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Understanding electrified interfaces

Stephan N. Steinmann^{1*}, Zhi Wei Seh^{2*}

¹Univ Lyon, ENS de Lyon, CNRS, Laboratoire de Chimie UMR 5182, Lyon, France

²Institute of Materials Research and Engineering, Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis, Singapore 138634, Singapore

*E-mail: stephan.steinmann@ens-lyon.fr; sehzw@imre.a-star.edu.sg

Understanding electrified interfaces is crucial to enabling a multitude of applications, including photo(electrocatalysis), super- and pseudocapacitors, batteries, etc. However, reaching an atomistic understanding of electrified interfaces remains challenging and will require the combination and development of refined computations and experiments.

Electrified interfaces are a key component of a variety of technologies, including (photo)electrocatalysis for the production of chemicals (for example, H₂, NH₃ and CO₂ reduction products)¹, super- and pseudocapacitors, large-scale redox flow batteries and portable lithium-ion batteries.

Electrified interfaces consist of an electrode and a liquid or solid electrolyte. This contact leads to the formation of an electric double layer. Practical electrodes expose a high surface area to maximize the contact with the electrolyte. Since molecules and ions coming from the bulk need to reach the electrode, these interfaces are generally non-crystalline and are, thus, complex at the atomic level. Moreover, if an (electro-)chemical reaction occurs at the electrified interface, the system is in a non-equilibrium state. Therefore, single-crystal surface models do not adequately describe electrified interfaces, and atomistic modelling is pushed to its limits.²

[H1] The challenge of atomistic description

For a realistic description of the physical and chemical processes in large, disordered systems, such as electrified interfaces, atomistic simulations need to be performed over sizeable timescales (for nanoseconds if coupled to biased exploration, otherwise even longer). Furthermore, electronic structure methods or interatomic potentials that capture the polarization in the presence of an electrochemical potential need to be considered to capture (electrochemical) reactivity. The experimental characterization of electrified interfaces is also challenging. Compared to the bulk electrode and electrolyte, the number of atoms forming the interface is generally small, so they tend to be difficult to detect experimentally. Furthermore, the non-crystalline nature of practical electrified interfaces prohibits the use of diffraction techniques, which are the most suitable methods to achieve atomic resolution. Nevertheless, advanced surface-sensitive techniques, such as operando variants of spectroscopies and microscopies, promise (near) atomic resolution and chemical characterization of electrified interfaces in the next decade under operating conditions.

To gain a deeper understanding of electrified interfaces, and thus, finer handles to design improved interfaces, the community needs to embrace the challenge of reaching an atomistic description.¹ Here, we suggest three complementary avenues to tackle this challenge: (a) autonomous workflows, (b) machine learning and (c) integrated computations and experiments. Our discussion is geared towards electrocatalysis; however, most aspects also apply to other electrified interfaces.

[H1] Computational screening and autonomous workflows

High-throughput and high-performance computing enables fast computational screening. Single crystal surfaces without a detailed description of the electrolyte are highly simplified models for electrified interfaces. Their simplicity enables efficient screening of electrode materials for various systems, such as catalysis and batteries. The systematic use of computations can guide experiments, but should also incorporate a feasibility component, that is, addressing the stability of the proposed active sites and materials. The screening of surfaces for assessing their activity and stability does not, in principle, require significant user knowledge and, thus, lends itself for high-throughput computing.³ However, the corresponding infrastructure for system setup and analysis largely relies on inefficient, in-house scripting and programming. Therefore, these approaches require human intervention and remain time-consuming in practice. One of the potential ways to address these issues is to develop autonomous workflows.

Autonomous workflows are highly beneficial to perform detailed mechanistic studies. In particular, they can be used in evaluation of relevant surface states as a function of the operating conditions (electrochemical potential, solvent and supporting electrolyte), evaluation of energies of various reaction intermediates by automatic ‘docking’ of intermediates on the surface, and determination of their energies as a function of the electrochemical potential by grand-canonical density functional theory (DFT). The identified intermediates should also be allowed to ‘back-couple’ to the surface state, i.e., the intermediates, rather than species derived from the solvent and electrolyte, can become the dominating species on the surface. In addition, to make experimentally relevant predictions, micro-kinetic models are required to describe the overall activity and selectivity. However, such models rely on the determination of the relevant activation energies, for which no generally accepted method exists for reactions at electrified interfaces.

[H1] Limitations of machine learning

Machine learning has the potential to change our workflows and (atomic) vision of electrified interfaces. Here, we focus on atomistic modelling, which excludes more global system-based machine learning techniques, such as surrogate models and data-driven rationalizations and predictions.⁴ At the atomic scale, machine learning can play several roles, including the generation of relevant geometries for high-throughput computing and autonomous workflows, automation of decision making during autonomous workflows (for example, which intermediates to follow, which transition states are relevant), and powering of atomistic simulations, that is, replacing costly DFT computations by faster energy evaluations. The possibility to reach (near) DFT accuracy for orders of magnitude larger systems with orders of magnitude lower computational cost is enticing: it would allow computations of larger, and

thus more realistic, models for electrified interfaces as compared to what is attainable with DFT. However, powering atomistic simulations with machine learning potentials is not trivial, in particular, for electrified interfaces.

The fundamental problem is that the interatomic potentials of many low-cost machine learning potentials do not consider atomic charges and polarizability. These physically motivated quantities may not be necessary for the computation of organic molecules and certain materials,⁵ but are key to the understanding of electrified interfaces. The electronic structure (and thus, the chemical properties) of electrodes, adsorbates and molecules depend on the electrochemical potential. If electrons are properly described in the simulations, the electrochemical potential can be accounted for by surface charge, electric fields, or explicit cation-electron pairs, since all three methods allow tuning of the Fermi level and thus the energy of electrons.² By contrast, low-cost machine learning potentials do not define a Fermi level. System-specific potentials can still mimic similar effects via geometrical parameters, which may explain the attractiveness of such approaches.^{6,7} However, this pragmatic solution leads to 'disposable' interatomic potentials (force fields), that is, these potentials are useful only for the specific application for which they have been designed.

To overcome the limitations of machine learning potentials and to enable computation of electrified interfaces, more physically motivated functional forms need to be developed and adopted.⁸ In addition, training sets should be made available in the form of curated datasets, similar as for molecular chemistry (quantum-machine.org). For example, the NOMAD Repository and Archive (nomad-lab.eu) could be used to centralize the available datasets and to compare results from various computational setups for identical systems. Combining datasets of various origins via machine learning (typically transfer learning) would allow the 'homogenization' of inhomogeneous data, further increasing the reusability of the original data.

[H1] Integrating computations and experiments

A general challenge for electrified interfaces is the lack of a gold standard for electronic energy evaluations for surfaces and solids. By contrast, in molecular chemistry, complete basis set coupled cluster singles, doubles and perturbative triples, or CCSD(T), computations are widely accepted as gold standard for all but the most problematic electronic structures. Carefully converged quantum Monte Carlo simulations could provide the required accuracy for interfaces; however, the computational cost is currently only compatible with small model systems.⁹ In other words, the accuracy of commonly available DFT data compared to the reality (i.e., experiment or exact quantum mechanics) might be insufficient to produce experimentally relevant data. As a consequence, reproducing DFT data at a lower computational cost (i.e., via machine learning potentials) might not be sufficient to achieve physically relevant results. Therefore, experimental validation of computational insights remains indispensable for the foreseeable future.

To validate computational models, surface-sensitive operando techniques need to be developed to characterize electrified interfaces in detail. Such techniques can be broadly classified into spectroscopic and microscopic methods. Spectroscopic techniques, such as X-ray photoelectron spectroscopy, extended X-ray absorption fine structure, Fourier-transform

infrared spectroscopy, Raman spectroscopy and ultraviolet-visible spectroscopy, can provide valuable information about the chemical species present at interfaces. For example, ambient pressure X-ray photoelectron spectroscopy performed at a synchrotron can be used to characterize solid/liquid interfaces, provided that the electrolyte layer is thin enough (< 20 nm) to allow measurement.¹⁰ Scanning probe microscopy, such as scanning tunnelling microscopy, atomic force microscopy and scanning electrochemical microscopy, enable high-resolution topographic imaging of interfaces with atomic resolution. For example, scanning electrochemical microscopy, which uses a scanning tip as a miniaturized electrode, can be applied to study the local electrochemical behaviour and surface reactivity of liquid/solid/gas interfaces.¹⁰ Liquid phase-transmission electron microscopy has also emerged as a promising technique to study real-time morphological and compositional changes in the presence of flowing electrolytes under controlled electrochemical conditions. However, several challenges remain in the operation of this technique. The electron beam can induce radiolysis and sample damage, in addition to creating artificial hot spots with high electrochemical activity near the electrode tip.¹⁰ Thus, operando characterization techniques need to be explored that reflect real electrochemical conditions, ideally, operating high-throughput using smart automation and robotics.

Finally, high-quality data collected by experimental techniques can be fed into computational models to validate and refine them in a tight feedback loop. Machine learning using deep generative models also enables the inverse design for a directed, automated search of the entire chemical space. Given a specified materials property, the ultimate goal of inverse design is to predict a feasible, optimal structure and composition within the chemical space.

In summary, integrating computations and experiments will transform the way we understand and discover new electrified interfaces and materials in the future.

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Author contributions

Both authors contributed to researching data, discussion of content, writing and reviewing/editing the manuscript.

Competing interests

The authors declare no competing interests.

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