

Machine Learning the Energetics of Electrified Solid-Liquid Interfaces

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We present a response-augmented machine-learning (ML) approach to the energetics of electrified metal surfaces. We leverage local descriptors to learn the work function as the first-order energy change to introduced bias charges and stabilize this learning through Born effective charges. This permits the efficient extension of ML interatomic potential architectures to include finite bias effects up to second order. Application to OH at Cu(100) rationalizes the experimentally observed pH dependence of the preferred adsorption site in terms of a non-Nernstian charge-induced site switching.

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Predictive-quality first-principles modeling and simulation has become indispensable for studying electrochemical interfaces. By accessing the detailed atomic structure and prevailing interactions, it provides deep mechanistic insight and generates ideas for the design of improved electrocatalysts [1–4]. Compared to its analog usage at solid-gas interfaces and thermal catalysis, first-principles modeling of electrified solid-liquid interfaces nevertheless still lags behind [5], largely because of difficulties to describe the extended double layer (DL) that builds up at biased conditions. Even within common approximations like implicit solvation [6–9], the description of complex and potential-dependent (near-surface) dynamics remains a challenging computational burden.

In this respect, application of machine-learning interatomic potentials (MLIPs) [10–12] as fast surrogates to the first-principles calculations is highly appealing. MLIPs access longer time and larger length scales, a prerequisite to derive reliable macroscopic insights from the atomistic interfacial structures and reactions [13–16]. Notwithstanding, the necessity to accurately capture the local fields that build up at the electrified interface prevents the straightforward usage of established short-range MLIP architectures [17]. To this end, an important strand of ongoing developments centers on incorporating long-range electrostatic interactions [18–25]. While this has led to a successful modeling of the atomistic structure of the interface at the potential of zero charge [26], there are still challenges at applied electrode potential

conditions. For instance, underlying charge equilibration schemes can suffer from unphysical, partially metallic behavior of the electrolyte, leading to overpolarization in the presence of electric fields [27], while the need to solve for electrostatic potentials and atomic charges self-consistently generally increases the computational costs, thereby reducing the very efficiency gain sought with MLIPs. Explicit training of short-range MLIPs for different charge states in turn requires larger amounts of training data and is typically not size extensive [19,28].

As such, a complementary strand of developments appears promising: models incorporating the effects of electric fields by machine-learning relevant response effects. With previous works addressing isolated molecules [29–33], bulk solids [34–36], or liquid water [37–40], we here transfer this concept to electrified interfaces formed between a liquid electrolyte and a metallic electrode. We do this with the understanding that the explicit account of local electrostatic fields generated by electronic bias charges is crucial for modeling adsorbed species and solvent molecules in the immediate interfacial layer(s) [41–46]. In contrast, knowledge about water and ion distributions in the further (diffuse) DL is predominantly important for appropriate referencing to experimental conditions, i.e., relating local bias charges q to the applied electrode potential ϕ_E .

In this spirit, we present the Response Analysis in z -Orientation (RAZOR) model, which machine learns the first-order derivatives of the potential energy and forces for interfacial species at extended interfaces with respect to q , while an appropriate referencing is achieved by effectively describing the extended DL part at the level of an implicit solvent model. By treating q as a perturbation to the charge-free energy, RAZOR offers a robust and computationally efficient extension of common MLIPs to the case of finite biases up to second order. Using OH adsorbed on Cu(100) as a prototypical showcase, we demonstrate that

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RAZOR MLIP-based molecular dynamics (MD) simulations at applied bias reliably describe non-Nernstian, interfacial behavior and reveal a potential-dependent switching of the adsorption site.

The general objective targeted here is to derive stabilities of interfacial states as a function of ϕ_E , measured relative to a universal potential reference. Practical calculations largely address this in half-cell setups where only a single electrode and the DL are present. The stability of an interface configuration α is then described by the electronically grand-canonical free energy $\Omega^\alpha(\phi_E)$, where α summarizes the configuration's chemical composition Z_i and atomic positions $\mathbf{r}_i$. Energetics at constant-potential conditions can be obtained either via grand-canonical methods, e.g., using a potentiostat [47–50], or by post-processing electronically canonical free energies $F^\alpha(q)$ at constant q via Legendre transformation [51–55].

Focusing on the latter route, we Taylor expand the q dependence of the total-energy component of $F^\alpha(q)$ around $q = 0$ (subscript 0),

$$\begin{aligned} E^\alpha(q) &= E_0^\alpha + \left. \frac{\partial E^\alpha}{\partial q} \right|_0 q + \frac{1}{2} \left. \frac{\partial^2 E^\alpha}{\partial q^2} \right|_0 q^2 + \dots \\ &= E_0^\alpha + \phi_0^\alpha q + \frac{1}{2} \frac{1}{C_{\text{el},0}^\alpha} q^2 + \dots \end{aligned} \quad (1)$$

Here, ϕ_0^α is α 's work function (divided by the electronic charge e) and $C_{\text{el},0}^\alpha$ is the second-order response parameter, both at $q = 0$. We refer to the latter as the *electronic capacitance* $C_{\text{el},0}^\alpha$ (see Refs. [51,54,56,57] and the discussion therein). The force on any atom i in α at q is, correspondingly,

$$\begin{aligned} \mathbf{F}_i(q) &= - \frac{\partial E^\alpha(q)}{\partial \mathbf{r}_i} \\ &= \mathbf{F}_{0,i} - \frac{\partial \phi_0^\alpha}{\partial \mathbf{r}_i} q - \frac{1}{2} \frac{\partial (C_{\text{el},0}^\alpha)^{-1}}{\partial \mathbf{r}_i} q^2 + \dots, \end{aligned} \quad (2)$$

which clarifies that machine learning the three contributions E_0^α , ϕ_0^α , and $C_{\text{el},0}^\alpha$ (all at $q = 0$), as well as their respective $\mathbf{r}_i$ derivatives, is necessary to build a second-order correct surrogate model for $E^\alpha(q)$.

Many MLIP architectures exist to learn E_0^α and $\mathbf{F}_{0,i}$ in field-free environments. Second generation MLIPs express the total energy E_0^α as the sum of contributions $\varepsilon(\mathbf{d}_i)$ from every atom i in the system [10,58–62],

$$E_0^\alpha = \sum_{i \in \alpha} \varepsilon_{0,i} = \sum_{i \in \alpha} \varepsilon_0(\mathbf{d}_i). \quad (3)$$

These contributions depend on the local atomic environment of the respective atom as encoded into a descriptor vector $\mathbf{d}_i$, typically respecting fundamental symmetries. Therefore, the actual learning of the $\varepsilon_0(\mathbf{d}_i)$ requires only

first-principles data at $q = 0$ and is stabilized by simultaneously learning on the equally provided forces

$$\mathbf{F}_{0,i} = - \frac{\partial E_0^\alpha}{\partial \mathbf{r}_i}. \quad (4)$$

To the best of our knowledge, no machine-learning model exists that immediately predicts work functions, i.e., interfacial potential drops ϕ_0^α . However, recent MLIP models have included external electric field response to describe bulk structures and liquid water [29,30,34,35,40], using logics analogous to Eq. (1), albeit as a function of the electric field vector $\mathbf{E}$ instead of q . In this case, the first-order terms are the structure's Cartesian polarization vector $\mathbf{P}^\alpha$ and the Born effective charge rank-2 tensor $\hat{\mathbf{Z}}_i^*$ [35,36,63] defined by

$$- \frac{\partial \mathbf{P}^\alpha}{\partial \mathbf{r}_i} = - \frac{\partial^2 E^\alpha}{\partial \mathbf{E} \partial \mathbf{r}_i} = - \frac{\partial^2 E^\alpha}{\partial \mathbf{r}_i \partial \mathbf{E}} = \frac{\partial \mathbf{F}_i}{\partial \mathbf{E}} = \hat{\mathbf{Z}}_i^*. \quad (5)$$

At extended planar metal electrodes, excess charges yield interfacial fields perpendicular to the surface, suggesting that the broken-symmetry situation at charged interfaces is equivalent to a uniaxial electric field along the z direction with $\mathbf{E} = E_z \mathbf{e}_z = (0, 0, E_z)^T$. Then, only the z -projected quantities are of relevance: the scalar P_z^α instead of the polarization vector $\mathbf{P}^\alpha$ and the Cartesian vector $\mathbf{Z}_i^*$ instead of the full tensor $\hat{\mathbf{Z}}_i^*$.

The intensive potential drop ϕ_0^α can furthermore be connected to the extensive interface polarization P_z^α (total dipole moment) through the Helmholtz equation [44,64–66]

$$P_z^\alpha = \epsilon_0 A \Delta \phi_0^\alpha = \epsilon_0 A (\phi_0^\alpha - \phi_0^{\text{ref}}). \quad (6)$$

Here, ϵ_0 is the dielectric constant of vacuum, A is the cell's surface area, and ϕ_0^{ref} is the work function of a reference state (e.g., the slab without adsorbates). Equation (6) shows that machine learning the first-order q response is essentially an identical problem as learning the first-order E_z response, except with exchanged learning targets

$$P_z^\alpha \leftrightarrow \epsilon_0 A \Delta \phi_0^\alpha, \quad (7)$$

$$\mathbf{Z}_i^* \leftrightarrow \epsilon_0 A \frac{\partial \mathbf{F}_i}{\partial q} = - \epsilon_0 A \frac{\partial \phi_0^\alpha}{\partial \mathbf{r}_i}. \quad (8)$$

While $\Delta \phi_0^\alpha$ is available from first-principles calculations at $q = 0$, obtaining $\mathbf{Z}_i^*$ necessitates calculating q derivatives of $\mathbf{F}_i$. As detailed in Sec. SIV.2 of Supplemental Material (SM) [67], we evaluate these numerically by performing calculations at $+q$ and $-q$ for each interfacial structure in the training set. While this formally triples the first-principles computational costs for the training of a RAZOR MLIP, use of the electron density of the charge-neutral calculation for

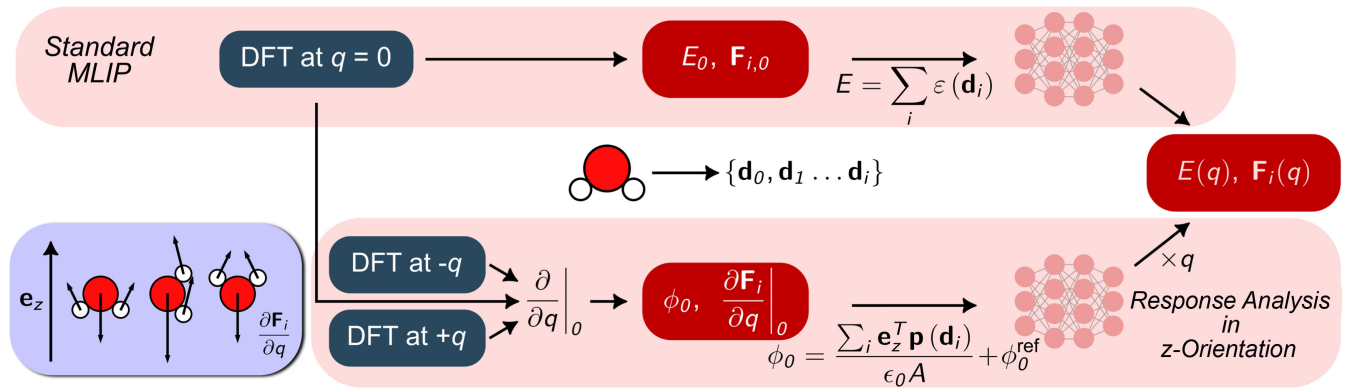


FIG. 1. Schematic workflow showing how combining the response analysis in z -orientation (RAZOR) approach with a standard MLIP provides the energy E^α and atomic forces $\mathbf{F}_i$ of an interfacial configuration α at excess bias charge q . RAZOR machine learns the energy change associated with the response parameter $\phi_0^\alpha = \partial E^\alpha / \partial q$ at $q = 0$, stabilized by including $-\partial \phi_0^\alpha / \partial \mathbf{r}_i = \partial \mathbf{F}_i / \partial q$, equivalent to the Born effective charges $\mathbf{Z}_i^*$ (inset on the left).

SCF initialization reduces this in practice to less than a doubling.

The analogy to Eqs. (3) and (4) suggests that the extensive quantity P_z^α [See Eq. (7)] can be learned using established MLIP architectures by expanding the z component of the total dipole moment into atomic contributions $p_{z,i}$,

$$P_z^\alpha = \sum_{i \in \alpha} p_{z,i} = \sum_{i \in \alpha} p_z(\mathbf{d}_i), \quad (9)$$

stabilized by the atomic contributions $\mathbf{Z}_i^*$; cf. Eq. (8) and Fig. 1.

This leaves the electronic capacitance $C_{\text{el},0}^\alpha$ as the last quantity in Eq. (1). As detailed in the End Matter, implicit solvent models typically yield $C_{\text{el},0}^\alpha$ values with weak dependencies to $\mathbf{r}_i$, in which case they must not be directly integrated into the machine-learning framework.

With configuration- and bias-dependent energetics $E^\alpha(q)$ provided by the RAZOR MLIP, it is straightforward to derive free energies $F^{Z_i}(q)$, and thus the desired electronically grand-canonical free energies $\Omega^{Z_i}(\phi_E)$, for a defined chemical composition Z_i (see the End Matter and Sec. SIII of SM for more details [67]).

We illustrate this workflow and the capabilities of the RAZOR-MLIP approach by considering the potential-dependent adsorption behavior of OH on Cu(100) in aqueous electrolyte, which is of interest in the context of CO_2 reduction at cathodic potentials and surface restructuring at anodic potentials [68–70]. The RAZOR MLIP is based on the NequIP neural network architecture [61], and the training is performed with density-functional theory (DFT) data generated with QUANTUM ESPRESSO and the implicit solvent model QUANTUM ENVIRON [6,71–73], with further details provided in Sec. SII of SM [67,74].

NVT MD simulations in supercells with (4×4) surface unit cells and for $T = 300$ K were run at different q and various OH coverages. With analog results for other coverages reported in SM [67], we focus here on the 0.5

monolayer (ML) case, which is considered the highest possible Cu(100) OH coverage [75]. As summarized in Fig. 2, we obtain a charge-induced change of the stable adsorption site. At very negative q , OH binds exclusively at the twofold bridge site and lies almost parallel to the surface (average angle $\langle \varphi \rangle \sim 20^\circ - 30^\circ$), whereas at positive q values it prefers the fourfold hollow site with an almost upright orientation (average angle $\langle \varphi \rangle \approx 75^\circ$). The switch between the two sites (and the concomitant OH-orientation change) occurs within a narrow charge range $0.02e \lesssim q \lesssim 0.05e$ per Cu surface atom and is accompanied by a strong work function change of ~ 1.5 V. Outside the transition region, charging and temperature effects are small and MD-averaged work functions closely align with those of DFT-optimized ($q = 0$, $T = 0$ K), fully ordered $c(2 \times 2)$ bridge and hollow reference structures; cf. Fig. 2.

In Fig. 2, we include the constant-charge OH adsorption free energies $\Delta F_{\text{ads}}^\circ(q)$, computed via the free energy difference (per OH) between the OH-covered and clean Cu(100) slabs, as well as the conventional OH chemical potential μ_{OH}° (see Sec. SIII.3 of SM for details [67]). The comparison to *ab initio* thermodynamics (AITD) [53,76] shows excellent agreement (Fig. 2, bottom panel), e.g., for the site switch as derived from the crossing of the free energy curves of the static DFT reference structures. Notably, this agreement prevails over the entire wide range of bias charges, supporting the validity of RAZOR’s second-order expansion.

By transforming the constant-charge $\Delta F_{\text{ads}}^\circ(q)$ to the corresponding constant-potential $\Delta \Omega_{\text{ads}}(\phi_E)$, we finally reach experimental conditions. Specifically, we employ computational hydrogen electrode referencing to the chemical potential [1], and measure ϕ_E versus the reversible hydrogen electrode (RHE). Figure 3 shows the corresponding results in both acidic and alkaline conditions (see SM for other coverages [67]). Strikingly, this shows that the aforementioned charge-dependent site switch

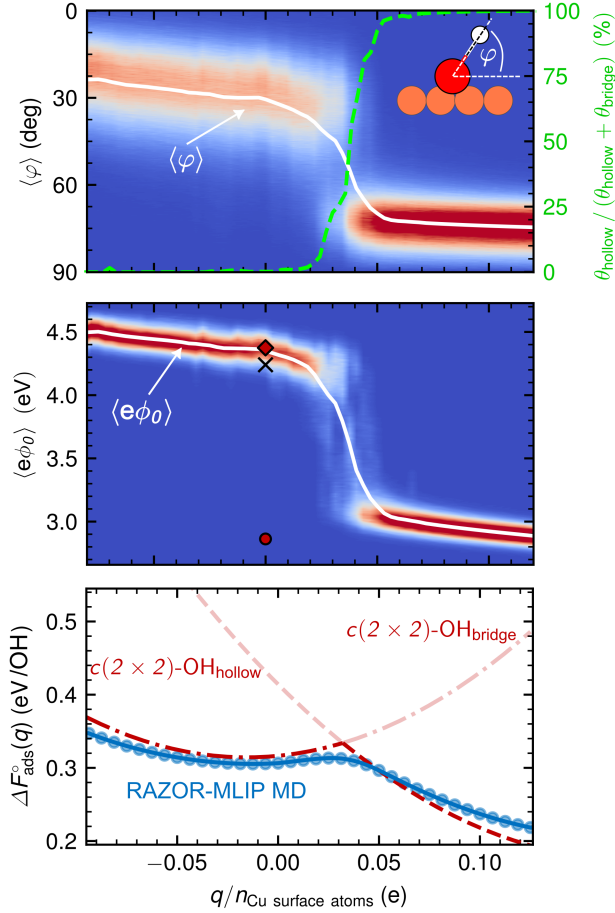


FIG. 2. RAZOR-MLIP-based MD simulations for a 0.5 ML OH-covered Cu(100) surface at different q (per Cu surface atom). Top panel: probability distribution of the OH-bond angle φ (see inset), together with the average $\langle \varphi \rangle$ (white line) and the fractional coverage of hollow and bridge sites $\theta_{\text{hollow}}/(\theta_{\text{hollow}} + \theta_{\text{bridge}})$ (green line), revealing a charge-induced switch of the adsorption site. Middle panel: corresponding data for the work function $e\phi_0$. Additionally shown are the $e\phi_0$ of DFT-optimized, ($q = 0$, $T = 0$ K) reference structures: clean Cu(100) (cross), $c(2 \times 2) - \text{OH}_{\text{bridge}}$ (diamond), and $c(2 \times 2) - \text{OH}_{\text{hollow}}$ (circle). Bottom panel: constant-charge adsorption free energy $\Delta F_{\text{ads}}^{\circ}(q)$ (blue circles) compared to results from DL-corrected *ab initio* thermodynamics for the reference $c(2 \times 2) - \text{OH}_{\text{hollow}}$ (dashed red line) and $c(2 \times 2) - \text{OH}_{\text{bridge}}$ (dash-dotted red line) structures.

manifests itself in a pH dependence of the preferred OH adsorption site: bridge sites in alkaline and hollow sites in acidic conditions, exactly as deduced in experimental studies by Kunze *et al.* [68] and Cruickshank *et al.* [77].

The agreement between RAZOR MLIP, AITD, and experiments is most gratifying. For one, it provides confidence in the AITD approaches, at least for systems of intermediate complexity such as the interface considered here with only one adsorbate species on well-defined adsorption sites. On the other hand, it confirms the correctness and robustness of the RAZOR-MLIP-based MD at

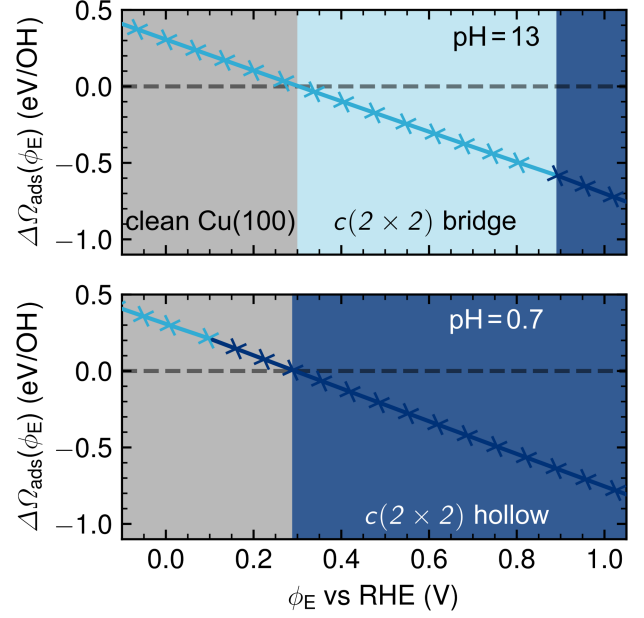


FIG. 3. Adsorption free energy $\Delta \Omega_{\text{ads}}(\phi_E)$ of 0.5 ML OH at Cu(100) versus the potential ϕ_E on the reversible hydrogen electrode (RHE) scale. The charge-dependent adsorption site (cf. Fig. 2) translates to a potential-induced site switch, with light (dark) blue crosses corresponding to bridge (hollow) site adsorption. This induces a pH dependence at the onset potentials for OH adsorption above $\phi_E \gtrsim 0.3$ V, i.e., when $\Delta \Omega_{\text{ads}}(\phi_E)$ becomes negative. At alkaline $pH = 13$ conditions, the preferred adsorption site is bridge (upper panel), whereas at acidic $pH = 0.7$ conditions it is hollow (lower panel).

applied bias, whose true prospective strength lies in the ability to tackle more complex situations. Even the present, relatively simple system requires long timescales to reach convergence. As detailed in Fig. S14 of SM [67], the interfacial transformation dynamics upon switching of the charge state can, for instance, take several hundred picoseconds, highlighting the importance of fast MLIP-surrogate total-energy methods.

In summary, the present response analysis in z -orientation framework extends existing MLIP approaches to provide computationally efficient and robust access to interfacial atomistic structures and energetics at electrified extended metallic electrodes. Rather than striving to directly machine learn applied bias conditions, it is rooted in perturbation theory to capture surface charging effects up to second order. This reduces the additional learning effort to a MLIP for the work function as the relevant linear response parameter, at only a modest increase in required first-principles training data. RAZOR can be directly implemented with any existing MLIP architecture, which makes it particularly useful in times where general, foundational models become increasingly accurate [78–82]. While we expect RAZOR to work without issue for nonplanar metallic electrodes [44], semiconducting electrodes are intrinsically more challenging and will require further research [83,84].

The first showcase application to the potential-dependent thermodynamics and dynamics of adsorbed OH on Cu(100) already reproduces the experimentally reported non-Nernstian pH dependence of the preferred adsorption site. Yet, this is only a glimpse of the predictive-quality electrochemical modeling capabilities enabled by RAZOR-MLIP acceleration, with future work concentrating on explicitly solvated complex interfacial environments. Specifically, we emphasize the possibility of performing large-scale potentiostated, constant-potential simulations or using the local work function decomposition ansatz to develop approximation-free, local descriptions of electrochemical driving forces [54,85,86] and simulating local work function variations such as those probed in Kelvin probe force microscopy [87].

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Data availability—The data that support the findings of this article are openly available [88].

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End Matter

Electronic capacitances of metallic electrodes— $C_{\text{el},0}^\alpha$ can be understood from a series circuit of capacitors $(C_{\text{Q},0}^\alpha)^{-1} + (C_{\text{XC},0}^\alpha)^{-1} + (C_{\text{DL},0}^\alpha)^{-1}$, with the three terms being the quantum, the exchange correlation, and the DL capacitance, respectively [56,83]. $C_{\text{Q},0}^\alpha$ is related to the spatial variation of the local density of states at the Fermi level and is somewhat analogous to the molecular polarizability. For the metallic electrodes studied here, the contributions of $C_{\text{Q},0}^\alpha$ and $C_{\text{XC},0}^\alpha$ to $C_{\text{el},0}^\alpha$ are negligible [56,83]. Thus, $C_{\text{el},0}^\alpha$ is defined predominantly by $C_{\text{DL},0}^\alpha$, which in the present description subsumes all second-order energy contributions due to the collective response of the DL.

In fully explicit atomistic descriptions, $C_{\text{el},0}^\alpha$ ($C_{\text{DL},0}^\alpha$) could be determined by integrating out degrees of freedom that reach deep into the bulk electrolyte, requiring exhaustive sampling [26,89,90]. Within an MLIP approach, such a sampling could be achieved by including a long-range electrostatic description [18–21,23–25], albeit with an increase in computational effort. Here, we instead use an implicit solvent model which provides an acceptable estimate for the major contributions of the deeper DL [9,45,53,73]. As we have already computed different q states to machine learn ϕ_0^α , calculating $C_{\text{el},0}^\alpha$ brings no additional first-principles computational cost. While $C_{\text{el},0}^\alpha$ in implicit solvent models is often rather independent of specifics of interface geometries like adsorption sites, it does depend on the overall interface composition Z_i and termination, e.g., surface coverage θ [43–45] (see Fig. S8 of SM [67]). If we therefore consider $C_{\text{el},0}^\alpha$ to only be a function of Z_i (also known as the surface coverage θ_i of species i), all force contributions at a fixed composition vanish and the second-order energy variation $\propto C_{\text{el},0}^{-1}$ remains configuration independent. As a result, $C_{\text{el},0}$ does not influence configurational distributions at given q at a fixed composition and must thus not be directly integrated into the machine-learning framework.

Grand-canonical free energies—As explained in more detail in Sec. SIII of SM [67], canonical free energies $F^{Z_i}(q)$ are determined via MD simulation at q and the subsequent thermodynamic integration

$$F^{Z_i}(q) = F_0^{Z_i} + \int_0^q \frac{\partial F^{Z_i}}{\partial q} \bigg|_{q'} dq' = F_0^{Z_i} + \int_0^q \langle \phi^\alpha \rangle_{q'} dq'. \quad (\text{B1})$$

$F_0^{Z_i}$ is the free energy at $q = 0$, obtained via standard referencing methods [42] and $\langle \phi^\alpha \rangle_q$ is the average work function of the sampled configurations α of the given interface composition Z_i at q .

In this Letter, we approximate (see Sec. SIII.1 of SM for more details [67])

$$\langle \phi^\alpha \rangle_q \approx \langle \phi_0^\alpha \rangle_q + \frac{q}{C_{\text{el},0}}, \quad (\text{B2})$$

where $\langle \phi_0^\alpha \rangle_q$ is the learned work function at $q = 0$, and $q/C_{\text{el},0}$ is the aforementioned, configuration-independent capacitive response of the implicit solvent model. The transformation to a specified ϕ_E is then achieved by an appropriate charge-potential mapping $q(\phi_E)$, given as the charge that minimizes the “formation free energy” of the interface at ϕ_E [53],

$$q(\phi_E) = \text{argmin}_q \{F^{Z_i}(q) - q\phi_E\}. \quad (\text{B3})$$

The so-determined, optimal formation free energy is identical to the grand potential of the system

$$\Omega^{Z_i}(\phi_E) = \min_q \{F^{Z_i}(q) - q\phi_E\}, \quad (\text{B4})$$

the Legendre transform of the free energy $F^{Z_i}(q)$. Equations (B1)–(B4) thus suffice to translate the constant-charge simulations to relevant quantities at constant-potential conditions, i.e., $q(\phi_E)$ and $\Omega^{Z_i}(\phi_E)$.