually numerically less demanding. As far as liquid electrolytes are concerned, such an initial averaging leads to the implicit solvent model [34], i.e., the representation of the liquid as a polarizable dielectric continuum. Whereas implicit solvent models have been used intensively in solvation science for decades [35], such approaches have only recently been implemented into periodic DFT codes, but widely used since then [34, 36–38]. In principle, the implicit solvent approach is best-suited to reproduce the properties of liquids consisting of non-polar molecules [39]. Hence, their application to aqueous electrolytes requires special care due to the strong polar nature of the water molecule. And indeed, quantitative and even qualitative differences between implicit solvent and AIMD simulations can result, as for example found for the determination of adsorption energies of small molecules and radicals at water/metal

interfaces [40].

Hence, there is certainly a need for reliable benchmark studies of the properties of electrochemical interfaces. Yet, the large numerical effort associated with running AIMD simulations still prevents systematically performing benchmark studies. A possible solution might be the on-the-fly active learning on interatomic potentials [41], as recently demonstrated for the determination of hydration free energies at water-platinum interfaces [42]. For selected configurations, still first-principles electronic structure calculations need to be performed in order to monitor the electron distribution that is underlying particular structures, as an understanding of electrochemical interfaces is not complete without such an analysis.

#### IV. INSIGHTS GAINED FROM AB INITIO MOLECULAR DYNAMICS SIMULATIONS OF ELECTROCHEMICAL INTERFACES

I will now give some recent examples of ab initio molecular dynamics simulations of electrochemical interfaces that provided some conceptual advances. Note that this list is by no means exhaustive. Early first-principles electronic structure calculations addressing the structure of water-metal interfaces, in particular with respect to the close-packed (111) surfaces, were performed for ice-like bilayer structures [8, 43–45] which resemble the densest layer of ice Ih. In the first layer of this bilayer structure, the water molecules are bound to the top sites of the underlying metal surface through their oxygen atoms which resembles the adsorption of a water monomer [44]. For the second layer, two different configurations are possible, the so-called H-up and H-down structures. These two structures lead to work functions that differ by more than 2 eV which correspond to an electrode potential difference that is larger than the stability window of water of 1.23 V [28]. AIMD simulations of two water layers on several close-packed metal surfaces could demonstrate that the results of work function experiments for adsorbed water layers can only be reproduced if already the first layer assumes a disordered liquid-like structure [28]. However, the question remained whether there are some structural elements of such ice-like water bilayers that are still present at water/metal interfaces at room temperatures.

This particular question was addressed in detail by Le *et al.* [11, 46]. They introduced the notation of watA molecules that are located adjacent to the metal surface with their oxygen atom pointing to the surfaces and watB molecules with the opposite orientation. These

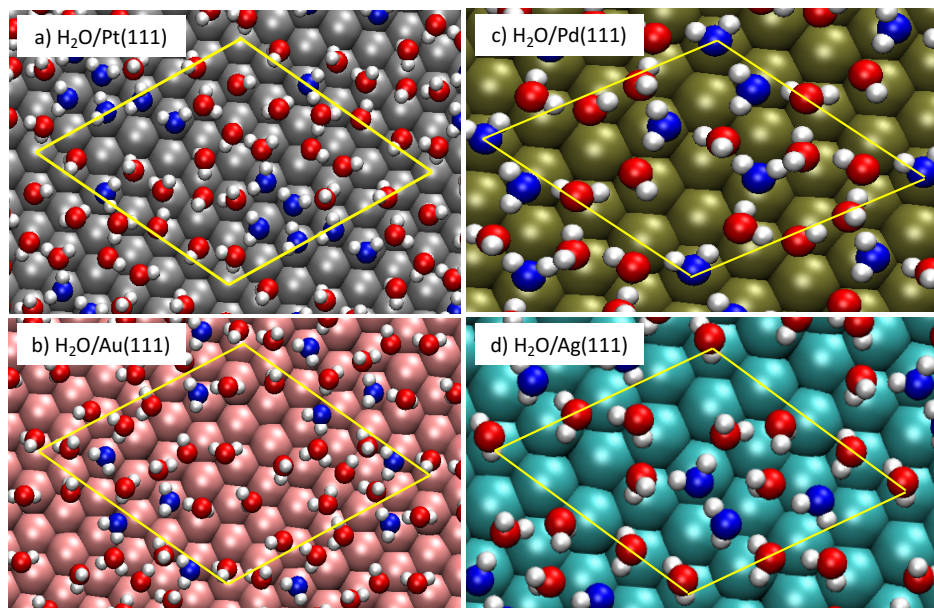


FIG. 2. Snapshots of AIMD simulations of the surface water configurations on Pt(111), Au(111), Pd(111) and Ag(111), taken from DFT-MD simulations at 330 K [46]. Blue and red oxygen atoms represent the watA and watB water molecules, respectively. Reprinted from Ref. [46], with the permission of Elsevier.

two kinds of configuration are illustrated in Fig. 2 using snapshots of AIMD simulations of water on Pt(111), Au(111), Pd(111) and Ag(111) [46], where the blue and red oxygen atoms represent watA and watB water molecules. They watA molecules correspond to strongly bound water molecules that are rather strongly located close to the metal top sites. However, as Fig. 2 demonstrates, at the more strongly interacting Pt(111) and Pd(111) surfaces the watA molecules are closer to the top sites than on the more weakly interacting Au(111) and Ag(111) surfaces.

Another AIMD study with potential control [10] showed that the coverage of the watA molecules depends on the electrode potential: at higher potential at which the electrode is more positively charged, the density of watA molecules increases as the negatively charged oxygen atoms bind more strongly. Le *et al.* [46] further differentiated between watB-down and watB-up molecules. Whereas watA and watB-down water molecules only form three hydrogen bonds on the average due to the interaction with the metal surface, the watB-up molecules are almost fully coordinated, i.e., they are already coordinated as the liquid bulk



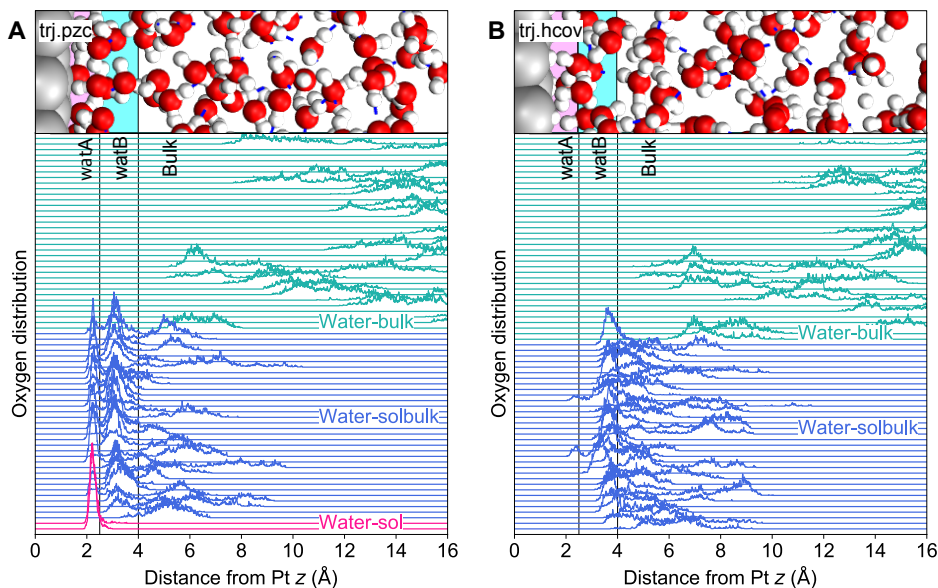


FIG. 3. Distribution of the oxygen atoms according to AIMD simulations of six water layers in a  $(6 \times 6)$  geometry with a run time of 40 ps of (A) a pure water film on clean Pt(111) and (B) a fully hydrogen-covered Pt(111) surface [10]. Reprinted from Ref. [8] under the Creative Commons Attribution License (CC BY).

water molecules.

Although the lateral position of watA molecules is rather restricted to the top sites, they constantly exchange their vertical position with the upper layers. This is illustrated in Fig. 3 where the distribution of selected water molecules along a 40 ps AIMD trajectory of six water layers in a  $(6 \times 6)$  geometry are shown. On clean Pt(111), there are two watA molecules that stay the whole run time adsorbed to Pt(111), but all other watA molecules move between the water layers, even farther away into the bulk water layers. On the hydrogen-covered Pt(111) surface, which is the stable phase at low electrode potentials, watA molecules hardly exist, and if so, only for a very short time. In addition, the watB water molecules are further away from the metal surface compared to uncovered Pt(111). In both cases, the bulk water molecules constantly move back and forth with respect to their distance from the metal surface. This demonstrates the very dynamical nature of water molecules in liquid water at electrochemical interfaces.

Finally I will touch an important topic that has recently drawn a lot of attention, namely the role of solvated ions in the water layers close to the electrochemical electrolyte/electrode

interface. A recent experimental study of the CO<sub>2</sub> electroreduction reaction (CO<sub>2</sub>RR) on Cu, Au and Ag electrodes by Monteiro *et al.* [23] found that CO is only produced if metal cations such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> or Cs<sup>+</sup> are added to the electrolyte. In the same paper, AIMD simulations were reported that had been performed in order to shed light on the role of cations in the CO<sub>2</sub> reduction. According to the simulations, the presence of partially desolvated metal cations stabilize the CO<sub>2</sub> intermediate mediated through a short-range electrostatic interaction, and this enables its reduction. Later, the results of the AIMD simulations were questioned [47] as apparently the observation of the CO<sub>2</sub> reduction required freezing the carbon atom of the CO<sub>2</sub> molecule. Due to this constraint, an activated bent CO<sub>2</sub> resulted in the presence of cations nearby which then dissociated [23]. Without such a constraint, the CO<sub>2</sub> molecule would just desorb from the surface [47]. It should be further noted that another study proposed that the main role of cations is to modify local electric fields, which suppresses hydrogen evolution while enhancing the CO<sub>2</sub>RR at the same time [48].

AIMD simulations are in principle not the appropriate tool to discover reaction mechanisms due to their limited run time, except for spontaneous events that are non-activated or hindered by very small barriers. Possible reaction mechanisms at electrochemical interfaces might be derived from a rational approach involving educated guesses. Furthermore, one has to take into account the liquid nature of the electrolyte along the reaction path which requires to calculate free energies instead of just total energies. These free energies can in fact be determined using constraint AIMD simulations, for example within the Blue Moon ensemble [49, 50].

The application of this technique with respect to the determination of the reaction mechanism and the corresponding barrier heights in the CO<sub>2</sub>RR and the competing hydrogen evolution reaction [51] is shown in Fig. 4. In the presence of two K<sup>+</sup> cations at the water/Au(110) interface, the CO<sub>2</sub> reduction becomes facile with CO<sub>2</sub> activation being the rate-determining step hindered by a barrier of 0.67 eV. At the same time, the hydrogen evolution becomes hindered by a barrier of 1.27 eV in the rate-limiting Volmer step. Thus in principle the mechanism proposed by Monteiro *et al.* [23] is confirmed. However, one still has to take into account that the operation of this mechanism requires a rather high potassium concentration of more than 1M, whereas in the experiment the cation effect was shown to set in at mM cation concentrations. Certainly the cation concentration might be higher directly

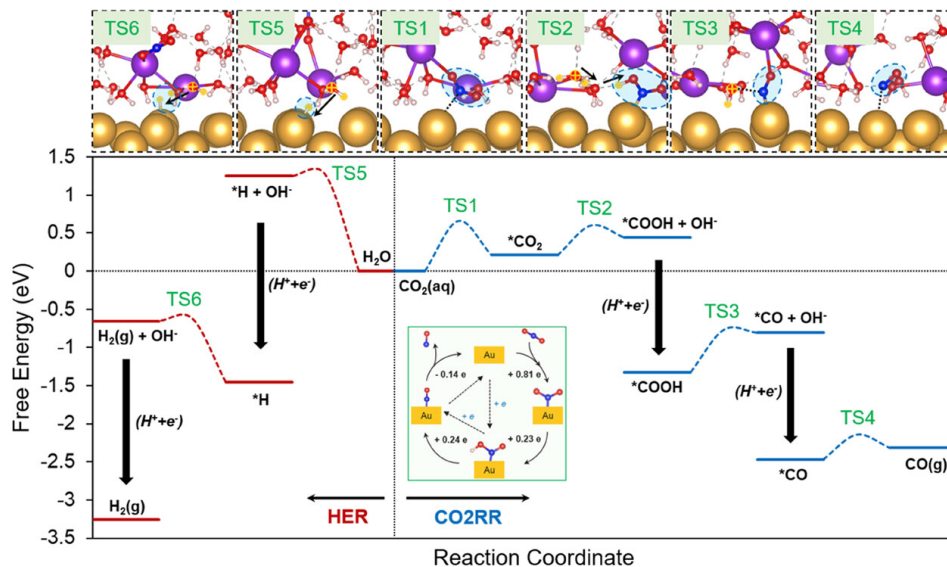


FIG. 4. Calculated free energy diagrams of the  $\text{CO}_2$  reduction reaction and the competing hydrogen evolution reaction at the water/Au(110) in the presence of K cations using a  $(2 \times 3)$  unit with in total 44 water molecules. The upper panel exhibits snapshots of the transition state configurations. In addition, the charge transfer to the key intermediates is shown in the inset. Reprinted from Ref. [51], with the permission of the American Chemical Society.

at the electrolyte/electrode interface than in the bulk electrolyte due to non-specific adsorption, but our knowledge about cation concentrations directly at electrode surfaces is rather limited. Recently it had been argued based on ab initio molecular dynamics simulations that larger cations exhibit a higher tendency to approach electrode surfaces [25]. However, an increase by three orders of magnitude with respect to the bulk electrolyte concentration appears to be unlikely. An atomistic understanding of cation effects in electrocatalytic reactions certainly requires further research efforts.

## V. CONCLUSIONS

A reliable description of structures and processes in interfacial electrochemistry on the atomistic level requires quantum chemical approaches which at the same time take the statistical nature of the electrolyte appropriately into account. Ab initio molecular simulations are in principle well-suited for this purpose, in particular as they can be performed under potential control and also allow to derive free energies. Still they are hampered by

their high computational demand which also prevents systematic studies for many different electrochemical conditions. Yet, there is certainly a need for benchmark studies based on reliable molecular dynamics simulations. They might be obtained by a combination of first-principles electronic structure calculations with intermediate simulation steps obtained using interatomic potentials that are obtained by on-the-fly active learning. Thus for example a better understanding of cation effects in electrocatalytic reactions might be obtained which are not fully understood yet.

## VI. DECLARATION OF INTERESTS

none

## ACKNOWLEDGEMENT

This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe). Support by the German Research Foundation (DFG) through contract GR 1503/39-1 and the POLiS Cluster of Excellence, Project ID 390874152, and by the Dr. Barbara Mez-Starck-Foundation is gratefully acknowledged.

- 
- [1] R. Schlögl, The role of chemistry in the energy challenge, *ChemSusChem* 2010, 3, 209
  - [2] O.M. Magnussen, A. Groß, Toward an atomic-scale understanding of electrochemical interface structure and dynamics, *J. Am. Chem. Soc.* 2019, 141, 4777
  - [3] A.Y. Lozovoi, A. Alavi, J. Kohanoff, R.M. Lynden-Bell, Ab initio simulation of charged slabs at constant chemical potential, *J. Chem. Phys.* 2001, 115, 1661
  - [4] C.D. Taylor, S.A. Wasileski, J.S. Filhol, M. Neurock, First principles reaction modeling of the electrochemical interface: Consideration and calculation of a tunable surface potential from atomic and electronic structure, *Phys. Rev. B* 2006, 73, 165402
  - [5] S. Schnur, A. Groß, Challenges in the first-principles description of reactions in electrocatalysis, *Catal. Today* 2011, 165(1), 129
  - [6] N. Bonnet, T. Morishita, O. Sugino, M. Otani, First-principles molecular dynamics at a constant electrode potential, *Phys. Rev. Lett.* 2012, 109, 266101

- [7] S. Surendralal, M. Todorova, M.W. Finnis, J. Neugebauer, First-principles approach to model electrochemical reactions: Understanding the fundamental mechanisms behind Mg corrosion, *Phys. Rev. Lett.* 2018, 120, 246801
- [8] A. Groß, S. Sakong, Ab initio simulations of water/metal interfaces, *Chem. Rev.* 2022, 122, 10746
- Comprehensive review about the current status of ab initio molecular dynamics simulations of water/metal surfaces.
- [9] A. Groß, F. Gossenberger, X. Lin, M. Naderian, S. Sakong, T. Roman, Water structures at metal electrodes studied by ab initio molecular dynamics simulations, *J. Electrochem. Soc.* 2014, 161, E3015
- [10] S. Sakong, A. Groß, Water structures on a Pt(111) electrode from ab initio molecular dynamic simulations for a variety of electrochemical conditions, *Phys. Chem. Chem. Phys.* 2020, 22, 10431
- [11] J. Le, M. Iannuzzi, A. Cuesta, J. Cheng, Determining potentials of zero charge of metal electrodes versus the standard hydrogen electrode from density-functional-theory-based molecular dynamics, *Phys. Rev. Lett.* 2017, 119, 016801
- [12] C.Y. Li, J.B. Le, Y.H. Wang, S. Chen, Z.L. Yang, J.F. Li, J. Cheng, Z.Q. Tian, In situ probing electrified interfacial water structures at atomically flat surfaces, *Nat. Mater.* 2019, 18, 697
- [13] P. Li, J. Huang, Y. Hu, S. Chen, Establishment of the potential of zero charge of metals in aqueous solutions: Different faces of water revealed by ab initio molecular dynamics simulations, *J. Phys. Chem. C* 2021, 125, 3972
- [14] J.B. Le, J. Cheng, Modeling electrochemical interfaces from ab initio molecular dynamics: water adsorption on metal surfaces at potential of zero charge, *Curr. Opin. Electrochem.* 2020, 19, 129
- [15] X. Qin, T. Vegge, H.A. Hansen, CO<sub>2</sub> activation at Au(110)-water interfaces: An ab initio molecular dynamics study, *J. Chem. Phys.* 2021, 155, 134703
- [16] J.B. Le, A. Chen, L. Li, J.F. Xiong, J. Lan, Y.P. Liu, M. Iannuzzi, J. Cheng, Modeling electrified Pt(111)-H<sub>ad</sub>/water interfaces from ab initio molecular dynamics, *JACS Au* 2021, 1, 569
- [17] M.T. Darby, C.S. Cucinotta, The role of water at electrified metal-water interfaces unravelled from first principles, *Curr. Opin. Electrochem.* 2022, 36, 101118

- [18] S.W. Boettcher, S.Z. Oener, M.C. Lonergan, Y. Surendranath, S. Ardo, C. Brozek, P.A. Kempler, Potentially confusing: Potentials in electrochemistry, *ACS Energy Lett.* 2021, 6, 261
- Fundamental work convincingly demonstrating that there is some confusion in the application of the concept of potential to electrochemical systems
- [19] A. Groß, Reversible vs standard hydrogen electrode scale in interfacial electrochemistry from a theoretician’s atomistic point of view, *J. Phys. Chem. C* 2022, 126, 11439
- [20] S. Sakong, A. Groß, The electric double layer at metal-water interfaces revisited, *J. Chem. Phys.* 2018, 149, 084705
- [21] W. Schmickler, E. Santos, *Interfacial electrochemistry*, 2nd edn. (Springer Berlin / Heidelberg, 2010)
- [22] A. Groß, S. Sakong, Modelling the electric double layer at electrode/electrolyte interfaces, *Curr. Opin. Electrochem.* 2019, 14, 1
- [23] M.C.O. Monteiro, F. Dattila, B. Hagedoorn, R. García-Muelas, N. López, M.T.M. Koper, Absence of CO<sub>2</sub> electroreduction on copper, gold and silver electrodes without metal cations in solution, *Nat. Catal.* 2021, 4, 654
- Important experimental work together with theoretical support demonstrating the influence of cations on electrocatalytic reactions at electrochemical interfaces
- [24] J. Huang, M. Li, M.J. Eslamibidgoli, M. Eikerling, A. Groß, Cation overcrowding effect on the oxygen evolution reaction, *JACS Au* 2021, 1, 1752
- [25] J.T. Bender, A.S. Petersen, F.C. Østergaard, M.A. Wood, S.M.J. Heffernan, D.J. Milliron, J. Rossmeisl, J. Resasco, Understanding cation effects on the hydrogen evolution reaction, *ACS Energy Lett.* 2023, 8, 657
- [26] S. Trasatti, The “absolute” electrode potential—the end of the story, *Electrochim. Acta* 1990, 35, 269
- [27] J. Cheng, M. Sulpizi, M. Sprik, Redox potentials and pK<sub>a</sub> for benzoquinone from density functional theory based molecular dynamics, *J. Chem. Phys.* 2009, 131, 154504
- [28] S. Schnur, A. Groß, Properties of metal–water interfaces studied from first principles, *New J. Phys.* 2009, 11, 125003
- [29] M. Otani, I. Hamada, O. Sugino, Y. Morikawa, Y. Okamoto, T. Ikeshoji, Structure of the water/platinum interface—a first principles simulation under bias potential, *Phys. Chem. Chem.*

- Phys. 2008, 10, 3609
- [30] R. Khatib, A. Kumar, S. Sanvito, M. Sulpizi, C.S. Cucinotta, The nanoscale structure of the Pt-water double layer under bias revealed, *Electrochim. Acta* 2021, 391, 138875
- [31] A. Groß, Challenges in the modeling of elementary steps in electrocatalysis, *Curr. Opin. Electrochem.* 2023, 37, 101170
- [32] F. Gossenberger, T. Roman, A. Groß, Hydrogen and halide co-adsorption on Pt(111) in an electrochemical environment: a computational perspective, *Electrochim. Acta* 2016, 216, 152
- [33] E. Skulason, G.S. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. Jonsson, J.K. Norskov, Density functional theory calculations for the hydrogen evolution reaction in an electrochemical double layer on the Pt(111) electrode, *Phys. Chem. Chem. Phys.* 2007, 9, 3241
- [34] S. Ringe, N.G. Hörmann, H. Oberhofer, K. Reuter, Implicit solvation methods for catalysis at electrified interfaces, *Chem. Rev.* 2022, 122, 10777
- [35] A. Klamt, Conductor-like screening model for real solvents: A new approach to the quantitative calculation of solvation phenomena, *J. Phys. Chem.* 1995, 99, 2224
- [36] O. Andreussi, I. Dabo, N. Marzari, Revised self-consistent continuum solvation in electronic-structure calculations, *J. Chem. Phys.* 2012, 136, 064102
- [37] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T.A. Arias, R.G. Hennig, Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways, *J. Chem. Phys.* 2014, 140, 084106
- [38] N.G. Hörmann, N. Marzari, K. Reuter, Electrosorption at metal surfaces from first principles, *npj Comput. Mater.* 2020, 6, 136
- [39] A.R. Leach, *Molecular Modelling: Principles and Applications*, 2nd edn. (Pearson, Harlow, 2001)
- [40] H.H. Heenen, J.A. Gauthier, H.H. Kristoffersen, T. Ludwig, K. Chan, Solvation at metal/water interfaces: An ab initio molecular dynamics benchmark of common computational approaches, *J. Chem. Phys.* 2020, 152, 144703
- [41] R. Jinnouchi, K. Miwa, F. Karsai, G. Kresse, R. Asahi, On-the-fly active learning of interatomic potentials for large-scale atomistic simulations, *J. Phys. Chem. Lett.* 2020, 11, 6946
- [42] R. Jinnouchi, F. Karsai, C. Verdi, G. Kresse, First-principles hydration free energies of oxygenated species at water-platinum interfaces, *J. Chem. Phys.* 2021, 154, 094107

- [43] S. Meng, L.F. Xu, E.G. Wang, S. Gao, Vibrational recognition of hydrogen-bonded water networks on a metal surface, *Phys. Rev. Lett.* 2002, 89, 176104
- [44] A. Michaelides, Density functional theory simulations of water-metal interfaces: Waltzing waters, a novel 2D ice phase, and more, *Appl. Phys. A* 2006, 85, 415
- [45] Y. Gohda, S. Schnur, A. Groß, Influence of water on elementary reaction steps in electrocatalysis, *Faraday Discuss.* 2008, 140, 233
- [46] J. Le, A. Cuesta, J. Cheng, The structure of metal-water interface at the potential of zero charge from density functional theory-based molecular dynamics, *J. Electroanal. Chem.* 2018, 819, 87
- [47] D. Le, T.S. Rahman, On the role of metal cations in CO<sub>2</sub> electrocatalytic reduction, *Nat. Catal.* 2022, 5, 977
- Balanced theoretical study illustrating the challenges associated with the modelling of electrocatalytic through ab initio molecular dynamics simulations
- [48] J. Gu, S. Liu, W. Ni, W. Ren, S. Haussener, X. Hu, Modulating electric field distribution by alkali cations for CO<sub>2</sub> electroreduction in strongly acidic medium, *Nat. Catal.* 2022, 5, 268
- [49] G. Ciccotti, M. Ferrario, Blue moon approach to rare events, *Mol. Simul.* 2004, 30, 787
- [50] Y. Komeiji, Implementation of the blue moon ensemble method, *Chem-Bio Inf. J.* 2007, 7, 12
- [51] X. Qin, T. Vegge, H.A. Hansen, Cation-coordinated inner-sphere CO<sub>2</sub> electroreduction at Au-water interfaces, *J. Am. Chem. Soc.* 2023, 145, 1897
- Determination of free energy barriers in the CO<sub>2</sub> reduction through constrained ab initio molecular dynamics simulations