

Macro-Dipole-Constrained Learning of Atomic Charges for Accurate Electrostatic Potentials at Electrochemical Interfaces

Jing Yang^{✉,*}, Bingxin Li[✉], Samuel Mattoso[✉], Ahmed Abdelkawy[✉], Mira Todorova^{✉,†} and Jörg Neugebauer[✉]
Max Planck Institute for Sustainable Materials, Max-Planck-Str. 1, 40237, Düsseldorf, Germany



(Received 1 October 2025; accepted 17 February 2026; published 16 March 2026)

Large thermal fluctuations of the liquid phase obscure the weak macroscopic electric field that drives electrochemical reactions, rendering the extraction of reliable interfacial charge distributions from *ab initio* molecular dynamics extremely challenging. We introduce SMILE (Scalar Macro-dipole Integrated LEarning) charge partition, a macro-dipole-constrained scheme that infers atomic charges using only the instantaneous atomic coordinates and the total dipole moment of the simulation cell—quantities routinely available from standard density functional theory calculations. SMILE preserves both the global electrostatic field and the local potential without invoking any explicit charge-partitioning scheme. Benchmarks on three representative electrochemical interfaces—nanoconfined water, Mg^{2+} dissolution in water, and a kinked Mg vicinal surface under anodic bias—show that SMILE eliminates the qualitative errors observed for unconstrained charge decompositions. The method is computationally inexpensive and data-efficient, opening the door to charge-aware machine-learning potentials capable of bias-controlled, nanosecond-scale simulations of realistic electrochemical systems.

DOI: [10.1103/5hh2-wypm](https://doi.org/10.1103/5hh2-wypm)

Computational electrochemistry plays a crucial role in understanding and designing electrochemical processes at the atomic scale, including reactions at electrode interfaces, ion transport, and charge transfer phenomena [1–4]. While density functional theory (DFT) provides an accurate quantum mechanical description, its high computational cost severely limits the accessible length and timescales, impeding simulations of realistic systems and dynamics. On the other hand, classical force fields enable larger-scale simulations but often rely on fixed or simplified electrostatic models, lacking the flexibility to capture complex, environment-dependent charge distributions that are needed for modeling electrochemical interfaces, especially charge transfer reactions.

In recent years, machine-learning interatomic potentials (MLIPs) have emerged as promising tools that combine near-DFT accuracy with significantly reduced computational cost [5–7]. However, the most prevalent types of MLIPs [8–14] determine the forces and energies of a given atom uniquely by its local atomistic environment within a certain cutoff. This inherent short-sightedness of the descriptors

renders the models incapable of capturing long-range interactions accurately, limiting their applicability. Hence, incorporating long-range electrostatic interactions in MLIPs has been a major focus of ongoing research [15–21].

A key quantity in electrochemistry is the electrostatic potential $\phi(z)$, which describes the variation of the electric potential as a function of position perpendicular to the electrode-electrolyte interface. This potential governs the distribution of ions, influences charge transfer processes, and plays a central role in determining interfacial properties such as the double layer structure and the driving force for electrochemical reactions. An accurate reproduction of ϕ is therefore essential for realistically modeling the behavior of electrochemical systems at the atomic scale. However, none of the present MLIP approaches takes the electrostatic potential ϕ directly as a target property due to its inherent incompatibility with standard machine-learning (ML) framework. Unlike atomic energies and forces, ϕ is a continuous scalar field over 3D space computed as the solution to Poisson's equation. Numerically, computing gradients of ϕ with respect to model parameters is impractical due to the nonlocality of the Poisson operator and therefore ϕ is ill-suited to be included in the loss function of an ML model. Instead, one commonly explored approach is to train the model on a local charge partition scheme and include the long-range electrostatic interactions computed from the local charge distribution. For example, Hirshfeld charges [22] are used as reference for training the fourth-generation high-dimensional neutral network potentials [17,23,24]. The deep potential model [18] is trained on the centers of maximally localized Wannier functions

*Contact author: j.yang@mpi-susmat.de

†Contact author: m.todorova@mpi-susmat.de

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Open access publication funded by the Max Planck Society.

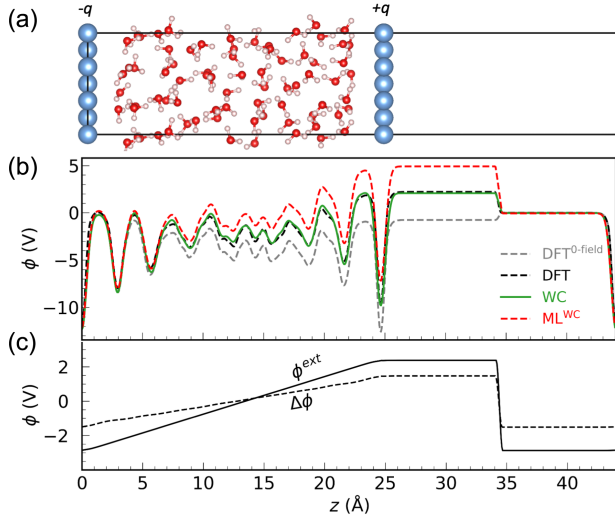


FIG. 1. (a) Atomistic model of the nanoconfined water between two Ne electrodes. The two electrodes carry opposite charges, creating a macroscopic field across the water layer. (b) The corresponding electrostatic potential calculated from DFT, Wannier centers (WCs), and the ML model learning from individual WCs (ML^{WC}), with an applied field of $E^{\text{ext}} = 0.2 \text{ V/\AA}$. The gray dashed line represents the zero field DFT reference. (c) The externally applied field ϕ^{ext} and the difference between the DFT electrostatic potential with and without field $\Delta\phi$. In the bulk water region, $\Delta\phi$ corresponds to an electric field smaller than E^{ext} , which results from the electronic screening of water.

(Wannier centers, WCs) [25,26] to calculate the corresponding long-range interaction. These MLIPs are used for simulating systems containing charge species and electric field [27–29] and for modeling dielectric response in polarizable media [30–33].

In this Letter, we demonstrate that machine-learning models that are solely trained to reproduce local charge decomposition schemes can result in significant errors in the long-range electrostatic potential $\phi(z)$. This shortcoming limits their application to electrochemical systems in which charge transfer processes are strongly influenced by the macroscopic electric field. To address this issue, we introduce two innovations: (1) incorporating the macro-dipole moment of the system as a surrogate for the electric field in the model’s cost function to ensure accurate reconstruction of the long-range electrostatic profile and (2) explicitly accounting for the electronic polarization of water, which escapes standard machine-learning potentials because of its relatively small magnitude in comparison to the intrinsic thermal fluctuation. The proposed approach is termed SMILE (Scalar Macro-dipole Integrated LEarning) charge partition.

To analyze and quantify the impact of large local fluctuations in the electrostatic potential on the accurate modeling of macroscopic fields in electrochemical systems, we have constructed a well-defined computational setup. This setup comprises a nanoconfined water slab that is sandwiched between two oppositely charged neon (Ne)

electrodes [Fig. 1(a)] [34,35]. This setup realistically describes local fluctuations at an electrochemical interface while providing full quantitative access to and control over the macroscopic field. Thus, it provides an ideal test bed for evaluating the capacity of local ML models to capture macroscopic electrostatics amid pronounced microscopic disorder, a challenge that is ubiquitous in realistic electrochemical interfaces. The net electrode charge, and thus the applied electric field across the water layer, is controlled by adjusting the Ne core charges while maintaining the cell’s overall charge neutrality. We impose a dipole correction along the surface normal (z) direction to ensure accurate long-range electrostatics [36]. *Ab initio* molecular dynamics (AIMD) simulations are performed using VASP [37,38]. A charge decomposition is performed on a selected set of molecular dynamics snapshots using WANNIER90 [39], and Bader charge decomposition [40,41]; full computational details are provided in Supplemental Material (SM) [42].

Figure 1(b) shows the electrostatic potential profile ϕ , along the z axis for a representative AIMD snapshot at an applied field of $E^{\text{ext}} = 0.2 \text{ V/\AA}$ (black line), compared with the zero-field case (gray dashed line). The close-to-linear dependence observed implies a nearly constant field in the water region. This is confirmed in Fig. 1(c) by plotting the difference potential, $\Delta\phi$, between the two field conditions. Bader charges fail to reproduce the macro dipole (see SM). Only the maximally localized Wannier functions accurately reproduce the macroscopic field from the WCs of individual water molecules [Fig. 1(b), green line], while small local deviations reflect the Gaussian approximation of the electron density.

In an ML approach, however, the WCs can no longer be obtained from electronic wave functions but exclusively from the local environment of each atom. We hence develop and apply an ML model (ML^{WC}) based on local ACE descriptors [13,50–52] that predicts the WC positions of individual water molecules, in the same spirit of the deep potential model with long-range electrostatic interaction [18]. The ML^{WC} model achieves state-of-the-art accuracy in WC positions with a mean squared root error (RMSE) of $0.004 \text{ \AA}$ [28,29]. However, despite this impressive local accuracy of 4 pm , the model systematically fails to reproduce the correct macroscopic field response, instead predicting an offset in the potential [Fig. 1(b), red line]. This failure is generic: it arises because large local fluctuations, which are inherent to electrochemical systems, decouple precise local charge prediction from accurate long-range electrostatics. Our finding thus reveals a fundamental limitation of strictly local ML approaches in capturing macroscopic electrostatic behavior in complex interfacial systems.

To elucidate the origin of this failure, we analyze how individual water dipoles respond to the applied electric field. Specifically, we define the electron charge center of

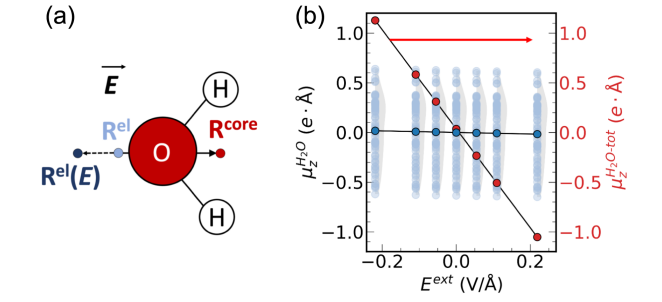


FIG. 2. (a) Schematic showing how a water molecule responds to an external electric field. The dipole moment of an individual water molecule is represented by $\mu^{\text{H}_2\text{O}} = 8e(\mathbf{R}^{\text{el}} - \mathbf{R}^{\text{core}})$, where $\mathbf{R}^{\text{core}}$ is the core charge center and $\mathbf{R}^{\text{el}}$ is the electron charge center. When an external field is applied, the electrons are polarized, leading to change of $\mathbf{R}^{\text{el}}$ and thus $\mu^{\text{H}_2\text{O}}$. (b) The dipole moments in the z direction of individual water molecules $\mu_z^{\text{H}_2\text{O}}$ (light blue dots) as a function of the applied field strength E^{ext} . The corresponding gray shades show their value distribution. The red dots are the sum of the dipole moment in the z direction $\mu_z^{\text{H}_2\text{O-tot}}$, which clearly shows a linear relationship with E^{ext} . The dark blue dots show $\mu_z^{\text{H}_2\text{O-tot}}$ averaged to each water molecule, which is almost horizontal on the given scale.

each water molecule as the center of mass of its WCs ($\mathbf{R}^{\text{el}}$), and calculate the molecular dipole moment as $\mu^{\text{H}_2\text{O}} = 8e(\mathbf{R}^{\text{el}} - \mathbf{R}^{\text{core}})$, where $\mathbf{R}^{\text{core}}$ denotes the core position [see schematic in Fig. 2(a)]. Upon application of an external field, the electron cloud of each water molecule is polarized, leading to a shift in the WC positions and a corresponding change in $\mu^{\text{H}_2\text{O}}$.

By tracking changes in the WC positions under varying external fields, we compute the dipole moment distributions for all water molecules. Figure 2(b) displays both the individual dipole moment projections along z ($\mu_z^{\text{H}_2\text{O}}$, light blue dots) and their sum ($\mu_z^{\text{H}_2\text{O-tot}}$, red dots) as a function of the applied field E^{ext} . While the total dipole response exhibits a clear linear dependence on E^{ext} —in agreement with the expected global polarization—the distributions of individual $\mu_z^{\text{H}_2\text{O}}$ remain essentially unchanged. This is further underscored by the nearly horizontal trend of the per-molecule-averaged $\mu_z^{\text{H}_2\text{O}}$ [dark blue dots in Fig. 2(b)].

This seemingly contradictory observation can be explained quantitatively. For a net change of $1 e\text{\AA}$ in the global dipole moment distributed across the 64 water molecules in our system, the average change in the individual molecular dipole $\mu_z^{\text{H}_2\text{O}}$ is just $0.016 e\text{\AA}$, 2 orders of magnitude smaller than the thermal fluctuations in $\mu_z^{\text{H}_2\text{O}}$ present in the system. This disparity presents a fundamental challenge for ML models trained to predict $\mathbf{R}^{\text{el}}$: the relevant signal—the material’s response to an external field—is almost entirely obscured by the intrinsic noise due to thermal motion and orientational disorder of water molecules. For WCs, this translates to a change of only $0.002 \text{\AA}$ change in $\mathbf{R}^{\text{el}}$, well below the resolution

achievable by local ML models. This limitation persists even at zero external field, due to the long-range field arising from spontaneous dipole fluctuations, and cannot be cured by adjusting model hyperparameters (see SM [42]).

Since the local descriptor entering the ML^{WC} model is not explicitly dependent on the macroscopic field, these models can only describe the local ionic screening but fail to capture the electronic polarization. Thus, in the absence of ionic screening (i.e., freezing in an AIMD snapshot) and applying an external field, the effective field in the water region $E_{\text{water}} \approx E^{\text{ext}}$. Indeed, as shown in Fig. 1(b), the internal electric field predicted by ML^{WC} is nearly twice that from DFT, corresponding to the missing dielectric screening factor ($\epsilon_\infty \approx 2$). These limitations apply generally to all ML models that use local charges as input. This systematic deviation is not observed in the x and y directions, along which no long-range electric field exists. The ML^{WC} model predicts the macro dipole in the x and y directions in good agreement with DFT reference (see SM [42]).

Given the failure of the local ML model to capture the long-range electrostatics, we propose an approach that extracts the local charges directly from the total macroscopic dipole moment μ_z^{tot} . In this approach, the dipole moment of each water molecule μ_i is a function of its local descriptor $\mathbf{D}^i$, such that

$$\mu^i = f(\mathbf{D}^i). \quad (1)$$

The sum of the predicted molecular dipoles has to match the total dipole along z axis,

$$\sum_i \mu_z^i = \mu_z^{\text{tot}}, \quad (2)$$

analogous to the procedure used in MLIPs, where atomic energies are learned subject to the constraint $\sum_i E^i = E^{\text{tot}}$. We denote the ML model employing Eq. (2) as SMILE0. Since in this approach the charge decomposition is done with the condition to minimize errors in the macro dipole, this schema guarantees an accurate description of the macroscopic field.

However, when applying this approach to a more realistic system with dissolved Mg^{2+} ion and charged electrodes [Fig. 3(a)], severe deviations between the electrostatic potential obtained by DFT [Fig. 3(b), black line] and the SMILE0 model [Fig. 3(b), orange line] are observed: while DFT shows strong screening as a nearly flat potential in the long range, the SMILE0 model predicts a pronounced field and a valley-shaped potential, indicative of underestimated screening.

This failure arises from the absence of electronic polarization in typical ML models. Conceptually, the total macro dipole can be separated into an electronic polarization term, $\mu_z^{\text{el-pol}}$, that is field-induced, and a local term, μ_i^{local} , that is field-independent,

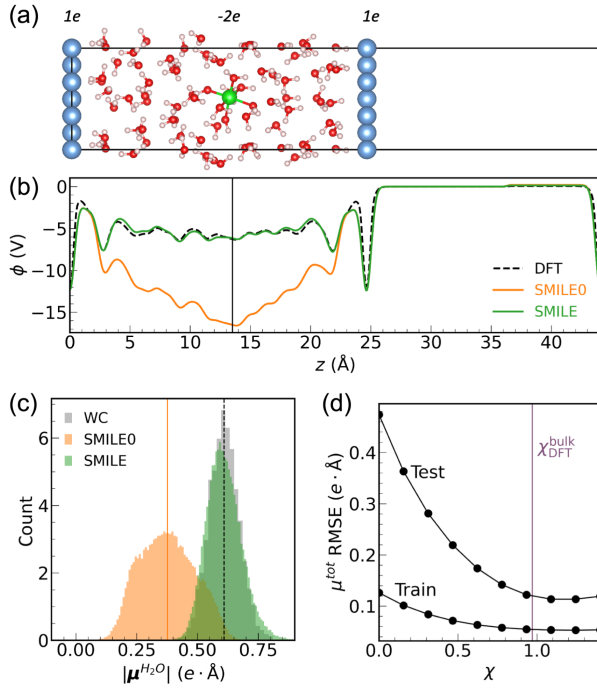


FIG. 3. (a) Atomistic structure of nanoconfined water with a dissolved Mg^{2+} ion. The compensating charge of the 2+ ion is evenly spread on the two Ne electrodes. (b) Predicted electrostatic potential ϕ of the SMILE0 and SMILE model, in comparison with DFT. The SMILE0 model is equivalent to SMILE at $\chi = 0$. The black vertical line represents the average position of the Mg ion. (c) The distribution of the individual water molecule dipole magnitude $|\mu^{\text{H}_2\text{O}}|$ of the two models, in comparison to the values computed with WCs. The vertical lines show the corresponding averaged values, for which the lines of WC and SMILE overlap. (d) The RMSE of the SMILE model as a function of χ . The purple vertical line shows the DFT-calculated electronic susceptibility of water $\chi_{\text{DFT}}^{\text{bulk}} = 0.96$.

$$\mu_z^{\text{tot}} = \mu_z^{\text{el-pol}} + \mu_z^{\text{local}}. \quad (3)$$

In the linear response regime, $\mu_z^{\text{el-pol}} = -\chi\mu_z^{\text{tot}}$, with χ being the electronic susceptibility ($\chi = \epsilon_\infty - 1$). The induced electronic polarization dipole counterbalances the applied field, therefore $\mu_z^{\text{el-pol}}$ and μ_z^{tot} have opposite signs. Thus, $\mu_z^{\text{tot}} = \mu_z^{\text{local}}/(1 + \chi)$, showing that the observed macro dipole is only a screened fraction of the static local dipoles, leading to a systematic underestimation of screening. Figure 3(c) confirms this, with the DFT-derived WC dipole distribution averaged at $0.61 \text{ e}\text{\AA}$, while SMILE0 yields $0.38 \text{ e}\text{\AA}$. Similar behavior is also observed in the system of nanoconfined water without dissolved ion (see SM [42]).

To account for the electronic polarization, we exploit the fact that in contrast to the ionic dielectric constant, which shows huge spatial fluctuations at the electrochemical interface, electronic polarization is remarkably homogeneous [see Fig. 1(c)]. Based on this insight, we reformulate the constraint in Eq. (2) as

$$\sum_i \mu_z^{i,\text{local}} = (1 + \chi)\mu_z^{\text{tot}}, \quad (4)$$

and denote this model as SMILE. Varying χ , we find the RMSE between reference and predicted dipoles is minimized at $\chi \approx 1.2$ [Fig. 3(d)], consistent across several water-solid interface systems. This optimal value slightly exceeds the DFT-calculated bulk value ($\chi_{\text{DFT}}^{\text{bulk}} = 0.96$), likely due to a reduced HOMO-LUMO gap of water in the interface region resulting in enhanced dielectric response [53].

With this correction, the SMILE model faithfully reproduces both the local dipole distribution [average $0.61 \text{ e}\text{\AA}$, Fig. 3(c)] and the long-range electrostatics [Fig. 3(b), green line], achieving an RMSE of $0.052 \text{ e}\text{\AA}$ for the macro dipole and $0.056 \text{ e}\text{\AA}$ for individual water dipoles. These results demonstrate the model's strong predictive power for both local and macroscopic electrostatics, resolving the inherent shortcomings of strictly local ML approaches. Given that the structural descriptors are invariant to rotations, the SMILE method captures the electric response in the three-dimensional space even though it is trained only on the z component of the macro dipole. We demonstrate this by comparing the resulting Born effective charges of the SMILE model against DFT reference, where a good agreement is observed (see SM [42]).

Another advantage of the proposed model is that it is flexible for learning the local dipole or the local charge. The latter assigns a point charge to each atom in the system. Practically, this is done by rewriting Eqs. (1) and (4) as

$$q_i = f(\mathbf{D}^i), \quad (5)$$

$$\sum_i q_i z_i = (1 + \chi)\mu_z^{\text{tot}}. \quad (6)$$

Here, q_i is the charge on atom i and z_i is the z coordinate of the corresponding atom. The model assigning atomic charges is arguably more flexible than the model predicting molecular dipoles because by assigning a dipole moment to each water molecule, the dipole-based model implicitly assumes charge neutrality for the individual molecule, thereby excluding intermolecular charge transfer.

We apply the model employing Eq. (6) to a realistic electrochemical system, an $\text{Mg}(1\ 2\ \bar{3}\ 15)$ vicinal surface under anodic potential [Fig. 4(a)]. The Mg-water interface is of particular interest due to the observed anomalous anodic hydrogen evolution reaction [54,55], and in recent years there have been a number of computational studies attempting to reveal the reaction pathway [34,56–58]. In this study, we employ a static potentiostat to apply anodic bias on the Mg surface, similar to the method in [34]. The evolution of the macro dipole and the electrode charge is shown in Fig. 4(b). The first 5 ps of the AIMD run is under open circuit condition, with no charge on the electrode;

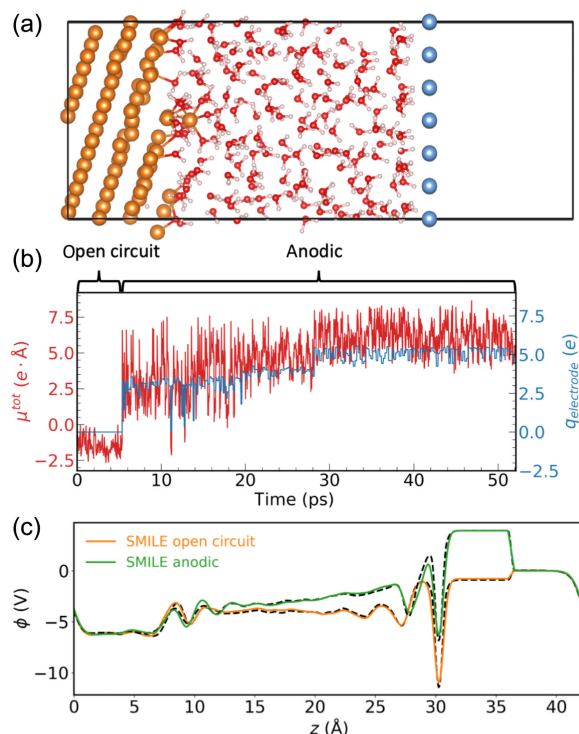


FIG. 4. (a) Atomistic model of the $\text{Mg}(1\ 2\ \bar{3}\ 15)$ -water interface. (b) The evolution of the macro dipole μ^{tot} and the electrode charge $q_{\text{electrode}}$ as a function of time in the AIMD simulation. The first 5 ps is under open circuit condition, followed by 45 ps of anodic bias. (c) The predicted electrostatic potential ϕ under open circuit condition and anodic bias predicted by the SMILE model (colored lines) in comparison to the DFT references (black dashed lines).

then an anodic bias is applied, which is gradually ramped up to 4 V.

The SMILE model consistently reproduces the electrostatic potential both under open circuit condition and under anodic bias [Fig. 4(c)]. The long AIMD trajectory allows us to average out the local fluctuations in ϕ and clearly observe the macroscopic field across the cell. While the ϕ profile is almost flat in the bulk of water under open circuit condition, the field under the 4V anodic bias averages to $0.15\text{ V}/\text{\AA}$. These long-range macroscopic fields are accurately captured by the SMILE model. We note here that both curves are obtained with a single model, which highlights the transferability of the model across applied potentials. In addition to water, the model is also applied to a molten salt LiF system. We again observe good agreement between the SMILE model and the DFT reference, demonstrating the transferability of the model to other types of liquid systems (see SM [42]).

In conclusion, for typical electrochemical interfaces, the polarization induced by an applied electric field is roughly 2 orders of magnitude smaller than the thermal dipole fluctuations of the liquid. As a result, machine-learning potentials that are trained only on locally partitioned

charges or dipoles tend to fit the noisy local variations and effectively discard the much weaker macroscopic component, which leads to unacceptably large errors in the long-range electrostatic field. Our macro-dipole-constrained SMILE approach restores the correct field while preserving the accuracy of the local charge distribution. The only additional information required is the scalar total dipole, which is readily obtainable from standard AIMD runs. Thus, the method avoids any ambiguous charge-partitioning step. Because the constraint is introduced as a loss-function term, it works with any descriptor and any neural-network architecture. Benchmarks on nanoconfined water, Mg^{2+} dissolution, and a biased Mg vicinal surface show that the macro-dipole constraint eliminates the qualitative errors in the electrostatic potential observed for unconstrained MLIPs and reproduces the full Poisson solution from the scalar charges alone. This flexible, easy-to-implement, and data-efficient strategy therefore opens the door to bias-controlled, nanosecond-scale simulations of realistic electrochemical interfaces and paves the way for systematic investigations of voltage-dependent processes in batteries, fuel cells, and electrocatalysis.

Acknowledgments—We acknowledge funding by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) through SFB1394, Project No. 409476157 and SFB1625, Project No. 506711657. J. Y. acknowledge support by the Alexander von Humboldt foundation.

Data availability—The data that support the findings of this article are openly available [59]; embargo periods may apply.

- [1] O. M. Magnussen and A. Groß, Toward an atomic-scale understanding of electrochemical interface structure and dynamics, *J. Am. Chem. Soc.* **141**, 4777 (2019).
- [2] G. Gonella, E. H. Backus, Y. Nagata, D. J. Bonhuis, P. Loch, A. Schlaich, R. R. Netz, A. Kühnle, I. T. McCrum, M. T. Koper *et al.*, Water at charged interfaces, *Nat. Rev. Chem.* **5**, 466 (2021).
- [3] S. Ringe, N. G. Hörmann, H. Oberhofer, and K. Reuter, Implicit solvation methods for catalysis at electrified interfaces, *Chem. Rev.* **122**, 10777 (2021).
- [4] M. Todorova, S. Wippermann, and J. Neugebauer, First-principles approaches and concepts to simulate electrochemical interfaces, *Nat. Rev. Chem.* **10**, 133 (2026).
- [5] V. L. Deringer, M. A. Caro, and G. Csányi, Machine learning interatomic potentials as emerging tools for materials science, *Adv. Mater.* **31**, 1902765 (2019).
- [6] Y. Zuo, C. Chen, X. Li, Z. Deng, Y. Chen, J. Behler, G. Csányi, A. V. Shapeev, A. P. Thompson, M. A. Wood *et al.*, Performance and cost assessment of machine learning interatomic potentials, *J. Phys. Chem. A* **124**, 731 (2020).
- [7] O. T. Unke, S. Chmiela, H. E. Saucedo, M. Gastegger, I. Poltavsky, K. T. Schütt, A. Tkatchenko, and K.-R. Müller,

- Machine learning force fields, *Chem. Rev.* **121**, 10142 (2021).
- [8] A. P. Bartók, M. C. Payne, R. Kondor, and G. Csányi, Gaussian approximation potentials: The accuracy of quantum mechanics, without the electrons, *Phys. Rev. Lett.* **104**, 136403 (2010).
- [9] J. Behler, Four generations of high-dimensional neural network potentials, *Chem. Rev.* **121**, 10037 (2021).
- [10] V. L. Deringer and G. Csányi, Machine learning based interatomic potential for amorphous carbon, *Phys. Rev. B* **95**, 094203 (2017).
- [11] I. S. Novikov, K. Gubaev, E. V. Podryabinkin, and A. V. Shapeev, The MLIP package: Moment tensor potentials with MPI and active learning, *Mach. Learn.* **2**, 025002 (2020).
- [12] R. Drautz, Atomic cluster expansion for accurate and transferable interatomic potentials, *Phys. Rev. B* **99**, 014104 (2019).
- [13] A. Bochkarev, Y. Lysogorskiy, S. Menon, M. Qamar, M. Mrovec, and R. Drautz, Efficient parametrization of the atomic cluster expansion, *Phys. Rev. Mater.* **6**, 013804 (2022).
- [14] S. Yue, M. C. Muniz, M. F. Calegari Andrade, L. Zhang, R. Car, and A. Z. Panagiotopoulos, When do short-range atomistic machine-learning models fall short?, *J. Chem. Phys.* **154**, 034111 (2021).
- [15] A. Grisafi and M. Ceriotti, Incorporating long-range physics in atomic-scale machine learning, *J. Chem. Phys.* **151**, 204105 (2019).
- [16] O. T. Unke and M. Meuwly, Physnet: A neural network for predicting energies, forces, dipole moments, and partial charges, *J. Chem. Theory Comput.* **15**, 3678 (2019).
- [17] T. W. Ko, J. A. Finkler, S. Goedecker, and J. Behler, A fourth-generation high-dimensional neural network potential with accurate electrostatics including non-local charge transfer, *Nat. Commun.* **12**, 398 (2021).
- [18] L. Zhang, H. Wang, M. C. Muniz, A. Z. Panagiotopoulos, R. Car *et al.*, A deep potential model with long-range electrostatic interactions, *J. Chem. Phys.* **156**, 124107 (2022).
- [19] M. Rinaldi, A. Bochkarev, Y. Lysogorskiy, and R. Drautz, Charge-constrained atomic cluster expansion, *Phys. Rev. Mater.* **9**, 033802 (2025).
- [20] S. Falletta, A. Cepellotti, A. Johansson, C. W. Tan, M. L. Descoteaux, A. Musaelian, C. J. Owen, and B. Kozinsky, Unified differentiable learning of electric response, *Nat. Commun.* **16**, 4031 (2025).
- [21] K. Joll, P. Schienbein, K. M. Rosso, and J. Blumberger, Machine learning the electric field response of condensed phase systems using perturbed neural network potentials, *Nat. Commun.* **15**, 8192 (2024).
- [22] F. L. Hirshfeld, Bonded-atom fragments for describing molecular charge densities, *Theor. Chim. Acta* **44**, 129 (1977).
- [23] Y. Shaidu, F. Pellegrini, E. Küçükbenli, R. Lot, and S. de Gironcoli, Incorporating long-range electrostatics in neural network potentials via variational charge equilibration from shortsighted ingredients, *npj Comput. Mater.* **10**, 47 (2024).
- [24] E. Kocer, A. Singraber, J. A. Finkler, P. Misof, T. W. Ko, C. Dellago, and J. Behler, Iterative charge equilibration for fourth-generation high-dimensional neural network potentials, *J. Chem. Phys.* **162**, 124106 (2025).
- [25] N. Marzari and D. Vanderbilt, Maximally localized generalized Wannier functions for composite energy bands, *Phys. Rev. B* **56**, 12847 (1997).
- [26] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Maximally localized Wannier functions: Theory and applications, *Rev. Mod. Phys.* **84**, 1419 (2012).
- [27] A. Gao and R. C. Remsing, Self-consistent determination of long-range electrostatics in neural network potentials, *Nat. Commun.* **13**, 1572 (2022).
- [28] C. Zhang, M. F. Calegari Andrade, Z. K. Goldsmith, A. S. Raman, Y. Li, P. M. Piaggi, X. Wu, R. Car, and A. Selloni, Molecular-scale insights into the electrical double layer at oxide-electrolyte interfaces, *Nat. Commun.* **15**, 10270 (2024).
- [29] J.-X. Zhu and J. Cheng, Machine learning potential for electrochemical interfaces with hybrid representation of dielectric response, *Phys. Rev. Lett.* **135**, 018003 (2025).
- [30] L. Zhang, M. Chen, X. Wu, H. Wang, W. E, and R. Car, Deep neural network for the dielectric response of insulators, *Phys. Rev. B* **102**, 041121 (2020).
- [31] A. Krishnamoorthy, K.-i. Nomura, N. Baradwaj, K. Shimamura, P. Rajak, A. Mishra, S. Fukushima, F. Shimojo, R. Kalia, A. Nakano, and P. Vashishta, Dielectric constant of liquid water determined with neural network quantum molecular dynamics, *Phys. Rev. Lett.* **126**, 216403 (2021).
- [32] B. Han, C. M. Isborn, and L. Shi, Incorporating polarization and charge transfer into a point-charge model for water using machine learning, *J. Phys. Chem. Lett.* **14**, 3869 (2023).
- [33] Q. Liang and J. Yang, Polarizable water model with *ab initio* neural network dynamic charges and spontaneous charge transfer, *J. Chem. Theory Comput.* **21**, 3360 (2025).
- [34] S. Surendralal, M. Todorova, M. W. Finnis, and J. Neugebauer, First-principles approach to model electrochemical reactions: Understanding the fundamental mechanisms behind Mg corrosion, *Phys. Rev. Lett.* **120**, 246801 (2018).
- [35] F. Deisenbeck, C. Freysoldt, M. Todorova, J. Neugebauer, and S. Wippermann, Dielectric properties of nanoconfined water: A canonical thermopotential approach, *Phys. Rev. Lett.* **126**, 136803 (2021).
- [36] J. Neugebauer and M. Scheffler, Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al (111), *Phys. Rev. B* **46**, 16067 (1992).
- [37] G. Kresse and J. Hafner, *Ab initio* molecular dynamics for liquid metals, *Phys. Rev. B* **47**, 558 (1993).
- [38] G. Kresse and J. Furthmüller, Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Phys. Rev. B* **54**, 11169 (1996).
- [39] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, WANNIER90: A tool for obtaining maximally-localised wannier functions, *Comput. Phys. Commun.* **178**, 685 (2008).
- [40] R. F. Bader and C. F. Matta, Properties of atoms in crystals: Dielectric polarization, *Int. J. Quantum Chem.* **85**, 592 (2001).

- [41] G. Henkelman, A. Arnaldsson, and H. Jónsson, A fast and robust algorithm for Bader decomposition of charge density, *Comput. Mater. Sci.* **36**, 354 (2006).
- [42] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/5hh2-wypm>, for computational details, which includes Refs. [43–49].
- [43] B. Hammer, L. B. Hansen, and J. K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, *Phys. Rev. B* **59**, 7413 (1999).
- [44] L. Li, T. Eggert, K. Reuter, and N. G. Hörmann, Electron spillover into water layers: A quantum leap in understanding capacitance behavior, *J. Am. Chem. Soc.* **145**, 22778–22784 (2025).
- [45] Z. Wang, M. Chen, J. Wu, X. Ji, L. Zeng, J. Peng, J. Yan, A. A. Kornyshev, B. Mao, and G. Feng, Constant-potential modeling of electrical double layers accounting for electron spillover, *Phys. Rev. Lett.* **134**, 046201 (2025).
- [46] L. Himanen, M. O. J. Jäger, E. V. Morooka, F. Federici Canova, Y. S. Ranawat, D. Z. Gao, P. Rinke, and A. S. Foster, DDescribe: Library of descriptors for machine learning in materials science, *Comput. Phys. Commun.* **247**, 106949 (2020).
- [47] J. Laakso, L. Himanen, H. Himm, E. V. Morooka, M. O. Jäger, M. Todorović, and P. Rinke, Updates to the DDescribe library: New descriptors and derivatives, *J. Chem. Phys.* **158**, 234802 (2023).
- [48] X. Gonze and C. Lee, Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory, *Phys. Rev. B* **55**, 10355 (1997).
- [49] A. Serva, L. Scalfi, B. Rotenberg, and M. Salanne, Effect of the metallicity on the capacitance of gold–aqueous sodium chloride interfaces, *J. Chem. Phys.* **155** (2021).
- [50] R. Drautz, Atomic cluster expansion for accurate and transferable interatomic potentials, *Phys. Rev. B* **99**, 014104 (2019).
- [51] Y. Lysogorskiy, C. v. d. Oord, A. Bochkarev, S. Menon, M. Rinaldi, T. Hammerschmidt, M. Mrovec, A. Thompson, G. Csányi, C. Ortner, and R. Drautz, Performant implementation of the atomic cluster expansion (pace) and application to copper and silicon, *npj Comput. Mater.* **7**, 97 (2021).
- [52] Y. Lysogorskiy, A. Bochkarev, M. Mrovec, and R. Drautz, Active learning strategies for atomic cluster expansion models, *Phys. Rev. Mater.* **7**, 043801 (2023).
- [53] S. Surendralal, Development of an *ab initio* computational potentiostat and its application to the study of Mg corrosion, Ph.D thesis, Ruhr-Universität Bochum, 2020, p. 71.
- [54] W. Beetz, XXXIV. On the development of hydrogen from the anode, *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **32**, 269 (1866).
- [55] G. L. Song and A. Atrens, Corrosion mechanisms of magnesium alloys, *Adv. Eng. Mater.* **1**, 11 (1999).
- [56] J. A. Yuwono, C. D. Taylor, G. S. Frankel, N. Birbilis, and S. Fajardo, Understanding the enhanced rates of hydrogen evolution on dissolving magnesium, *Electrochem. Comm.* **104**, 106482 (2019).
- [57] F. Deisenbeck, S. Surendralal, M. Todorova, S. Wippermann, and J. Neugebauer, Revealing the reaction pathway of anodic hydrogen evolution at magnesium surfaces in aqueous electrolytes, *J. Am. Chem. Soc.* **146**, 30314 (2024).
- [58] B. Li, N. M. Harrison, and A. P. Horsfield, Uncovering the electrochemical stability and corrosion reaction pathway of Mg (0001) surface: Insight from first-principles calculation, *Corros. Sci.* **241**, 112524 (2024).
- [59] J. Yang, AIMD simulations data, available on Edmond, 2026, [10.17617/3.FSA883](https://doi.org/10.17617/3.FSA883).