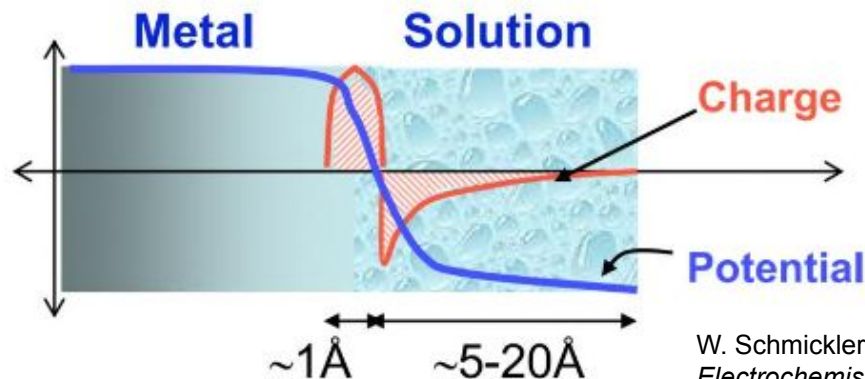# Applied voltage in atomistic simulations II: Methods for classical and ML-based MD

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CCCE Interfaces and Applied Voltage Working Group
November 25th, 2025

W. Schmickler & E. Santos, *Interfacial Electrochemistry*, **2010**

Outline

➢ Recap of definition of electrode potential and DFT/half cell methods

➢ Machine learning potentials in the grand canonical ensemble

➢ Methods for molecular dynamics under applied electrode bias
   ○ Constant Potential Method a.k.a. Siepmann-Sprik
   ○ External electric field approaches
   ○ Applicability of both with MLIPs

➢ Outlook for battery modeling: from training on half cells to simulating half cells to ultimately full cells

The electrode potential

NB: batteries are Galvanic—not electrolytic—cells so there isn't an external power supply
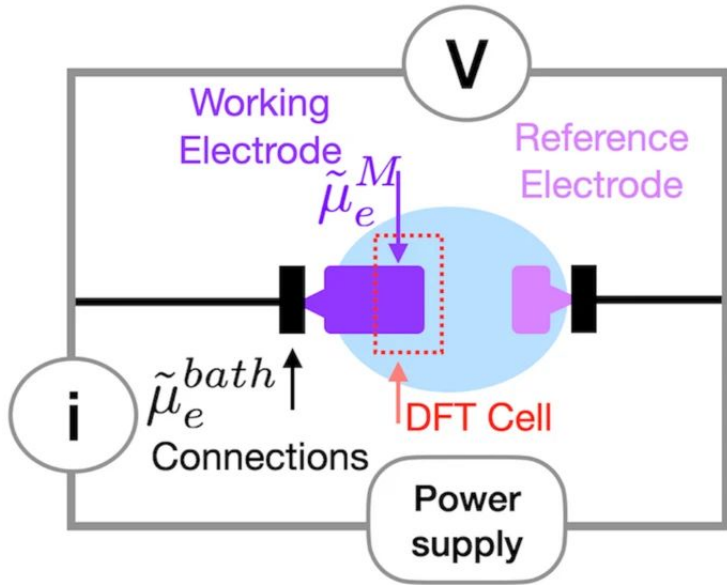
- Cell voltage is governed by the voltage difference between the anode and cathode
  - Experimentally this is often achieved using a reference electrode
- Electrons freely flow through the circuitry to maintain this voltage
- Periodic DFT cells can only realistically accommodate a half-cell: one electrode and its interface with electrolyte
- How can one apply and control an electrode potential that is necessarily defined relative to a counter electrode?

The electrode potential has several expressions

Abstract—A unifying derivation of the various concepts of "absolute" electrode potential is provided starting from a simple electrochemical cell. The approach proves that all kinds of "absolute" potential are implicit in the thermodynamics of the cell and all have the same conceptual validity. Therefore, the relevant question is not which is the true "absolute" electrode potential, but which provides the most convenient reference for a practical impact.

Comparison with Equation (2) shows that

$$_2E_a^M = (\phi^M - \phi^S) - \mu_e^M, \qquad (14)$$

also fulfils the requirements to be termed "absolute" electrode potential it is straightforward that $_2E_a^M$ implies the inner (Galvani) electric potential of the solution as the reference state. This is the potential

- Trasatti unified existing definitions using the rigorous thermochemical origins of electrode potentials
- Defined electrode potentials using computationally realizable terms, i.e. electrostatic (Hartree+nuclear) potential values and chemical potentials of electrons (Fermi energy)

Expressing electrode potential in a half-cell

is not the only available option. There are at least four different single potential definitions[3] each with different scales and reference systems, but all of them can be presented formally using the reduced absolute potential[3,44]

$$U^{\mathrm{M}}(\mathrm{abs}) = \Delta_{\mathrm{S}}^{\mathrm{M}}\phi - \mu_{\mathrm{e}}^{\mathrm{M}} + K \qquad (2)$$

where $\mu_{\mathrm{e}}^{\mathrm{M}}$ is an intrinsic material property and independent of the electrode potential. $\Delta_{\mathrm{S}}^{\mathrm{M}}\phi = \phi^{\mathrm{M}} - \phi^{\mathrm{S}}$ stands for the inner potential difference, i.e. the electrostatic potential difference between the bulk of electrode (M) and solution (S) as shown in Fig. 2. K is a constant and depends on the chosen scale, which in DFT simulations is typically chosen[6] as the electrostatic potential in vacuum or the inner potential of the implicit solvent, in which case $U_{\mathrm{vac}}^{\mathrm{M}}(\mathrm{abs}) = -\tilde{\mu}_{\mathrm{e}}^{\mathrm{M}} = -E_{\mathrm{F}}^{\mathrm{DFT}}$[3,45].
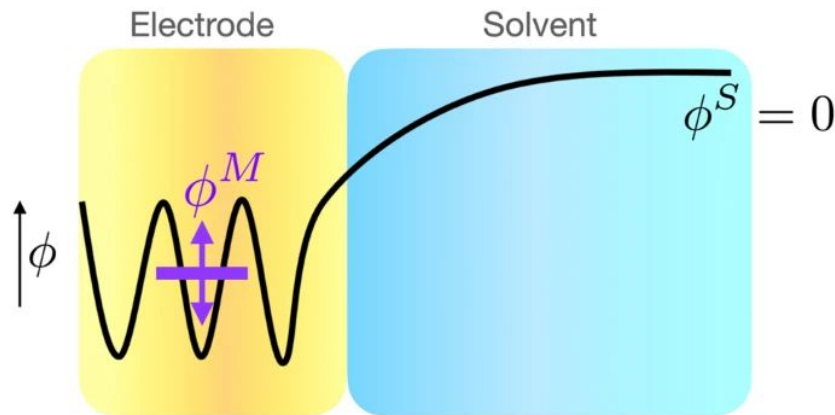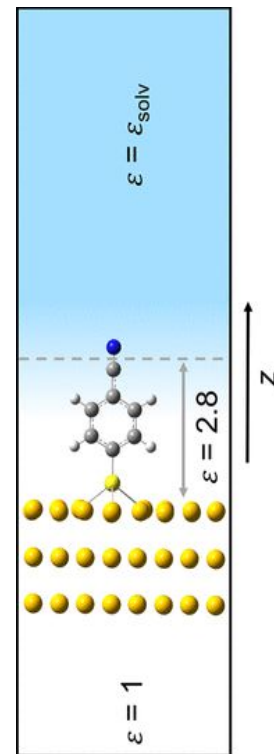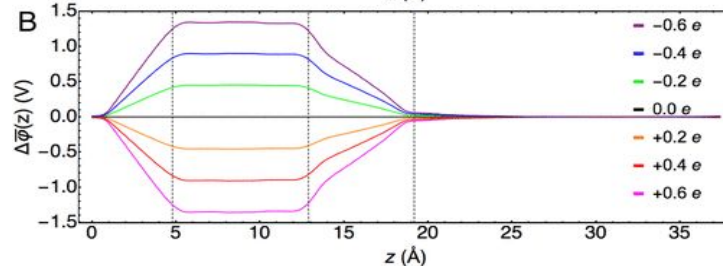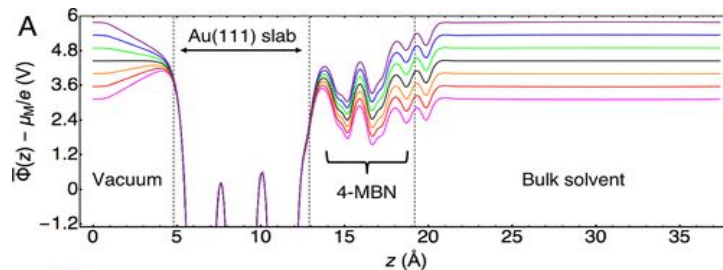

- Absolute potential can be expressed in terms of the electrostatic potential difference between deep in the metal and deep in solution as well as the intrinsic chemical potential of electrons in the metal (Fermi energy or inverse work function)
- DFT methods for half-cells in the grand canonical ensemble have been developed

Melander, Wu, Weckman, Honkala, *npj Comput. Mat.*, **2024**
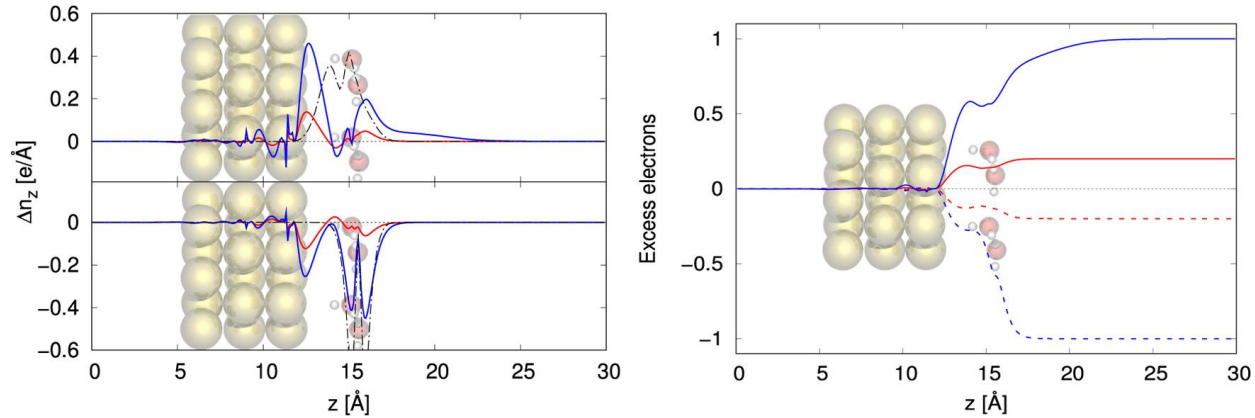
Electrode potential in practice: Static calculations
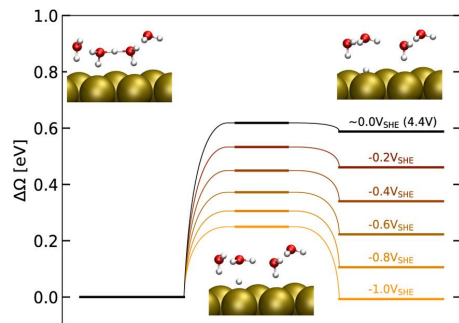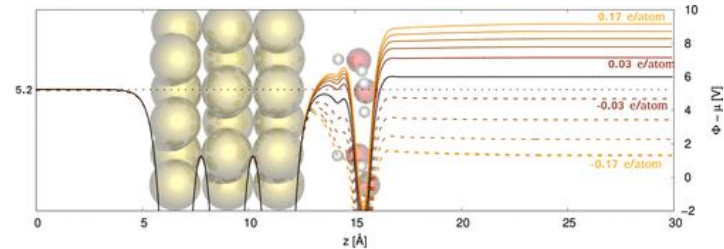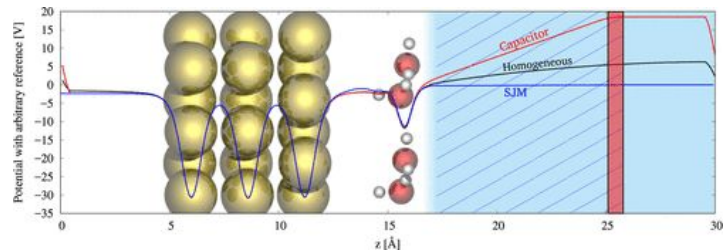
> ➤ Exploiting fractional charge and implicit solvation in periodic DFT calculations allows for smooth change to the applied voltage
> ➤ Differential capacitance governs the charge needed to apply a given potential

Kastlunger, Lindgren, Peterson, *JPC C*, **2018**
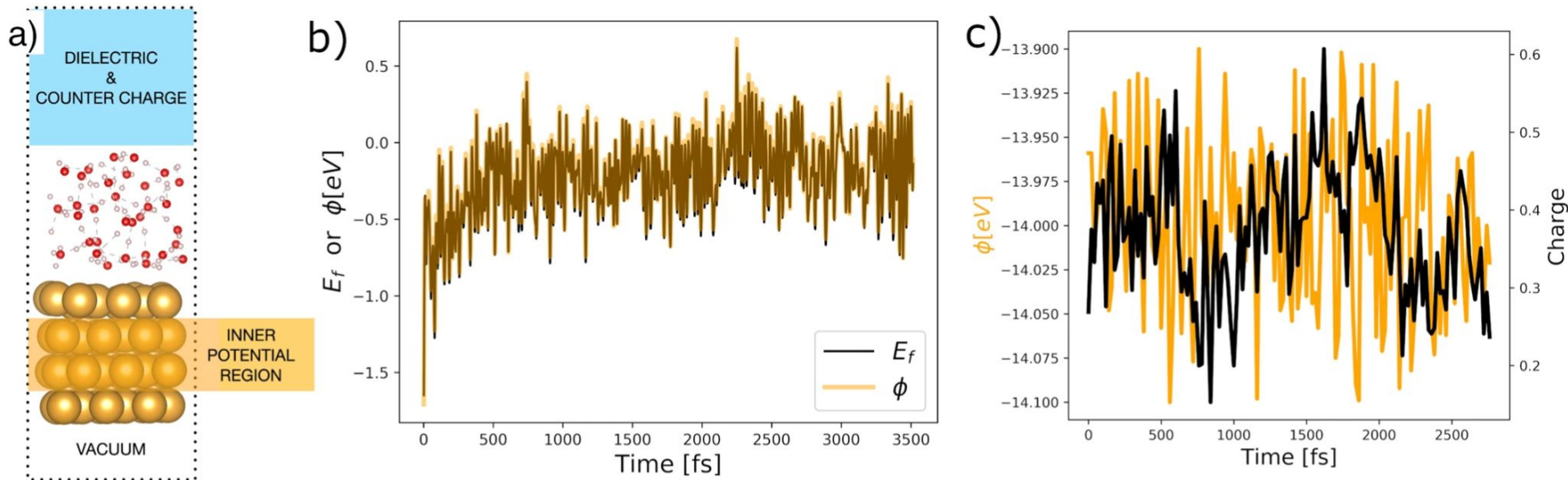
Goldsmith, Secor, Hammes-Schiffer, *ACS Cent. Sci.*, **2020**

Electrode potential in practice

- Note that a carefully constructed and bounded simulation cell allows for overwhelming localization of excess charge on one "active" surface

Kastlunger, Lindgren, Peterson, *JPC C*, **2018**

Dynamics exhibit the charge-potential relationship

- AIMD of water @ negatively polarized gold electrode done with both fixed charge and fixed (inner) potential
- Charge and potential behave like conjugate variables: fix one and the other fluctuates around an equilibrium value

Melander, Wu, Weckman, Honkala, *npj Comput. Mat.*, **2024**

Dynamics exhibit the charge-potential relationship
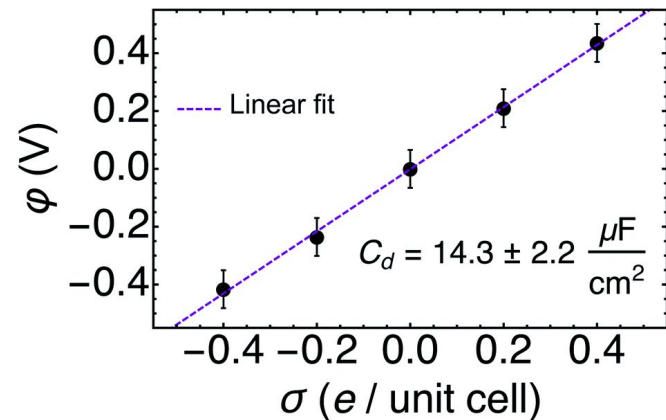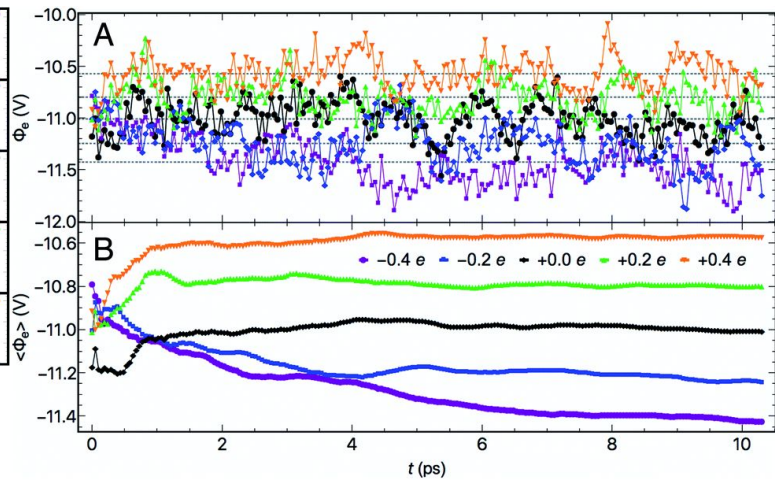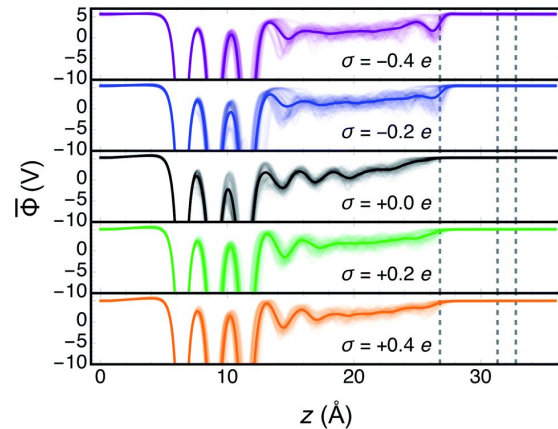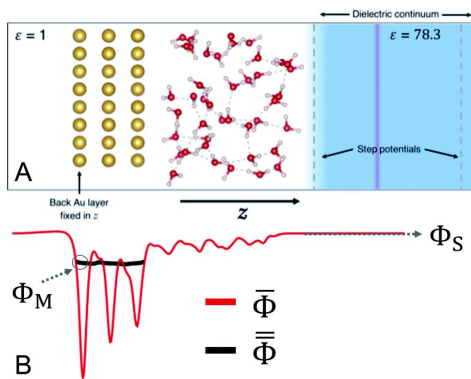
- AIMD of water @ gold electrode w/ 5 different constant charge values
- Average potential converges despite significant, persistent fluctuations
- Differential capacitance in agreement with experiment

Goldsmith, Calegari Andrade, Selloni, *Chem. Sci.*, **2021**

Machine learning in the GC ensemble

- Machine-learning in the GC ensemble for proton discharge on gold
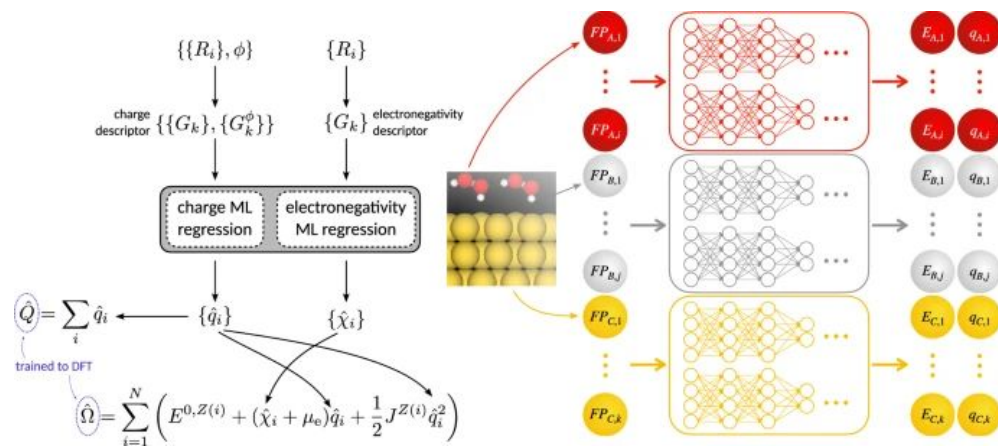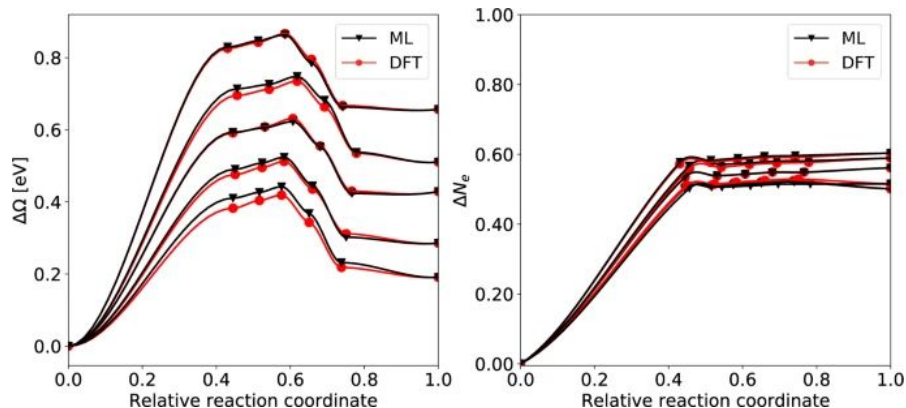- QEq-like approach coupled to GPAW periodic DFT with SJM for training
- One NN predicts charges from geometry + potential, one predicts electronegativities from geometry

$$\hat{Q} = \sum_i \hat{q}_i$$

trained to DFT

$$\hat{\Omega} = \sum_{i=1}^{N} \left(E^{0,Z(i)} + (\hat{\chi}_i + \mu_e)\hat{q}_i + \frac{1}{2} J^{Z(i)} \hat{q}_i^2 \right)$$

- Geometry encoding electronegativity → no need to designate surface/electrode atoms
- ML simulations reproduce Faradaic proton discharge at various voltages

Chen, Willard, Peterson et al., *npj Comp. Mat.,* **2023**

Machine learning in the GC ensemble

Constant-Potential Machine Learning Force Field for the Electrochemical Interface

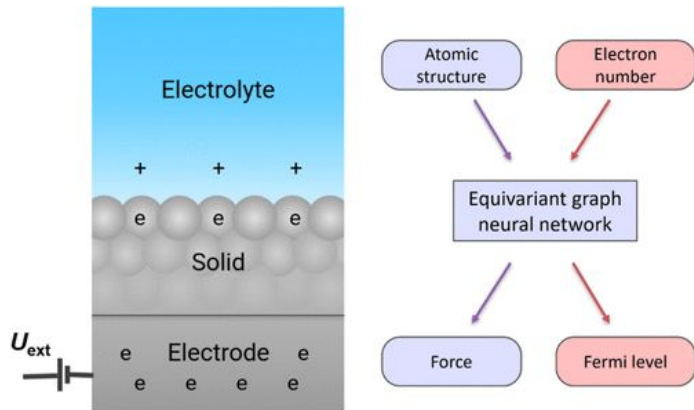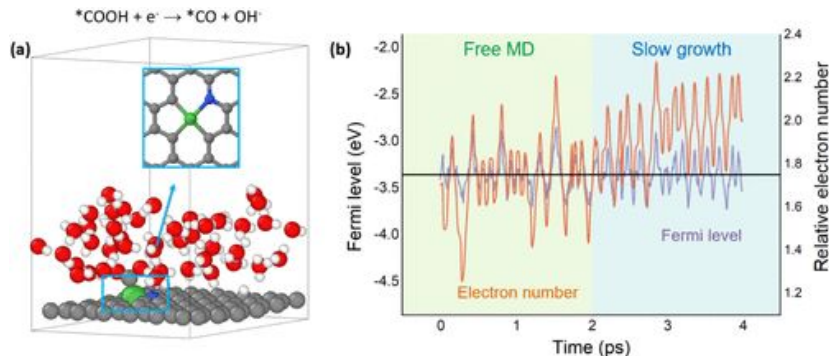Ruoyu Wang, Shaoheng Fang, Qixing Huang, and Yuanyue Liu*

Read Online

*COOH + e⁻ → *CO + OH⁻

- Fermi level can be learned in the training procedure
- This study trained at a single potential rather than one that can vary

Constant potential in charge-aware MD

Influence of surface topology and electrostatic potential on water/electrode systems 🛒

J. Ilja Siepmann; Michiel Sprik

In the CPM, the electric potential Ψ_i on each electrode atom is constrained at each simulation step to be equal to a preset applied external potential V, which is constant over a given electrode. This constraint leads to the following equation for the charge, q_i, on each electrode atom (where i indexes the atoms in the electrode):

$$V = \Psi_i = \frac{\partial U}{\partial q_i}, \qquad (1)$$

where U is the total Coulomb energy of the system.

Wang, Yang, Olmsted, Asta, Laird, *JCP*, **2014**

- Charges on <u>designated metal sites</u> satisfy a constraint according to the applied potential
- Equations of motion for *r* and q_i solved together

L3 L2 L1	-0.02 -0.01 0.00 0.01 0.02		R1 R2 R3
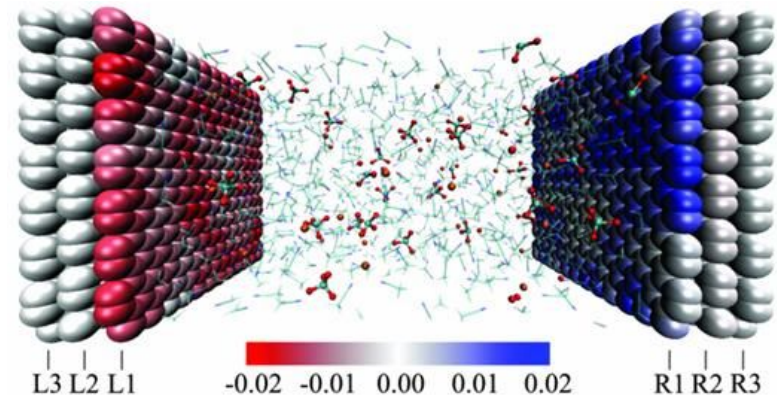
Model electrode in contact with aqueous electrolyte

- Ru2+/3+ "electrodes" in contact with aqueous NaCl
- Constant potential method engenders potential drop from one side of the cell to the other
- Electrostatic potentials in bulk solution are not flat at large biases, however
- Color coding shows how local polarization environment of electrode atoms allows for different partial charges

$$\nabla^2 \Psi = -\rho/\varepsilon_0$$

Willard, Reed, Madden, Chandler, *Faraday Discuss.,* **2009**
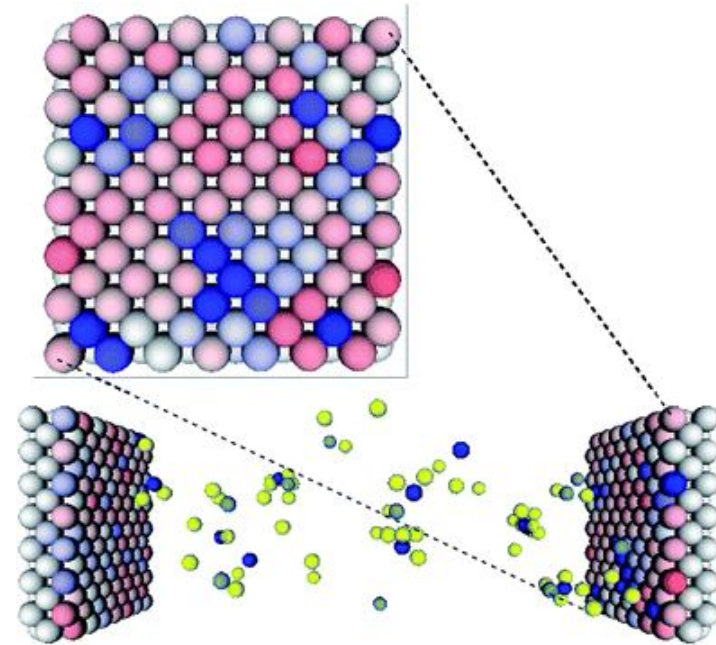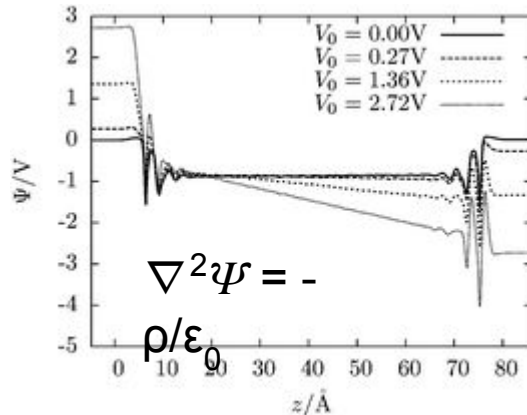
Model electrode in contact with aqueous electrolyte

- CPM for 2D periodic cell of graphene in contact with water
- SFG spectrum computed at various applied biases according to the method
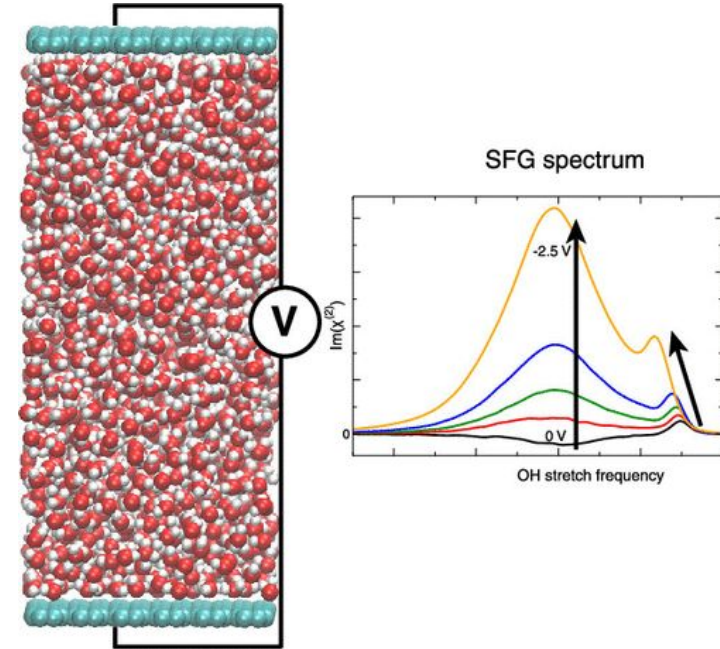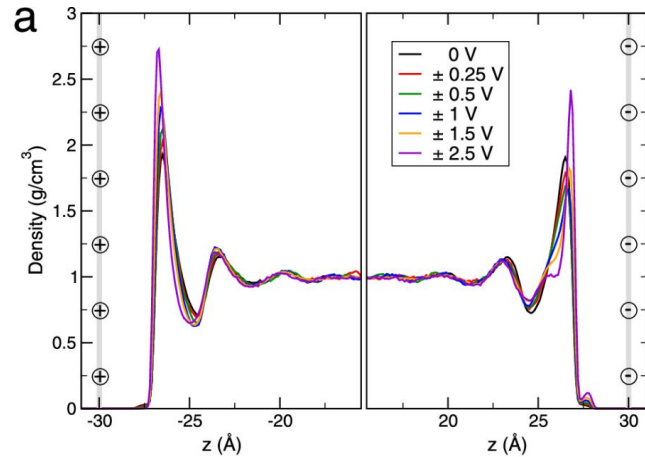
Zhang, Aguiar, Hynes, Laage, *JPCL,* **2020**

Coupling constant potential methods to MLIPs

- Siepmann-Sprik potentiostat can in principle be coupled to MLFFs
- DeepMD coupled to Siepmann-Sprik method adds the external potential as the long-range electrostatic part
  - Intra-system long-range electrostatics are also included via WCs
- Pt(111)-KF(aq) system studied
  - Pt cannot be described by WCs, so the electrode atoms had to be designated specifically for Siepmann-Sprik treatment

- There are not a lot of these examples, however

$$E(r, w, q) = E_{SR}(r) + E_{elec}(r, w, q).$$

Zhu & Cheng, *PRL,* **2025**
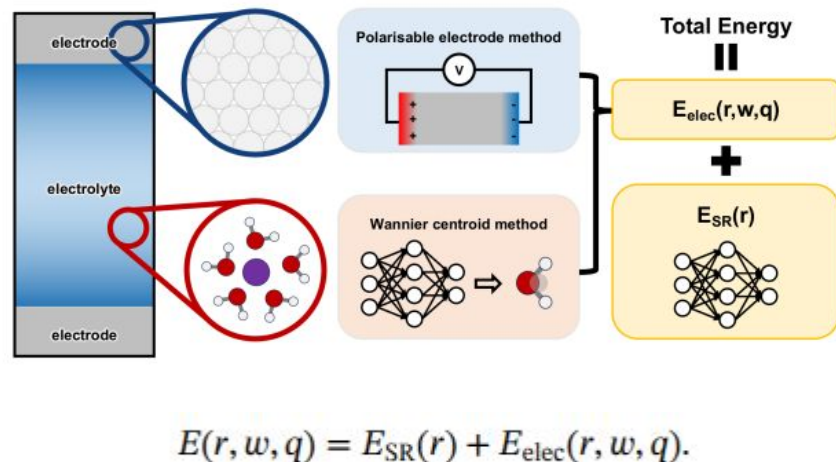
Coupling constant potential methods to MLIPs

- Li dendrite growth modeled with a MLFF+QEq model with constant potential method
- Lagrangian with piecewise scheme for applied potential on Li metal atoms

$$\mathcal{L} = E_{QEq} - \chi_{eq}\left(\sum_{i=1}^{N} Q_i - Q_{tot}\right) \qquad (3)$$

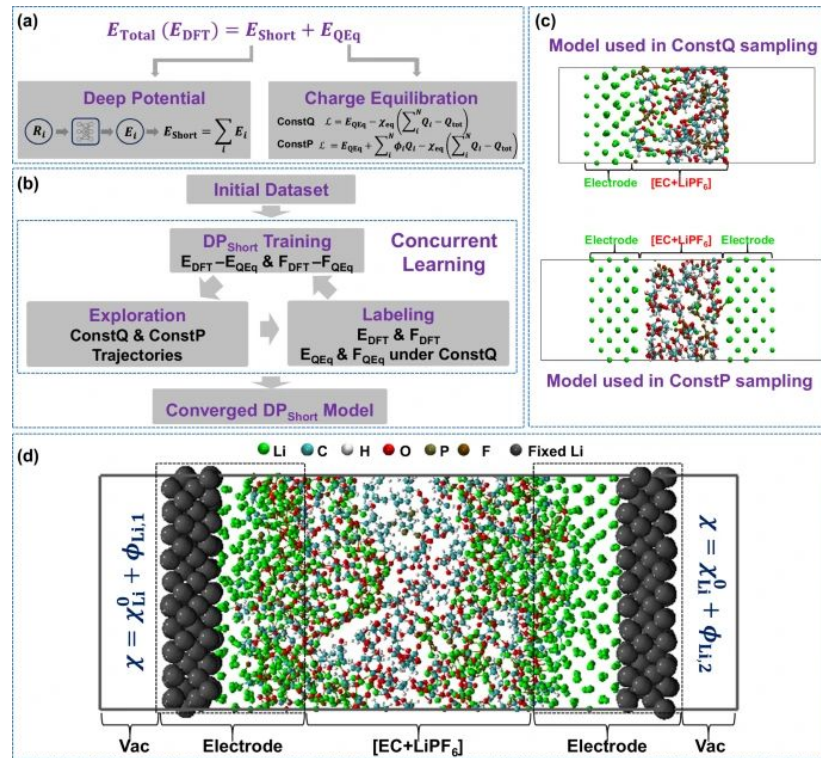The QEq charges $\{Q_i\}$ and the Lagrange multiplier χ_{eq} can thus be solved by

$$\begin{cases} \frac{\partial \mathcal{L}}{\partial Q_i} = 0 \\ \frac{\partial \mathcal{L}}{\partial \chi_{eq}} = 0 \end{cases} \qquad (4)$$

In the ConstP condition, we apply external potentials to electrode atoms with a set of predefined values $\{\phi_i\}$, and the grand energy of this system is given by

$$\Omega = E_{QEq} + \sum_{i=1}^{N} \phi_i Q_i \qquad (5)$$

where

$$\phi_i = \begin{cases} 0, & \text{if not Li} \\ 0, & \text{if Li, and} CN_{Li-Li} < CN_{Metal} \\ \phi_{Li,1}, & \text{if Li, } CN_{Li-Li} > CN_{Metal}, \text{and Li} \in \text{Anode side} \\ \phi_{Li,2}, & \text{if Li, } CN_{Li-Li} > CN_{Metal}, \text{and Li} \in \text{Cathode side} \end{cases} \qquad (6)$$

(a) $E_{Total}(E_{DFT}) = E_{Short} + E_{QEq}$
Deep Potential
$R_i \rightarrow E_i \rightarrow E_{Short} = \sum E_i$
Charge Equilibration
ConstQ $\mathcal{L} = E_{QEq} - \chi_{eq}\left(\sum_i^N Q_i - Q_{tot}\right)$
ConstP $\mathcal{L} = E_{QEq} + \sum_i^N \phi_i Q_i - \chi_{eq}\left(\sum_i^N Q_i - Q_{tot}\right)$

(b) Initial Dataset
DP_Short Training $E_{DFT} - E_{QEq}$ & $F_{DFT} - F_{QEq}$
Concurrent Learning
Exploration ConstQ & ConstP Trajectories
Labeling E_{DFT} & F_{DFT} E_{QEq} & F_{QEq} under ConstQ
Converged DP_Short Model

(c) Model used in ConstQ sampling — Electrode [EC+LiPF6]
Model used in ConstP sampling — Electrode [EC+LiPF6] Electrode

(d) Li • C • H • O • P • F • Fixed Li
$\chi = \chi_{Li}^0 + \phi_{Li,1}$ ... $\chi = \chi_{Li}^0 + \phi_{Li,2}$
Vac | Electrode | [EC+LiPF6] | Electrode | Vac

Xu et al., *Nat. Comm.*, **2025**

Applied potential vis-a-vis applied electric field

- A macroscopic electric field can impose a potential drop from one end of the cell to the other
- This can be equivalent to 2D CPM so long as the Ewald summation for finite field method is done in 2D PBC
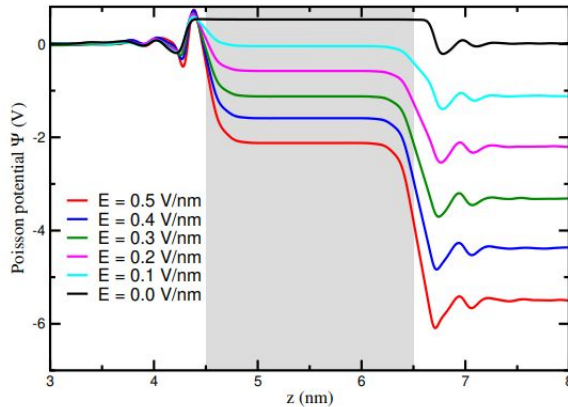
$$\Psi_j = \Psi_j^{PBC} - \mathbf{r}_j \cdot \mathbf{E}$$

- This method works even with empirical FFs
- "Double layer"-like potential drops at the interfaces and flat electrostatic potentials in bulk solid and bulk electrolyte
- Maybe an option at the multi-scale phase of the project

Dufils et al., *PRL,* **2019**
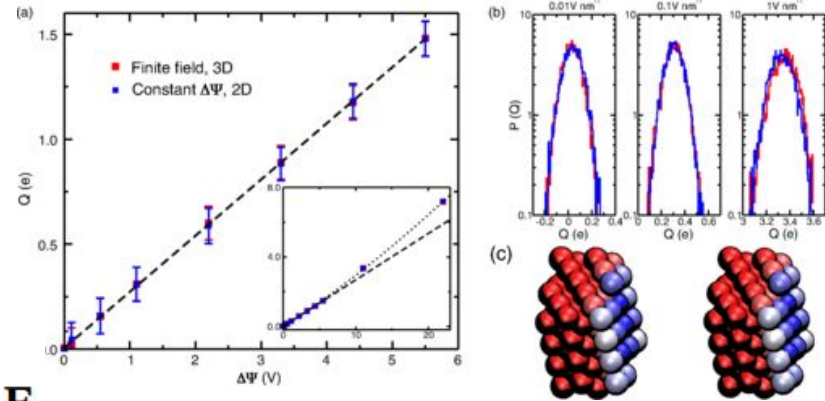
Applied *D*-field DeepMD
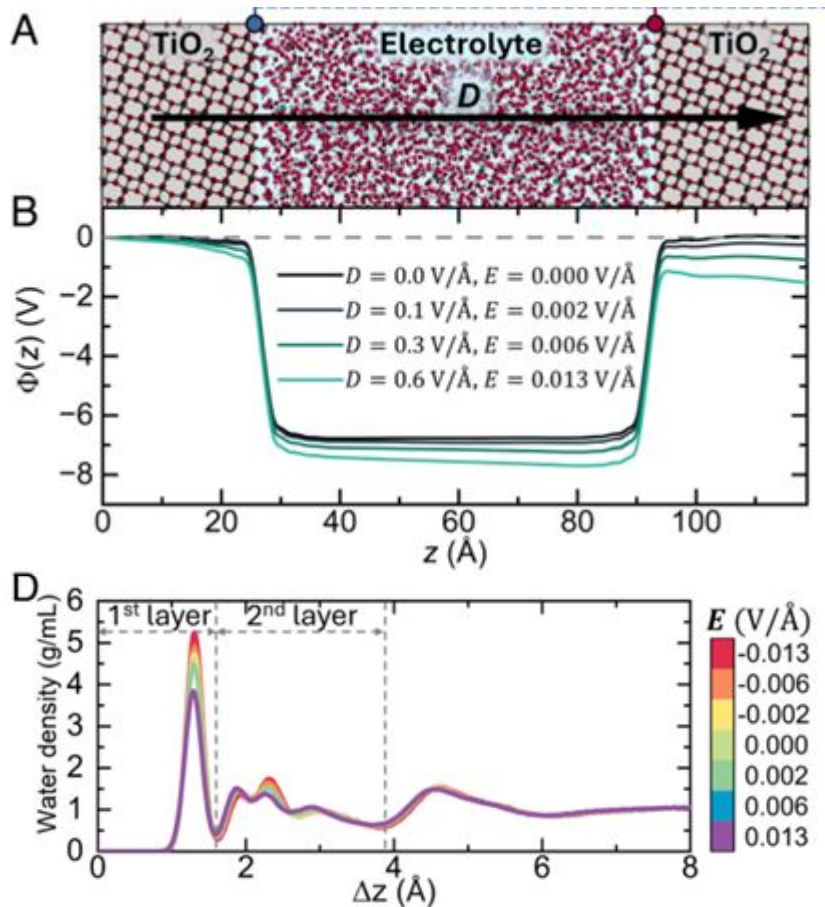
- Semiconductor-electrolyte interface studied with DPLR (Wannier function-based)
- Dynamics conducted with constant *D* field values: electrostatic potential drops a finite amount across the cell as a result
  - Const. *D* is the "open-circuit" condition
- Non-zero field in bulk solution is unphysical
  - Need to train in presence of field?
  - Finite size effect?
- Effects of field/potential on water structure and dissociation studied
- Constant *D* or *E* field methods may not be well-behaved for metallic electrodes

Zhang, Yu, Car, Selloni, *PNAS,* **2025**

Open questions for models and simulations

- Can models trained under half-cell conditions be transferred to full cell models?
  - Are grand-canonical models imbuing the same microscopic E fields as full cells?
- What happens in a CPM-MLFF setup when a Faradaic reaction occurs?
  - Is the electron/hole compensated for on the opposite electrode?
- What sorts of systems make sense to target, at least initially?
  - Large half cells?
  - Full cell with one PBC electrode? One side would possibly be a 'dummy' electrode
  - Full cells with anode and cathode? 2D PBC likely
- Practical concerns
  - GPAW+SJM is not very compatible with hybrid functionals; perhaps apply some corrections based on unbiased systems? Or need to develop software?
  - What integer number of voltages is sufficient in the training to describe a continuous range?