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## How can machine learning facilitate computational electrochemistry

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## ABSTRACT

Electrochemistry plays a central role in modern sustainable energy technologies, yet its computational modeling has long been constrained by the trade-off between the efficiency of classical force fields and the accuracy of *ab initio* methods. This limitation is particularly critical given the scarcity of experimental “ground truth” data for buried interfaces. This Perspective charts the transformative impact of machine learning on overcoming these long-standing spatiotemporal barriers. We begin with an overview of foundational methodologies, ranging from continuum models to *ab initio* molecular dynamics, to contextualize the unique physical requirements of the charged electrode–electrolyte interface. The discussion then focuses on the evolution of machine learning potentials, tracing their development from short-range local descriptors to advanced architectures capable of capturing long-range electrostatic interactions. A critical analysis is provided on the central challenge: accurately modeling the distinct dielectric responses of metallic conductors vs ionic insulators and the emergence of hybrid frameworks as a promising solution. Finally, we offer an outlook on the future of computational electrochemistry, arguing that the next frontier involves the synergistic integration of machine learning with multiscale modeling to bridge the gap between microscopic mechanisms and macroscopic device performance.

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## I. INTRODUCTION

Electrochemistry plays a central role in modern science and technology, underpinning advances in sustainable energy conversion and storage.<sup>1–3</sup> In particular, computation and simulation play an increasingly important role in the development of this field. While *in situ* and *operando* experimental techniques have advanced significantly,<sup>4–6</sup> observing structures and processes at the atomic level remains challenging, making computational modeling indispensable in extending the boundaries of electrochemical studies.<sup>7</sup>

As an inherently interdisciplinary field, computational electrochemistry builds upon theoretical electrochemistry,<sup>8–10</sup> surface science,<sup>11</sup> and computational chemistry.<sup>12</sup> It draws heavily

from ingredients in these upstream disciplines to model complex interfacial phenomena. Consequently, the field is deeply shaped by developments in these adjacent areas. In recent years, the rapid rise of machine learning (ML) has had a significant impact on these foundational subjects, offering new tools to overcome long-standing barriers.

A typical example of this “upstream” influence is the development of machine learning force fields [MLFFs, or machine learning potentials (MLPs)]. Trained on high-fidelity *ab initio* data, MLPs can reproduce potential energy surfaces (PES) with quantum-mechanical accuracy at a much lower computational cost. This capability seamlessly addresses the efficiency-accuracy trade-off that has long constrained computational chemistry, enabling molecular dynamics (MD), Monte Carlo (MC), and geometry optimization

tasks that were previously computationally prohibitive.<sup>13–15</sup> Computational electrochemistry has directly benefited from these advances. By leveraging MLPs, it is now feasible to sample solid/liquid interfaces with *ab initio* accuracy over extensive spatiotemporal scales.

This capability is vital for electrochemistry due to the scarcity of experimental “ground truth” data for interfacial structures. Unlike biological systems, where a wealth of experimental data exists to validate empirical models, the atomic-level properties of electrochemical interfaces are often inaccessible to direct measurement. As a result, simulation results at the *ab initio* level are usually taken as the primary reference for empirical parameterization. Seen from this perspective, MLPs serve not merely as an accelerator but as an essential bridge, generating the extensive sampling data required to understand microscopic mechanisms that are otherwise inaccessible to both experiment and static *ab initio* calculations.

However, simply importing ML techniques from upstream fields is insufficient. Computational electrochemistry faces unique challenges that extend beyond the scope of general computational chemistry. The most significant of these is the accurate description of the metal electrode/electrolyte interface, where two materials with fundamentally different dielectric properties meet: a metallic conductor (an electronic conductor but ionic insulator) and an electrolyte (an ionic conductor but electronic insulator). Capturing the distinct dielectric responses of these two phases simultaneously, specifically the nonlocal charge transfer in the metal vs the reorientation of solvent dipoles, remains the central challenge in simulating electrochemical interfaces with MLPs.

In this Perspective, we chart the significant impact of ML on computational electrochemistry by addressing the past, present, and future of this field. We begin in Sec. II with a brief overview of foundational methodologies, from continuum models to *ab initio* molecular dynamics (AIMD), to contextualize the unique physical requirements of the charged electrochemical interface. In Sec. III, we examine the evolution of MLPs, from short-range local descriptors to advanced architectures capable of capturing long-range electrostatic interactions. We highlight how hybrid frameworks have emerged as a solution to the dielectric mismatch problem. Finally, in Sec. IV, we offer an outlook on the future, arguing that the next frontier involves integrating ML with multiscale modeling to bridge the gap between various spatiotemporal scales.

## II. FOUNDATIONAL METHODOLOGIES AND PHYSICAL REQUIREMENTS

To effectively integrate ML into the study of electrochemical systems, it is necessary to first understand the unique physical constraints that govern the electrochemical interface. Unlike bulk systems, the metal electrode/liquid electrolyte interface represents a junction where the statistical mechanics of a liquid meet the complex electronic response of a solid. Generally speaking, the development of computational methods in this field has been driven by the need to take both these distinct behaviors into account, evolving from continuum models to explicit quantum mechanical (QM) descriptions. Understanding the successes and limitations of these foundational methods identifies the specific physical “ingredients,” such as interfacial polarization and chemisorption, that MLPs must successfully encode to be effective for electrochemical interfaces.

## A. The dielectric response of the electrolyte and electrode

In electrochemistry, an electrode is normally charged rather than neutral. To keep the electroneutrality of an electrochemical interface under equilibrium, ions in electrolyte solution with charges of equal magnitude and opposite sign will be attracted toward the electrode and then form the so-called electrical double layer (EDL) at the electrode/electrolyte interface. Classical electrochemistry conceptualizes this via the Gouy–Chapman theory, proposed in the early 20th century, which treats the electrode as a perfect conductor and the ionic solute as point charges interacting through a mean-field continuum solvent.<sup>8,9</sup> While this creates a useful baseline, the model notoriously fails at high potentials or concentrations, predicting unphysical capacitance values since it neglects the finite volume of ions.<sup>16,17</sup> Stern addressed this geometric limitation in 1924 by introducing a distance of closest approach, effectively splitting the interface into a rigid compact layer (Helmholtz layer) and a statistically distributed diffuse layer.<sup>10</sup> This results in the Gouy–Chapman–Stern (GCS) model, which treats the total differential capacitance ( $C_d$ ) as an inverse sum of two capacitors in series,<sup>16</sup>

$$C_d^{-1} = C_H^{-1} + C_{GC}^{-1}, \quad (1)$$

where  $C_H$  represents the capacitance of the sterically hindered compact layer and  $C_{GC}$  represents the diffuse layer. Despite decades of refinement,<sup>18–20</sup> continuum models derived from the GCS model often struggle to match experimental differential capacitance curves quantitatively.<sup>21,22</sup> One major source of this mismatch lies in the linear dielectric response assumption for interfacial water. In realistic systems, the dielectric constant of water is a complex function of spatial position and electrode potential due to factors such as Pauli repulsion and water chemisorption.<sup>21</sup> To capture these solvent effects, the field moved toward bottom-up atomistic simulations using MD simulations, which can explicitly reproduce the nonlinear dielectric behavior of water through empirical force fields like the extended simple point charge (SPC/E) water model.<sup>12,23</sup>

However, switching to atomistic MD simulations introduces a new, critical challenge that is particularly relevant to the design of MLPs: describing the dielectric response of the metallic electrode. Unlike the electrolyte, which is an ionic conductor but an electronic insulator, the metal electrode is an electronic conductor. Standard classical force fields, which assign fixed partial charges to atoms, cannot capture the dynamic redistribution of electron density that occurs in a metal when an external field is applied or a charged ion approaches. To resolve this without the cost of quantum mechanics, researchers developed polarizable electrode models, such as the core–shell (Drude oscillator) method<sup>24–26</sup> and the fluctuating charge methods.<sup>27–29</sup> Among them, the Siepmann–Sprik method, a type of fluctuating charge method, is one of the most pioneering and widely used approaches.<sup>27</sup> Moreover, it serves as a conceptual predecessor to the hybrid ML architectures discussed in Sec. III C. The Siepmann–Sprik method treats the electrode charge distribution  $\rho(r)$  not as fixed points but as a superposition of Gaussian functions centered on atoms, allowed to fluctuate to minimize the electrostatic energy of systems,<sup>27</sup>

$$\rho(r) = \sum_i \frac{q_i}{(2\pi\sigma_i^2)^{3/2}} \exp\left[-\frac{(r-r_i)^2}{2\sigma_i^2}\right], \quad (2)$$

where  $q_i$  and  $\sigma_i$  represent the magnitude and width of the Gaussian charge on atom  $i$ . Because the electrostatic energy is quadratic with respect to  $q_i$ , the charge distribution that satisfies constant potential conditions can be solved efficiently. This “*can be considered an extreme simplification of density functional theory.*”<sup>27</sup> Furthermore, the Siepmann–Sprick method can be understood as a simplified subset of the Charge Equilibration (QEq) scheme proposed by Rappe and Goddard.<sup>30</sup> While the full QEq energy formalism includes terms with electronegativity and atomic hardness to describe contributions from chemical potential,<sup>31,32</sup> the Siepmann–Sprick method considers only electrostatic interaction (i.e., electric potential). Despite its simplicity, the Siepmann–Sprick method effectively captures key aspects of polarization at electrochemical interfaces (in particular, for single-element single-crystal electrodes) and remains one of the most widely used polarizable electrode methods in the classical force field.<sup>28,33–37</sup> Remarkably, the Siepmann–Sprick method has also been integrated into hybrid quantum mechanics/molecular mechanics (QM/MM) frameworks,<sup>38</sup> where it successfully reproduces both long-range interactions and adsorption energies consistent with full Density Functional Theory (DFT) calculations. The promising result indicates that the Siepmann–Sprick method is a good candidate for describing the electronic dielectric response of the metal electrode.

## B. The quantum nature of electrochemical interfaces: chemisorption and electron spillover

While the classical methods mentioned earlier provide a reasonable description of electrostatics, they fundamentally miss the quantum nature at electrode/electrolyte interfaces. Specifically, two quantum phenomena are relevant to capture the behavior of realistic interfaces: electron spillover and specific adsorption (i.e., chemisorption). Classical models typically assume the metal charge is confined to the atomic nuclei, but in reality, the electron density “spills over” into the interface. The jellium model, which treats the metal as an electron gas in a uniform positive background, was the first to elucidate this effect.<sup>39,40</sup> It revealed that this spillover creates a substantial surface dipole, often conceptualized as a “negative capacitance” component that modifies the total interfacial capacitance.<sup>41–43</sup> Omitting this effect in classical MD leads to systematic errors in capacitance predictions, necessitating empirical fixes such as placing image planes in the vacuum rather than on the surface atoms.<sup>44,45</sup> Recent *ab initio* studies on platinum electrodes have shown that this is not merely a surface but an interfacial effect. Polarization charges induced by spillover can extend into the second water layer, highlighting a complex interplay between the metal electrons and the electrolyte species.<sup>46</sup>

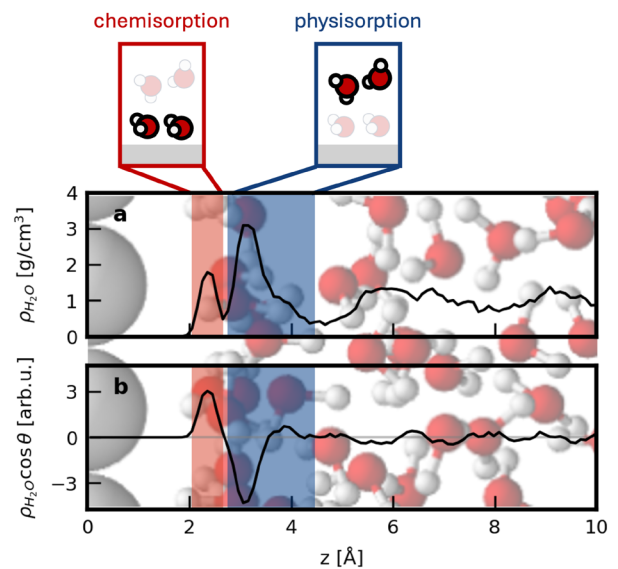
A description of the electrolyte at the QM level is as essential as that of the electrode. For example, water on transition metals does not just act as nearly rigid dipoles that reorient in response to electric fields. The d bands of transition metals hybridize with the  $1b_1$  and  $3a_1$  orbitals of water, resulting in strong chemisorption.<sup>47</sup> This chemical bonding between water and metal dramatically alters the EDL structure and capacitance, effects that are omitted in classical force fields.<sup>48</sup> Early attempts to capture this with DFT relied on static “ice-like” bilayer models to approximate the solvent layers.<sup>49–51</sup> While these static models provided qualitative agreement with some vacuum experiments,<sup>52–55</sup> they are fundamentally limited

by their neglect of entropy effects. At room temperature, the liquid interface is highly disordered, and properties like the work function are extremely sensitive to the fluctuating orientation of water molecules.<sup>56</sup> Consequently, static QM calculations are insufficient, necessitating a transition to full dynamical simulations.

## C. *Ab initio* molecular dynamics as the benchmark

To bridge the gap between QM accuracy and the statistical sampling required for liquids, *ab initio* molecular dynamics (AIMD) has emerged as an important benchmark in computational electrochemistry. By calculating potential energy surfaces (PES) on the fly from the electronic structure at every time step, AIMD captures both the bond-breaking chemistry and the entropic disorder of the electrolyte.<sup>57</sup> Although computationally expensive, AIMD has been pivotal in revealing the atomistic structure of the EDL, particularly in the Helmholtz layer. A key finding from decades of AIMD simulations is the material-dependent nature of interfacial water structuring. On inert metals like Au or Ag, the water density profile exhibits only broad features or tails near the surface, indicative of weak physisorption.<sup>58–64</sup> In contrast, on catalytically active metals like Pt or Pd, AIMD reveals sharp, well-defined density peaks corresponding to a strongly chemisorbed water layer.<sup>60,62,64–68</sup>

This distinction in interfacial water structures has profound electronic consequences. On Pt(111), for instance, the chemisorbed water layer preferentially adopts an “oxygen-down” orientation, creating a dipole pointing toward the metal, while the subsequent physisorbed layer is more disordered with a net dipole pointing toward the solution<sup>61,69</sup> (see Fig. 1). The analysis of the electronic density of states confirms that the water layer closest to metals is chemisorbed, characterized by a broadening and shifting of the



**FIG. 1.** Distribution profiles of (a) water density and (b) dipole orientation along the surface normal ( $z$ -coordinate) at Pt(111)/water interfaces. Adapted with permission from Le *et al.*, Phys. Rev. Lett. **119**, 016801 (2017). Copyright 2017 American Physical Society.

water  $1b_1$  orbital states.<sup>60,70</sup> These microscopic details directly govern macroscopic observables, such as the differential capacitance. On weakly interacting Au(111), the capacitance is dominated by ion transport and solvent reorientation, resulting in a nearly constant capacitance–potential curve.<sup>71</sup> In contrast, for Pt(111), adsorption of chemisorbed water is potential-dependent. Le *et al.* demonstrated that this phenomenon is responsible for the characteristic bell-shaped capacitance curve observed experimentally for Pt, a feature that classical models completely fail to reproduce.<sup>48</sup> While the exact partitioning of capacitance contributions between reorientation and chemisorption remains a topic of active research,<sup>64,72,73</sup> the consensus is that an explicit quantum mechanical treatment is a necessity for active electrocatalysts.

Beyond pristine surfaces, AIMD has proven indispensable for understanding complex reaction environments. It has provided critical insights into how adsorbates like hydrogen and hydroxyl modify the interfacial water structure,<sup>66,68,70,74–81</sup> how solvated cations influence adsorbate stability through noncovalent interactions,<sup>82,83</sup> and how the connectivity of the hydrogen bond network dictates proton transfer kinetics.<sup>84–88</sup> However, the bottleneck remains the computational cost. Typically, AIMD is restricted to small systems (hundreds of atoms) and short timescales (tens of picoseconds). This prohibits the direct simulation of mesoscopic phenomena such as slow ion diffusion,<sup>89</sup> long-term EDL relaxation,<sup>90</sup> or the behavior of complex nanostructures.<sup>91</sup> This well-known spatiotemporal barrier has motivated the search for more computationally efficient methods that can retain *ab initio* accuracy, a challenge for which ML has emerged as a particularly powerful solution.

### III. MACHINE LEARNING MOLECULAR DYNAMICS SIMULATION

#### A. Short-range machine learning potentials based on local chemical environment descriptors

Widely used *ab initio* methods such as Kohn–Sham DFT typically involve self-consistent field (SCF) iterations. This leads not only to high computational cost but usually also to a superlinear scaling with the number of atoms in the system, e.g.,  $\mathcal{O}(N^3)$  for Kohn–Sham DFT.<sup>92,93</sup> This superlinear scaling limits the application of *ab initio* calculations to large systems. Based on the “nearsightedness” of electronic interactions in many-atom systems,<sup>94,95</sup> Behler and Parrinello developed a neural network-based MLP known as the Behler–Parrinello neural network (BPNN).<sup>96</sup> In this framework, the total energy  $E$  of the system is expressed as a sum of atomic energies  $E_i$ , each predicted from a local chemical environment descriptor  $\mathcal{D}_i$  within a cutoff radius  $r_{cut}$ ,

$$E = \sum_i E_i(\mathcal{D}_i). \quad (3)$$

For each atom in the system, a descriptor vector can be constructed using local structural information (e.g., interatomic distances, bond angles), which is then input into a ML model to predict atomic energies. Contemporaneously, Csányi and co-workers developed the Gaussian Approximation Potential (GAP) framework.<sup>97</sup> Often combined with the Smooth Overlap of Atomic Positions (SOAP) descriptor,<sup>98</sup> this method utilizes Gaussian process regression to interpolate energy surfaces based on the similarity of local atomic environments. Collectively, the BPNN and GAP-SOAP frameworks

cemented the validity of the local atomic energy decomposition ansatz, establishing the two pioneering paradigms upon which high-dimensional machine learning potentials are built.

To improve model accuracy, significant testing and tuning of basis functions are often required. This challenge is broadly known in ML as feature engineering.<sup>99,100</sup> Recently, deep learning has offered an alternative. Instead of manually tuning basis sets, neural networks can be trained to “construct” appropriate basis functions.<sup>101</sup> One prominent example of integrating deep learning into MLPs is Deep Potential (DP), where an embedding network transforms physical inputs (e.g., distances and angles) into symmetry-preserving descriptors, which are then used to fit the potential energy surface.<sup>102,103</sup> Graph neural networks (GNNs) are another typical example of deep learning-based MLPs, which have gained popularity in recent years.<sup>104–111</sup> In these models, atoms are treated as nodes, connected to neighboring atoms within  $r_{cut}$  by edges. Each node is associated with a vector descriptor that is updated iteratively through convolutions involving neighboring atoms. This process is known as message passing,<sup>112</sup> and it allows GNNs to effectively capture longer-range structural information at reasonable computational cost. Based on the GNN framework, Kozinsky *et al.* developed Neural Equivariant Interatomic Potentials (NequIP), which use E(3)-equivariant convolutions and explicitly incorporate higher-order geometric tensors such as relative atomic positions.<sup>108</sup> NequIP demonstrates superior accuracy, transferability, and data efficiency compared to conventional MLP approaches. Notably, the development of MLPs and their applications in chemistry and materials science have experienced explosive growth in the recent decade. While an exhaustive survey of this rapidly evolving landscape lies beyond the scope of this Perspective, we direct interested readers to the comprehensive review in Ref. 113.

As mentioned in Sec. II, an appropriate description of EDLs with both electrodes and electrolytes at the QM levels, which is a prerequisite to capture properties like differential capacitances, typically involves hundreds of atoms and tens of picoseconds. MLPs provide a straightforward solution for some of the cases, i.e., structural and energy information. Overall, short-range MLPs based on local descriptors have been applied to long-timescale simulations and property investigations of solid–liquid interfaces.<sup>114–127</sup> From the resulting trajectories, mechanistic insights into processes such as surface defect diffusion<sup>114</sup> and proton transfer<sup>115,118,124</sup> can be gained. Thermodynamic quantities like free energy changes<sup>114,118,124</sup> and kinetic properties such as diffusion coefficients<sup>126</sup> can also be extracted. Note that free energy changes estimated from trajectory-derived state population ratios are reliable only for low-barrier processes. For more complex quantities, e.g., redox potentials, acidity constants, and solvation free energies, techniques such as free energy perturbation must be employed.<sup>120,125,128</sup> Moreover, by incorporating ML models that predict atomic dipoles or polarizabilities, interfacial vibrational spectra can be computed,<sup>116,123,129,130</sup> bridging the gap between simulation and experiment.

Despite their success in simulating numerous interfacial properties, short-range MLPs lack explicit long-range interactions. As a result, they cannot ensure charge neutrality in the bulk electrolyte region when applied to systems with ions.<sup>131</sup> This highlights the importance of incorporating long-range interactions into MLP frameworks for accurate simulation of electrochemical interfaces.

## B. Long-range machine learning potentials

In MLPs based on local chemical environment descriptors, the energy is expressed as a sum of atomic energies that depend on local chemical environments. While this locality assumption works well for describing short-range interatomic interactions, it may break down when applied to systems with ions.<sup>131–133</sup> Although GNNs can include the structural information in the distance in an implicit way, the computational cost grows rapidly with the number of message-passing layers. As a result, this is not a practical strategy for describing long-range interactions such as electrostatics.

To capture long-range electrostatic interactions at a reasonable computational cost, methods inspired by classical force fields, in particular the separation of short and long-range contributions, have been introduced in several studies.<sup>134–139</sup> In these approaches, short-range interactions are still described using short-range MLPs, while long-range electrostatics are computed analytically, for example, using Ewald summation. In some implementations, fractional atomic charges are predicted via ML models based on local chemical environments. These models have significantly improved the accuracy over short-range MLPs in systems such as ionic crystals. However, the use of monopole (i.e., fractional charge) representations is fundamentally insufficient for capturing, for example, electrical conductivity<sup>140–142</sup> and dielectric properties.<sup>143,144</sup> To reproduce polarization distributions, Zhang *et al.* developed the Deep Potential Long Range (DPLR) framework,<sup>139</sup> in which the Deep Wannier (DW) model predicts the average position of the centers of the maximally localized Wannier functions (MLWFs) (i.e., Wannier centers) associated with each central atom, which are referred to as Wannier centroids. This strategy reduces the dominating error in electrostatic interactions from monopole–dipole terms to dipole–quadrupole terms. The definition of Wannier centroids requires artificial assignment of MLWFs to central atoms (based on spatial distributions). This, however, prohibits the electron transfer during simulations. In order to overcome the limitation of the Wannier centroid-based method, new iterative schemes such as the self-consistent field neural network (SCFNN)<sup>145</sup> and Deep Wannier Iterative Refinement (DWIR)<sup>146</sup> models have been proposed to predict Wannier centers in the systems. Using *ab initio* simulations as reference, DWIR accurately reproduces the nonlocal distribution of hydrated electrons, indicating its capability for treating both closed- and open-shell systems, and providing a powerful tool for studying electron transfer processes. In addition, Cheng treated the charges as intermediate quantities and trained for only potential energy surfaces in the CACE-LR model.<sup>147</sup> Since this “intermediate-charge” framework does not require the calculation of MLWFs, it is a feasible and efficient way to involve long-range interactions, especially for metallic systems.

The methods mentioned earlier predict charge distributions (based on atomic fractional charges or Wannier centroids) from local chemical environments. This means that these methods, like their counterparts of classical force fields, struggle to handle nonlocal charge transfer. As introduced in Sec. II A, such nonlocality is often described through the QEq schemes or the Siepmann–Sprik model<sup>27,30–32</sup> in classical force fields. Based on these classical methods, Behler and co-workers proposed the fourth-generation high-dimensional neural network potential (4th-HDNNP), which uses a neural network to predict electronegativities for the QEq framework

and optimizes atomic hardness for each element.<sup>148</sup> This method has successfully described nonlocal charge transfer induced by electronegativity differences in systems such as (Al-doped) MgO, and achieved quantitative agreement with *ab initio* results in properties such as adsorption energies. In contrast to the above strategies, which systemically extend MLP frameworks by incorporating classical long-range corrections, Grisafi and Ceriotti introduced nonlocality directly into descriptor construction. In the Long-Distance Equivariant (LODE) framework, an atom-density potential is constructed to incorporate long-range interactions.<sup>149</sup> This method not only preserves the additivity of the model but also provides physical interpretability by allowing users to define the type of long-range interactions via a tunable decay power in the atomic density kernel.

## C. Dielectric response of electrochemical interfaces in machine learning potentials

In addition to describing long-range electrostatic interactions, another major challenge in applying MLPs to electrochemical interface simulations lies in accurately describing dielectric response. In the presence of a non-zero electric field, the Hamiltonian of the system is given by<sup>150</sup>

$$H = H_{\text{PBC}} - \Omega P \cdot \mathcal{E}, \quad (4)$$

where  $H_{\text{PBC}}$  is the Hamiltonian under periodic boundary conditions,  $P$  is the polarization,  $\mathcal{E}$  is the applied electric field, and  $\Omega$  is the volume of the simulation cell. This implies that in order to describe the dielectric response accurately, one must also describe the polarization. Moreover, conductors and insulators exhibit fundamentally different dielectric responses, making the choice of descriptor and model architecture system-dependent.

The species at electrochemical interfaces responds to the electric field in the following ways, i.e., the translation of ions, the reorientation of solvent molecules, the vibration/elongation of bonds and the polarization of electrons.<sup>151</sup> For commonly used aqueous electrolytes, which are ionic conductors and electronic insulators, the first three mechanisms dominate near the potential of zero charge, while electronic polarization (i.e., electronic dielectric response) contributes relatively little. For example, bulk water at ambient conditions has a dielectric constant of  $\sim 78$ , of which the electronic contribution accounts for only 1.8.<sup>152</sup> For such systems, the electronic component of the dielectric response can be inferred from local chemical environments.<sup>130</sup> In the DPLR framework introduced in Sec. III B, the electronic response is captured by tracking the displacement of Wannier centroids.<sup>139</sup> Using this method, Zhang *et al.* computed the static dielectric constants of NaCl solutions at various concentrations and analyzed the molecular mechanisms behind the observed concentration dependence.<sup>153,154</sup> By examining the dipole moments of water molecules and the connectivity of the hydrogen bonding network, they attributed the negative correlation between dielectric constant and salt concentration to the disruption of hydrogen bonding by the hydration shells of the ions. Furthermore, Zhang *et al.* investigated the structure and differential capacitance of TiO<sub>2</sub>/NaCl interfaces at different pH values.<sup>131</sup> Their MD simulations revealed a higher differential capacitance under alkaline conditions, consistent with experimental results. This

trend was attributed to the stronger screening by  $\text{Na}^+$  ions compared to  $\text{Cl}^-$  ions, i.e.,  $\text{Na}^+$  tends to accumulate closer to the solid surface, compressing the electrical double layer and increasing the capacitance. Unlike DPLR, which explicitly predicts polarization distributions, the perturbed neural network potential (PNNP) developed by Joll *et al.* modifies atomic forces under zero-field conditions to infer dielectric behavior.<sup>155</sup> However, PNNP can only describe the response to external fields via finite-field methods and cannot account for intrinsic electric fields caused by heterogeneity within systems (i.e., polarization field).

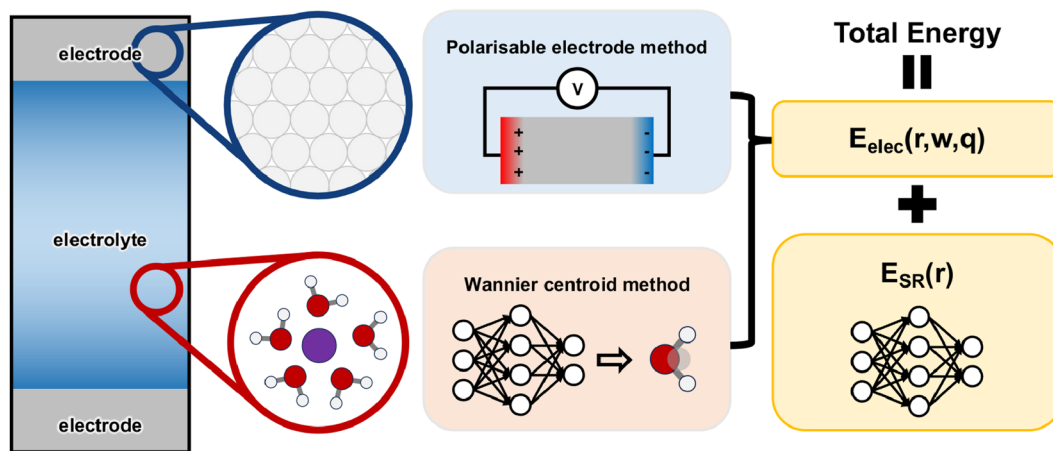
Under strong electric fields, the dielectric saturation in translational and orientational contributions makes the electronic contribution increasingly important. In the SCFNN approach discussed in Sec. III B, the local electric field is included as an input variable in addition to the local chemical environment.<sup>145</sup> This allows SCFNN to capture non-zero-field behavior and reproduce the dielectric saturation of bulk water under high electric fields.<sup>156</sup> Nevertheless, SCFNN relies on iterative solutions, making it computationally expensive. Given that electronic response in electrochemical interfaces generally follows linear response theory,<sup>127,151</sup> an alternative is to predict molecular polarizability from local environments and use this to correct the potential energy surface.<sup>129,139</sup>

In contrast to electrolytes, metal electrodes are electronic conductors and ionic insulators. Their dielectric response is dominated by electronic redistributions and strongly influenced by nonlocal effects. Therefore, local-environment-based approaches are invalid. While the 4th-HDNNP method discussed in Sec. III B can model element-induced nonlocal charge transfer in metals,<sup>148</sup> it does not guarantee accurate polarization distributions. This limitation has been addressed in subsequent charge-equilibration-based ML models,<sup>157,158</sup> which have been successfully applied to describe dielectric response in systems with nonlocal dielectric response. Another strategy discussed in Sec. III B, in which long-range information is embedded directly into the descriptor, can also be extended to cases under non-zero electric fields. For example, by incorporating the LOD framework<sup>149</sup> into symmetry-adapted learning of three-dimensional electron densities (SALTED),<sup>159,160</sup>

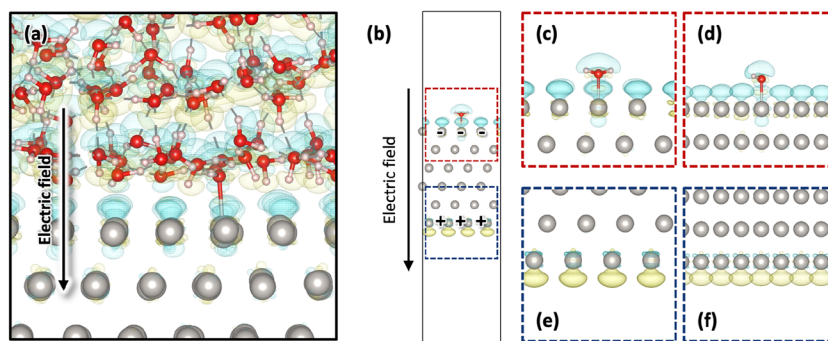
Grisafi *et al.* successfully reproduced DFT-calculated electron densities and their response to electric fields in metallic slabs.<sup>161</sup>

In brief, metals (which are ionic insulators and electronic conductors) and electrolytes (which are ionic conductors and electronic insulators) show distinct dielectric properties. As a result, most ML methods can describe only one or the other. Approaches that predict electronic polarization from local environments fail to capture nonlocal charge transfer in metals,<sup>148</sup> while QEq-based models tend to overestimate the polarizability of electronic insulators.<sup>157,162,163</sup> Instead of describing the dielectric response at metal/electrolyte interfaces within one ML model, the authors proposed a hybrid ML framework, ec-MLP<sup>164</sup> (see Fig. 2). This idea is built on the basis of the recent *ab initio* study that elucidated the localized nature of the interfacial dielectric response.<sup>127</sup> In this study, the electronic dielectric constant decays sharply from infinity to a small value when leaving metal slabs. Even at the water layer in contact with metals (i.e., chemisorbed water), the electronic dielectric constant is smaller than 3, indicating a localized electronic dielectric response in this region. This localized interfacial dielectric response can be further visualized by the spatial distribution of polarization charges. In Fig. 3(a), the polarization charges from metal slabs are localized in d-orbitals of metals and do not extend into the water region. Furthermore, the influence of water chemisorption is elaborated in Figs. 3(b)–3(f). Compared with those of the Pt atoms without water adsorption, the d-orbital of the Pt atom with water adsorption moves toward the Pt slabs. This is consistent with the prediction of the jellium model that the dielectrics suppresses the electron spillover.<sup>43</sup>

Building on the above-mentioned physical insight, the hybrid ML model ec-MLP captures this behavior by integrating two specialized components, i.e., a local-descriptor-based DW model<sup>130</sup> to describe the dielectric response in the electrolyte and a Siepmann–Sprik model<sup>27</sup> to handle nonlocal charge transfer in the electrode. However, the correlation between PES accuracy and the accuracy of physical properties is not always straightforward. It is therefore necessary to validate methods against properties obtained from AIMD. Benchmarks confirm that the hybrid model meets



**FIG. 2.** Schematic illustration of the machine learning model for electrochemistry (ec-MLP). Reprinted with permission from J.-X. Zhu and J. Cheng, Phys. Rev. Lett. **135**, 018003 (2025). Copyright 2025 American Physical Society.



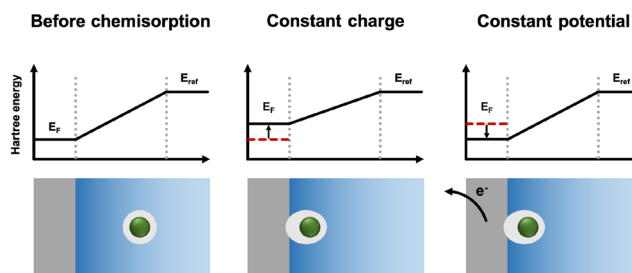
**FIG. 3.** (a) Spatial distribution of polarization charges on the Pt(111)/water interface at a given electric field. The isosurfaces are illustrated with an isovalue of  $5.7 \times 10^{-5}$  e/bohr<sup>3</sup>. (b) Spatial distribution of polarization charges in the system where water monomer adsorbs at the Pt(111) surface at a given electric field. The zoom-in views of the region in the red box are shown in (c) and (d), while those of the region in the blue box are shown in (e) and (f). The isosurfaces are illustrated with an isovalue of  $2 \times 10^{-4}$  e/bohr<sup>3</sup>. In all figures, the polarization charges are shown in yellow and cyan for charge accumulation and depletion, respectively.

this standard, accurately describing not only potential-dependent interfacial water structuring but also the bell-shaped differential capacitance curve of Pt(111)/electrolyte interfaces. Notably, the core strength of the framework lies not in these specific choices of ML models but in its “hybrid” design. The components for both the electrolyte and electrode are replaceable, allowing the framework to evolve. Underscoring this flexibility, a recent study by Cheng and co-workers successfully integrated a different MLP (i.e., CACE-LR) for the electrolyte component, demonstrating the capacity of the hybrid scheme for adaptation and improvement.<sup>165</sup>

#### D. Applicability regime and computational cost of hybrid frameworks

While ec-MLP demonstrates an effective way to describe the dielectric response at electrochemical interfaces, it is instructive to place it within the broader context of computational methodologies. As summarized in Table I, each method occupies a distinct niche defined by the trade-off between spatiotemporal scale and dielectric accuracy. Hybrid frameworks uniquely fill the gap between classical efficiency and quantum accuracy, specifically for electrified interfaces.

However, to fully leverage the strategic advantage highlighted in Table I, it is crucial to define the physical limits of the hybrid architecture. Since these frameworks partition the system into distinct dielectric regions, their validity hinges on whether interfacial phenomena can be accurately captured without a unified electronic structure. A primary concern in this regard is the description of chemisorption. Intuitively, the partial charge transfer between



**FIG. 4.** Illustration of the electron redistribution and the associated current flow through the external circuit during a chemisorption process under constant potential conditions. The green balls and the gray ellipses represent the nuclei and the electrons of the adsorbate.

an adsorbate and the electrode might appear incompatible with an electrolyte model where species carry fixed integer charges (as in the standard DW implementation). However, as elucidated by Schmickler and Santos,<sup>17</sup> chemisorption can be equivalently described through two alternative physical pictures: one involving partially charged adsorbates interacting with image charges and the other, as adopted in the ec-MLP, involving electronic polarization at the interface. As illustrated in Fig. 4, the partial charge transfer associated with chemisorption can be effectively captured via the electron redistribution within the adsorbates (i.e., the displacement of Wannier centroids) under the constant potential constraint.

For redox processes involving distinct oxidation states (e.g.,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ), the current framework can determine redox potentials

**TABLE I.** Comparison of computational methods for electrochemical interfaces with comparable computational resources.

Method	Spatiotemporal scale	Accuracy	Cost	Application
AIMD	$\sim 10$ ps, $10^3$ atoms	High (explicit electronic structure)	High	Reaction mechanisms
Classical FF	$\sim 100$ ns, $10^4$ atoms	Low (fixed charges)	Low	Ion diffusion
Short-range MLP	$\sim 100$ ns, $10^4$ atoms	Medium (local environment only)	Medium	Zero-field interfaces
ec-MLP	$\sim 10$ ns, $10^4$ atoms	High (with dielectric response)	Medium	EDL modeling

via thermodynamic integration methods. By distinguishing oxidation states as different atom types (associated with different predefined Wannier centroid charges), the energetics of the transition between states can be rigorously computed. Furthermore, this can be addressed in a more general manner by upgrading the sub-models. For instance, replacing the standard Deep Wannier model with the DWIR model<sup>146</sup> allows for the simulation of variable total electron numbers in the electrolyte, thereby capturing oxidation state changes dynamically without manual atom typing.

The modular nature of the hybrid framework also allows for significant improvements in the electrode description. Currently, the Siepmann–Sprick model minimizes electrostatic interaction using spherical Gaussian charges with fixed widths. To model complex materials like alloy electrodes, one can integrate ML-driven QEq methods,<sup>148,157,158</sup> where electronegativity and atomic hardness are predicted from the local chemical environment. This extension offers two key advantages: First, it accounts for the chemical potential differences between elements. Second, it allows for a rigorous definition of the Fermi level via the derivative of the potential energy with respect to the total electron number. By approximating the variation of the total electron number as the variation within the metal electrode, this framework enables the calculation and control of the electrode potential relative to a specific reference. In addition, for cases where the precise spatial distribution of electrons is critical, the descriptions for electrode charge densities can be upgraded from simple spherical Gaussians to the SALTED framework,<sup>161</sup> which reproduces full DFT-level charge densities.

A fundamental challenge that remains for hybrid frameworks is the description of species exchange between subsystems, such as metal ion deposition [ $M^+(aq) + e^- \rightarrow M(s)$ ]. This process requires a particle to transition from the electrolyte submodel (ionic) to the electrode submodel (metallic). This is an inherent difficulty shared with hybrid modeling methods such as QM/MM.<sup>166</sup> A naïve solution is an “abrupt partitioning update” where species are reassigned on-the-fly based on spatial criteria. This idea has been applied in a ML-driven QEq model to study solid-electrolyte interphase formation in Li-ion batteries.<sup>167</sup> However, as known in the QM/MM community, this abrupt partitioning update can introduce spatial and temporal discontinuities. A more robust solution lies in “adaptive partitioning,” where a buffer zone ensures a smooth transition between descriptions.<sup>166,168,169</sup> While defining smoothing functions between subsystems is non-trivial in QM/MM, ML offers a unique opportunity to learn these smoothing functions from *ab initio* data, representing a promising frontier for the development of ec-MLP.

Finally, regarding computational cost, it is instructive to compare the hybrid framework with alternative implementations like SALTED. While the cost varies with the choice of sub-models, the hybrid architecture generally outperforms unified nonlocal ML schemes. In the referenced study of the Au(100)/NaCl interface,<sup>170</sup> SALTED was employed to achieve a QM/MM accuracy: only the metal slab (a  $4 \times 4$  surface unit cell with 7 layers) was described by the ML model to reproduce the electron density at the QM level, while the electrolyte was treated with a classical force field. In contrast, the ec-MLP framework aims to describe the *entire* system, including electrodes and electrolytes, at the *ab initio* level. Despite this significantly increased complexity in describing the electrolyte, the current graphics processing unit (GPU)-accelerated

implementation of ec-MLP can achieve a simulation speed  $\sim 50$  times faster than the central processing unit (CPU)-based SALTED/MM setup reported in the literature. This demonstrates that the hybrid architecture is highly efficient and well-suited for scaling to mesoscopic systems over nanosecond timescales.

#### IV. MACHINE LEARNING BEYOND MOLECULAR DYNAMICS

The trajectory of computational electrochemistry is deeply intertwined with the broader development of computational chemistry. Consequently, it is instructive to examine the trends in this parent field to understand the current landscape. We performed a bibliometric analysis of the chemistry literature using the Web of Science Core Collection. As shown in Fig. 5, the application of ML to atomistic modeling (i.e., MLPs) has grown rapidly over the last decade. This surge is driven by the central focus of chemistry: the accurate description of bond breaking and formation, which requires methodologies with atomic resolutions. In contrast, the integration of ML with continuum modeling is less frequent and growing slowly. While indispensable, this focus on the atomistic scale addresses only one piece of a much larger puzzle.

Electrochemical processes are inherently multiscale, spanning microscopic charge transfer processes to macroscopic mass transport phenomena, a complexity that cannot be captured within a single simulation. As detailed in an enlightening article from a recent Lorentz workshop,<sup>173</sup> while various methods exist for different spatiotemporal scales, the crucial task of bridging the gaps between them has been less of a focus. In Fig. 1 of Ref. 173, three typical simulation types (atomistic modeling, microkinetic modeling, and transport modeling) with increasing length and time scales are shown. However, these scales might be convoluted in reality. For example, water chemisorbed on Pt (atomistic modeling) influences the ion transport close to surfaces (transport modeling), which will further alter reaction kinetics (microkinetic modeling).<sup>46,174</sup> This is where ML can provide a transformative solution. When building MLFFs, ML can be considered an effective tool to embed the

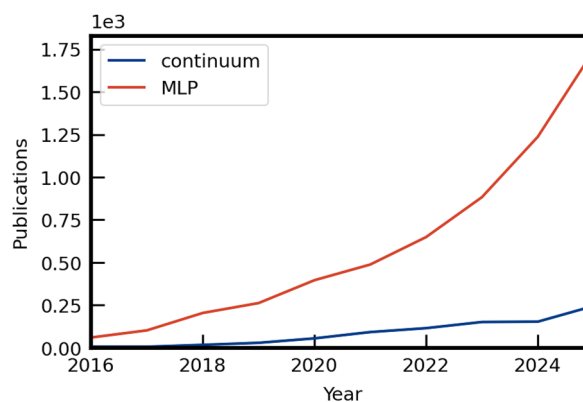


FIG. 5. Annual publication trends (2016–2025) comparing the application of machine learning in atomistic modeling (red line) vs continuum modeling (blue line) within the fields of chemistry. The data are retrieved from the Web of Science Core Collection, and the details of the query are referred to in Refs. 171 and 172.

electronic structure information into atomic structures and bridge the gap between MM and QM. As insightfully illustrated in a recent perspective by Wang *et al.*,<sup>175</sup> this bridging can be envisioned as a detailed “ladder” of models connecting the QM and MM accuracy, where each rung represents a different trade-off between flexibility and efficiency. While one end of this ladder is the above-mentioned MLPs or MLFFs, the other end is to find the optimal parameters for existing (classical) force fields. For instance, leveraging automatic differentiation algorithms, frameworks like DiffTRe<sup>176,177</sup> and DMFF<sup>178–182</sup> have been developed to systematically refine force field parameters against high-fidelity reference data or even experimental observables.

As expected, there have also been some studies to bridge the gaps between coarse-grained (CG) simulations and all-atom simulations<sup>183–185</sup> and continuum modeling and all-atom simulations.<sup>186–189</sup> However, these studies normally focus on biological systems and have not been transferred to electrochemical systems. A primary reason for this is the lack of “ground-truth” data for the upper levels of the multiscale ladder. Unlike biological systems, where a wealth of experimental data can be used for validation, the properties needed to parameterize an empirical model of electrochemical interfaces are often difficult to measure in the experiment. This highlights the critical importance of MD simulations driven by MLPs. Although the choice of computational setup still matters, simulations at the *ab initio* level provide the most reliable reference data currently available for many interfacial properties, especially at the microscopic level. Therefore, the continued development of accurate and efficient MLPs is not merely an end in itself. It is also the essential foundation upon which a robust, data-driven multiscale modeling ladder for computational electrochemistry can be built. By generating reference data, MLMD provides the necessary information to train and validate each successive link, from the microscopic and mesoscopic, all the way to the macroscopic scale.

In this Perspective, we have centered our discussion on the methodological advancements in computational electrochemistry, particularly the great impact of MLFFs. While these tools represent a significant leap forward, we acknowledge that the role of ML is far broader, with powerful applications in, for example, data curation<sup>190</sup> and the construction of scientific knowledge maps.<sup>191</sup> Ultimately, ML should be viewed not as an all-encompassing solution in itself, but as a versatile toolkit. When combined with physical principles and domain expertise, these tools empower us to formulate new strategies and work toward solving the grand challenges in the field of (computational) electrochemistry.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**Jia-Xin Zhu:** Conceptualization (equal); Writing – original draft (lead); Writing – review & editing (equal). **Jun Cheng:** Conceptualization (equal); Writing – review & editing (equal).

## DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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