Grand-Canonical Variational Theory of Oscillatory Fields at Electrified Metal-Solution Interfaces

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Abstract The oscillatory fields near the electrode surface are not considered in the classical models of electrical double layer (EDL), while holding immense importance for stability, activity, and selectivity of interfacial reactions. Here, we develop a unified theoretical framework for oscillatory fields in the EDL under constant potential conditions, combining an orbital-free DFT treatment of electrons on the metal side and a statistical field theory of charged fluids on the electrolyte side. The resulting grand potential is a hybrid functional of electron density, electric potential, and solvent polarization, referred to as density-potential-polarization functional theory (DPPFT). Built on the DPPFT, an EDL model for the Ag(110)-KPF₆ aqueous interface is parameterized with experimental double layer capacitance (C_{dl}) data. The calibrated model is then employed to study the influence of electronic, ion, and solvent properties on the EDL structure and capacitance. C_{dl} profiles at different crystal faces and in various electrolyte solutions are rationalized coherently. We reveal that intensified ion layering leads to elevated capacitances at the potential of zero charge (PZC) and narrowed ionic peaks in the C_{dl} profile. Contrary to classical models, the DPPFT model allows co-ions to have an appreciable density near the electrode surface, opening an avenue to decipher the origin of the anomalous anion effects on electrochemical CO₂ reduction. The presented framework adds much-needed realism to the modelling of EDLs.

Keywords density-potential-polarization functional theory, statistical field theory, constant potential, differential capacitance, electric double layer, oscillatory fields, layered structure

1 Introduction

The physics at electrified interfaces is the foundational basis of numerous research fields, including but not limited to electrochemistry [1–4], nanofluidics [5–7], biology [8,9], and geological science [10]. In a nutshell, when an electronic conductor, often a metal, is immersed into an ionic conductor, often an aqueous solution, electronic and ionic charge of same magnitude but opposite sign assemble at the interface between the adjacent phases, forming an electric double layer (EDL).

Understanding the interactions between electrons, ions, and solvent molecules within the EDL has been a topic of intense research for the past two centuries. Current textbook understanding is neatly condensed into the Gouy-Chapman-Stern-Grahame (GCSG) model [11,12], which describes the EDL as an inner compact layer and an outer diffuse layer. The inner layer is further divided into an inner Helmholtz plane (IHP) of specifically adsorbed ions and an outer Helmholtz plane (OHP) at the position of the closest nonspecifically adsorbed ions. Ion densities in the diffuse layer are determined by the interplay between electrostatic, thermal, and short-range hard-sphere forces. The GCSG model is well-established for mercury-like metals [13–15], as well as for sd metals like Ag and Au [16–21]. Applicability of the GCSG model for Pt-type electrodes remains a topic of heated discussion [22–25].

The GCSG model and its variants are often criticized for the absence of two characteristic features of an EDL. The first one is metal electronic effects [26,27]. The second one is the absence of oscillations in the electric potential and ion densities in the nanoscale region just outside the electrode surface that appear in every atomistic or molecular simulation [28–30]. Addressing metal electronic effects, the jellium models developed in the 1980s allow us to understand the dependency of the inner layer capacitance on the nature of the metal [31–33]. Nowadays, Kohn-Sham density functional theory (DFT) based models provide a largely satisfactory description of metal electronic effects. Oscillatory fields were first sensed by surface force apparatus (SFA) in the pioneering work by Pashley and Israelachvili *et al.* [34–36] Later, advances in experimental techniques such as atomic force microscopy (AFM) [37,38], have enabled their more detailed investigation. For instance, Mugele *et al.* detected oscillatory forces on mica and amorphous silica surfaces in aqueous solution using an ultra-sharp AFM tip with a radius of 1-2 nm [38].

The oscillatory fields near the electrode surface are crucial for the stability of colloidal particles and macromolecules like DNA, as well as the activity and selectivity of electrochemical reactions. Recently, Kornyshev *et al.* gave a historical account of interests in the former aspect [39], and herein, we complement their account by focusing on the latter aspect. All electrochemical reactions occur in the EDL, and the oscillatory fields dramatically change the local reaction conditions for reactions, including the concentration of the reactant(s) and product(s), electrostatic driving force, and solvent reorganization free energy. Early on, these local reaction conditions were accounted for in the Frumkin corrections based on the notation of a reaction plane [3,40–45]. The reaction plane may be a good approximation in the mean-field type GCSG model, while it

becomes problematic in the presence of oscillatory local reaction conditions. Instead, the notation of a reaction volume considering the discreteness and oscillatory distribution of charges near the electrode surface is necessary [46,47].

On the theory side, the oscillatory fields in the EDL can be captured by phenomenological theories of structured liquids. For this end, Berthoumieux *et al.* employed the Landau-Ginzburg approach where solvent interactions are described as a functional of the solvent polarization [39,48,49]. In this theory, electric potential and solvent polarization are two coupled field variables of the electrolyte solution. The oscillations of electric potential and solvent polarization, alongside the layered structure of ions, are delineated by this theory [39]. Recently, Blossey and Podgornik have developed a comprehensive continuum theory rooted in statistical field theory, in which they further coupled the ion charge density with the solvent polarization, enabling the description of short-range interactions between ions and solvent [50–52]. These literature works have described the electrolyte solution. This treatment neglects the built-in electric field at the metal surface and its influence over the oscillatory fields. It is unclear how the built-in electric field distorts the oscillatory fields in the EDL.

While the two key drawbacks of the GCSG model can be treated by Kohn-Sham DFT and Landau–Ginzburg theory, a unified framework considering the interactions between electrons on the metal side and classical oscillatory fields on the electrolyte side is, to the best of our knowledge, missing. This work addresses this gap by developing a computationally efficient, grand-canonical, variational theory for metal electronic effects and oscillatory fields in the EDL. In the remainder of this paper, we first formulate the grand potential of the EDL by combining the orbital-free density functional theory (OFDFT) of quantum mechanical electrons and the statistical field theory of charged fluids on the electrolyte side. The theory describes the grand potential of the EDL as a functional of three field variables, *i.e.*, the electron density, the electric potential, and the solvent polarization field, hence referred to as a density-potential-polarization functional analysis of the grand potential. The DPPFT model is parameterized with experimental data for the differential capacitance (C_{dl}) of the Ag(110)-KPF₆ aqueous interface. The calibrated model is then employed to study the influence of model parameters, including electronic structure parameters, ionic properties, and solvent properties, on the interfacial structure and C_{dl} profiles.

2 Theory development

2.1 Grand potential of EDL

The metal comprises cationic cores and electrons, while the electrolyte comprises cations, anions, and solvent molecules (denoted by cc, e, c, a, s subscripts). The grand potential Ω of the electrochemical interface is obtained by a Legendre-transformed from the Helmholtz free energy *F*,

$$\Omega = F - \int_{r} \left(n_{\rm e} \tilde{\mu}_{\rm e} + \sum_{i={\rm a,c,s}} n_{i} \tilde{\mu}_{i} \right) \tag{1}$$

where $\tilde{\mu}_{e}$ and $\tilde{\mu}_{i}$ are electrochemical potentials of electrons and electrolyte component *i*, and n_{e} and n_{i} represent their number densities. The subscript of the integral sign denotes the integral variable. *r* represents the spatial coordinates, and \int_{r} is a short-hand notation for $\iiint dxdydz$. Following ref. [53,54], the Helmholtz free energy is decomposed as,

$$F = F_{\mathbb{Q}} + F_{\mathbb{C}} + F_{\otimes} \tag{2}$$

where $F_{\mathbb{Q}}$ describes the quantum-mechanical interactions of the inhomogeneous electron gas in the metal, $F_{\mathbb{C}}$ describes the classical interactions between all particles in both phases, and F_{\otimes} describes the short-range interactions between the metal and the electrolyte particles.

2.2 The metal

In the orbital-free DFT (OFDFT) formalism, $F_{\mathbb{Q}}$ is written as,

$$F_{\mathbb{Q}} = T_{\text{in}}[n_{\text{e}}, \nabla n_{\text{e}}, \dots] + U_{\text{XC}}[n_{\text{e}}, \nabla n_{\text{e}}, \dots]$$
(3)

where T_{ni} is the kinetic energy of non-interacting electrons and U_{XC} the exchange-correlation energy. They are functionals of electron density, ∇n_e , $\nabla^2 n_e$, etc. T_{ni} is described by Thomas-Fermi-von Weizsäcker (TFvW) theory [55–57],

$$T_{\rm ni}[n_{\rm e}] = \int_{r} e_{\rm au} a_0^{-3} t_{\rm TF} (1 + \theta_{\rm T} s^2)$$
(4)

with the volumetric kinetic energy that is given by the Thomas-Fermi theory, $t_{\rm TF} = \frac{3}{10} (3\pi^2)^{\frac{2}{3}} (n_{\rm e}a_0^3)^{\frac{5}{3}}$, the correction for gradient terms, $(1 + \theta_{\rm T}s^2)$, and the reduced gradient term, $s = \frac{1}{2} (3\pi^2)^{-\frac{1}{3}} |\nabla n_{\rm e}| (n_{\rm e})^{-\frac{4}{3}}$. $\theta_{\rm T}$ is a coefficient for the contribution of the gradient term in the kinetic energy. $e_{\rm au}a_0^{-3}$ is used to transform the expression from atomic units to SI units, with atomic energy $e_{\rm au} = \frac{e_0^2}{4\pi\epsilon_0 a_0}$, Bohr radius a_0 , elementary charge e_0 , and vacuum permittivity ϵ_0 .

The exchange-correlation energy $U_{\rm XC}$ is the sum of an exchange part $u_{\rm X}$ and a correlation part $u_{\rm C}$ [34],

$$U_{\rm XC} = \int_{r} (u_{\rm X} + u_{\rm C}) \tag{5}$$

 u_X and u_C are described by the Perdew-Burke-Ernzerhof (PBE) functional [58]. u_X is formulated as,

$$u_{\rm X} = e_{\rm au} a_0^{-3} u_{\rm X}^0 (1 + \theta_{\rm X} s^2) \tag{6}$$

with the volumetric exchange energy of a uniform electron gas, $u_X^0 = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{1}{3}} (n_e a_0^3)^{\frac{4}{3}}$. θ_X is a coefficient for the contribution of the gradient term in the exchange energy. Similarly, u_C is formulated as,

$$u_{\rm C} = e_{\rm au} a_0^{-3} (u_{\rm C}^0 + (n_{\rm e} a_0^3) \theta_{\rm C} t^2)$$
⁽⁷⁾

with the reduced gradient term $t = \frac{1}{4} \left(\frac{3}{\pi}\right)^{-\frac{1}{6}} a_0^4 |\nabla n_e| (n_e a_0^3)^{-\frac{7}{6}}$. θ_c is a coefficient for the contribution of the gradient term in the correlation energy. u_c^0 is the volumetric correlation energy of a uniform electron gas, for which we use the interpolation scheme of Perdew *et al.* [59], $u_c^0 = -2a_1(1 + a_2r_s)(n_ea_0^3)\ln(1/\xi + 1)$, with the term $\xi = 2a_1(a_3r_s^{1/2} + a_4r_s + a_5r_s^{3/2} + a_6r_s^2)$, the radius $r_s = (4\pi n_ea_0^3/3)^{-\frac{1}{3}}$, the coefficients $a_1 = 0.0310907, a_2 = 0.2137, a_3 = 7.5957, a_4 = 3.5876, a_5 = 1.6382, a_6 = 0.49294$.

Three aspects regarding the description of metal electrons need to be noted. Firstly, if we consider all electrons in the metal, pseudopotentials for the cationic cores are not required anymore. Secondly, the electrostatic potential energy of electrons and cationic cores is included in $F_{\mathbb{C}}$. Thirdly, the entropy of the electron gas can be implicitly considered in the parameters of electronic functionals, T_{ni} and U_{XC} , which are temperature-dependent as in ref [60].

2.3 The electrolyte solution

Following Blossey and Podgornik [50,51], the classical part is treated by field-theoretic continuum theory, encompassing both electrostatic and non-electrostatic interactions between classical particles. We consider an electrolyte containing a pair of monovalent ions. We first introduce four fields, *i.e.*, the charge density field of cations $\hat{\rho}_c$, the charge density field of anions $\hat{\rho}_a$, the polarization field \hat{P} and the overall charge density field $\hat{\rho}$. Their spatial distributions depend on the positions of cations r_c , anions r_a , solvent molecules r_s , and the orientations of solvent molecules n,

$$\hat{\rho}_{\rm c} = e_0 \sum_{N_{\rm c}} \delta(r - r_{\rm c}) \tag{8}$$

$$\hat{\rho}_{a} = -e_{0} \sum_{N_{a}} \delta(r - r_{a}) \tag{9}$$

$$\widehat{\boldsymbol{P}}(r) = p \sum_{N_c} \boldsymbol{n} \delta(r - r_s) \tag{10}$$

$$\hat{\rho}(r) = \hat{\rho}_{c}(r) + \hat{\rho}_{a}(r) + \nabla \cdot \hat{P}(r) + \rho^{ex}(r)$$
(11)

where N_c , N_a are the number of cations and anions and the summations over them iterate over the positions of all ions. N_s is the number of solvent molecules, and the summations iterate over the positions and orientations of all solvent molecules. p is the magnitude of solvent dipole moment. Here, n is defined as the normal vector pointing from the center of positive charge of a solvent molecule to that of negative charge of a solvent molecule. In this definition, the bound charge (polarization charge) distribution generated by the solvent polarization is expressed as,

$$\hat{\rho}_{\mathbf{b}}(r) = \nabla \cdot \hat{\boldsymbol{P}}(r) \tag{12}$$

The interaction energy of the classical part can be expressed as a functional of the above four fields and their gradients. Following ref. [50,51], it comprises of three parts,

$$\widehat{H}[\widehat{\rho}_{c},\widehat{\rho}_{c},\widehat{\rho},\widehat{P}] = \widehat{H}_{es}[\widehat{\rho}] + \widehat{H}_{corr}[\widehat{P}] + \widehat{H}_{sr}[\widehat{\rho}_{c},\widehat{\rho}_{a},\widehat{P}]$$
(13)

where \hat{H}_{es} is the total electrostatic energy between charged particles. For a given configuration, it can be expressed by a standard Coulomb interaction,

$$\widehat{H}_{es}[\widehat{\rho}] = \frac{1}{2} \int_{r,r'} \widehat{\rho}(r) G(r,r') \widehat{\rho}(r')$$
(14)

where $G(r,r') = \frac{1}{4\pi\epsilon_{\infty}|r-r'|}$ is the Coulomb interaction potential with its inverse operator being $G^{-1}(r,r') = -\epsilon_{\infty} \nabla^2 \delta(r-r')$, and ϵ_{∞} being the high-frequency dielectric permittivity accounting for the non-configurational polarization.

 H_{corr} is the correlational energy between solvent molecules, which originates from short-range interactions, due to the coupling between non-local polarization fields. Following ref. [50,51], we expand the coupling potential to fourth order, namely, \hat{H}_{corr} can be expressed as the quadratic functional of polarization field \hat{P} , its gradient $\nabla \cdot \hat{P}$, and its second order gradient $\nabla^2 \hat{P}$,

$$\widehat{H}_{\text{corr}}[\widehat{\boldsymbol{P}}] = \frac{1}{2\epsilon_0} \int_r \left(K_{\text{s}} \widehat{\boldsymbol{P}}^2 + K_{\alpha} \left(\nabla \cdot \widehat{\boldsymbol{P}} \right)^2 + K_{\beta} \left(\nabla^2 \widehat{\boldsymbol{P}} \right)^2 \right)$$
(15)

where K_s, K_α, K_β are phenomenological coefficients of expanded terms. K_s is dimensionless, while $K_{\alpha}^{\frac{1}{2}}, K_{\beta}^{\frac{1}{4}}$ have the dimension of length.

 \hat{H}_{sr} is the short-range interaction between the charge density of ions and the solvent polarization field. This term describes the coupling between the solvent polarization and the charge density of ions, which is related to the solvation of ions. To the lowest order, \hat{H}_{sr} can be expressed as a functional of ionic density field and the gradient of polarization field [50,51],

$$\widehat{H}_{\rm sr}[\widehat{\rho}_{\rm c},\widehat{\rho}_{\rm a},\widehat{\boldsymbol{P}}] = \alpha_{\rm c} \int_{r} \widehat{\rho}_{\rm c} \nabla \cdot \widehat{\boldsymbol{P}} + \alpha_{\rm a} \int_{r} \widehat{\rho}_{\rm a} \nabla \cdot \widehat{\boldsymbol{P}}$$
(16)

where α_c , α_a are two parameters that characterize the strength of short-range correlations between solvent and cations and between solvent and anions, respectively. In the classical interaction energy \hat{H} , the total solvation energy \hat{H}_{sol} , arising from all interactions between ions and solvent molecules, is then,

$$\widehat{H}_{\text{sol}}[\widehat{\rho}_{c},\widehat{\rho}_{a},\widehat{P}] = \int_{r} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \cdot P(r') + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r} G(r,r') \right) \nabla \cdot P(r') + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} G(r,r') \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left(\alpha_{c} + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \right) \nabla \left((17) + \int_{r'} \widehat{\rho}_{c}(r) \right$$

Since G(r, r') is positive, negative values of α_c and α_a indicate that short-range correlations effectively reduce the impact of electrostatic interactions between ions and surrounding solvent molecules. This destabilizes the solvation structure governed by electrostatic interactions, resulting in a less negative solvation energy. Conversely, positive values of α_c and α_a effectively enhance electrostatic interactions between ions and surrounding solvent molecules, strengthen the solvation structure, and result in a more negative solvation energy.

The grand canonical partition function Z_{gc} for the system with Hamiltonian \hat{H} , is defined as,

$$Z_{\rm gc}[T, \{\tilde{\mu}_i\}] = \sum_{N_{\rm s}} \sum_{N_{\rm c}} \sum_{N_{\rm a}} \lambda_{\rm s}^{N_{\rm s}} \lambda_{\rm c}^{N_{\rm c}} \lambda_{\rm a}^{N_{\rm a}} Z_{\rm c}$$
(18)

with

$$Z_{c}[T, \{N_{i}\}] = \frac{1}{\Lambda_{s}^{3N_{s}}\Lambda_{c}^{3N_{a}}} \frac{1}{N_{s}!N_{c}!N_{a}!} \int_{\mathbb{C}} \exp\left(-\beta\widehat{H}\left[\hat{\rho}_{c}, \hat{\rho}_{a}, \hat{\rho}, \widehat{P}\right]\right)$$
(19)

where $\lambda_i = e^{\beta \tilde{\mu}_i}$ is the fugacity of electrolyte component $i, \beta = \frac{1}{k_B T}$ is the thermal constant, with Boltzmann constant k_B . The thermal de Broglie wavelength, Λ_i , ensures a dimensionless partition function. Z_c is the canonical partition function with temperature T, and particle number $\{N_i\}$. The subscript \mathbb{C} represents the integral measure over all configurational coordinates of particles.

To develop the field theoretic representation of the partition function, we first introduce a set of collective fields by utilizing the sifting property of the Dirac delta functional. For example, given a functional $f(\hat{\varrho})$ of the field $\hat{\varrho}$, a collective field ϱ can be introduced using the sifting property of the Dirac delta functional $\delta(\varrho - \hat{\varrho})$, *i.e.*,

$$f(\hat{\varrho}) = \int_{\varrho} \delta(\varrho - \hat{\varrho}) f(\varrho)$$
⁽²⁰⁾

In such a way, we can introduce four collective fields ρ_c , ρ_a , ρ , P respectively corresponding to the previously defined fields $\hat{\rho}_c$, $\hat{\rho}_a$, ρ , \hat{P} in the integral kernel of Z_c in Eq. 19,

$$\exp\left(-\beta \widehat{H}[\widehat{\rho}_{c},\widehat{\rho}_{a},\widehat{\rho},\widehat{P}]\right) = \int_{\rho_{c}} \int_{\rho_{a}} \int_{P} \int_{\rho} \left(\prod_{\varrho=\rho_{c},\rho_{a},\rho,P} \delta(\varrho-\widehat{\varrho})\right) \exp\left(-\beta H[\rho_{c},\rho_{a},\rho,P]\right)$$
(21)

with,

$$H = \frac{1}{2} \int_{r,r'} \rho(r) G(r,r') \rho(r') + \frac{1}{2\epsilon_0} \int_r \left(K_{\rm s} \boldsymbol{P}^2 + K_\alpha (\nabla \cdot \boldsymbol{P})^2 + K_\beta (\nabla^2 \boldsymbol{P})^2 \right) + \alpha_{\rm c} \int_r \rho_{\rm c} \nabla \cdot \boldsymbol{P}$$

$$+ \alpha_{\rm a} \int_r \rho_{\rm a} \nabla \cdot \boldsymbol{P}$$
(22)

The collective fields are functions of spatial coordinates only. Further, the auxiliary field φ^* corresponding to the collective field ϱ in Eq. 21 can be introduced by Fourier transform to ϱ in the Dirac delta functional $\delta(\varrho - \hat{\varrho})$ [61], *i.e.*,

$$\delta(\varrho - \hat{\varrho}) = \int_{\varphi^*} \exp\left(-i \int_r \beta \varphi^*(\varrho - \hat{\varrho})\right)$$
(23)

In such a way, we introduce another four auxiliary fields $\phi_c^*, \phi_a^*, \phi^*, \mathcal{E}^*$ respectively corresponding to the collective fields ρ_c, ρ_a, ρ, P in Eq. 21. The auxiliary fields are functions of spatial coordinates only. Then Z_c is reformulated as,

$$Z_{\rm c} = \frac{1}{\Lambda_{\rm s}^{3N_{\rm s}}\Lambda_{\rm c}^{3N_{\rm c}}\Lambda_{\rm a}^{3N_{\rm a}}} \frac{1}{N_{\rm s}! N_{\rm c}! N_{\rm a}!} \int_{\mathbb{F}} \exp\left(-\beta \begin{pmatrix} H+i \int_{r} \boldsymbol{\mathcal{E}}^{*} \cdot \boldsymbol{P} + i \int_{r} \phi^{*} \rho \\ +i \int_{r} \phi^{*}_{\rm c} \rho_{\rm c} + i \int_{r} \phi^{*}_{\rm a} \rho_{\rm a} \end{pmatrix}\right) Z_{\rm c}^{0}$$
(24)

with

$$Z_{\rm c}^{0} = \int_{\mathbb{C}} \exp\left(i\beta \int_{r} \left(\boldsymbol{\mathcal{E}}^{*} \cdot \boldsymbol{\widehat{P}} + \phi^{*} \boldsymbol{\widehat{\rho}} + \phi^{*}_{\rm c} \boldsymbol{\widehat{\rho}}_{\rm c} + \phi^{*}_{\rm a} \boldsymbol{\widehat{\rho}}_{\rm a}\right)\right)$$
(25)

where the subscript \mathbb{F} denotes the integral measure over all collective fields and all auxiliary fields. The exponential term in Z_c^0 is evaluated as follows,

$$i\beta \int_{r} (\phi^{*}\hat{\rho} + \phi_{c}^{*}\hat{\rho}_{c} + \phi_{a}^{*}\hat{\rho}_{a} + \mathcal{E}^{*} \cdot \hat{P})$$

$$= i\beta \int_{r} \phi^{*} \left(e_{0} \sum_{N_{c}} \delta(r - r_{c}) - e_{0} \sum_{N_{a}} \delta(r - r_{a}) + p \sum_{N_{s}} \mathbf{n} \cdot \nabla \delta(r - r_{s}) \right)$$

$$+ \rho^{ex}(r) + i\beta e_{0} \int_{r} \phi_{c}^{*} \sum_{N_{c}} \delta(r - r_{c}) - i\beta e_{0} \int_{r} \phi_{a}^{*} \sum_{N_{a}} \delta(r - r_{a})$$

$$+ i\beta \int_{r} p \mathcal{E}^{*} \cdot \sum_{N_{s}} \mathbf{n} \delta(r - r_{s})$$

$$= i\beta p \sum_{N_{s}} \mathbf{n} \cdot (\mathcal{E}^{*}(r_{s}) - \nabla \phi^{*}(r_{s})) + i\beta e_{0} \sum_{N_{c}} (\phi^{*}(r_{c}) + \phi_{c}^{*}(r_{c}))$$

$$- i\beta e_{0} \sum_{N_{a}} (\phi^{*}(r_{a}) + \phi_{a}^{*}(r_{a})) + i\beta \int_{r} \phi^{*} \rho^{ex}$$

$$(26)$$

where the first equality is obtained by recalling the definition of fields in Eq. 8-11, and the second

equality utilizes the sifting property of the Dirac delta function, as shown in Eq. 20. Z_c^0 is then calculated as,

$$Z_{c}^{0} = \left(\int_{r} \exp(i\beta e_{0}\phi^{*} + i\beta e_{0}\phi_{c}^{*})\right)^{N_{c}} \left(\int_{r} \exp(-i\beta e_{0}\phi^{*} - i\beta e_{0}\phi_{a}^{*})\right)^{N_{a}} \left(\int_{r} d\boldsymbol{n} \exp(i\beta p\boldsymbol{n} + (\boldsymbol{\mathcal{E}}^{*} - \nabla\phi^{*}))\right)^{N_{s}} \exp\left(i\beta\int_{r}\phi^{*}\rho^{ex}\right)$$
(27)

The integration over n for solvent molecules can be done straightforward by going to spherical coordinates, *i.e.*,

$$\int d\boldsymbol{n} \exp(i\beta p\boldsymbol{n} \cdot (\boldsymbol{\mathcal{E}}^* - \nabla \phi^*)) = \frac{1}{4\pi} \int_0^{\pi} d\theta \sin \theta \int_0^{2\pi} d\omega \exp(i\beta p \cos \theta |\boldsymbol{\mathcal{E}}^* - \nabla \phi^*|)$$

$$= \frac{\sin(\beta p |\boldsymbol{\mathcal{E}}^* - \nabla \phi^*|)}{\beta p |\boldsymbol{\mathcal{E}}^* - \nabla \phi^*|}$$
(28)

where θ is the angle between \boldsymbol{n} and z axis, ω is the polar angle. Z_{gc} is rearranged into,

$$Z_{\rm gc} = \int_{\mathbb{F}} \exp\left(-\beta \left(H + i \int_{r} \boldsymbol{\mathcal{E}}^* \cdot \boldsymbol{P} + i \int_{r} \phi^* \rho + i \int_{r} \phi^*_{\rm c} \rho_{\rm c} + i \int_{r} \phi^*_{\rm a} \rho_{\rm a} - i \int_{r} \phi^* \rho^{\rm ex}\right)\right) W \tag{29}$$

with the series function,

$$W = \sum_{N_{s}} \sum_{N_{c}} \sum_{N_{a}} \frac{1}{\left(\frac{\lambda_{a}}{\Lambda_{a}^{3}} \int_{r} \exp(i\beta e_{0}\phi^{*} + i\beta e_{0}\phi_{c}^{*})\right)^{N_{c}}}{\left(\frac{\lambda_{a}}{\Lambda_{a}^{3}} \int_{r} \exp(-i\beta e_{0}\phi^{*} - i\beta e_{0}\phi_{a}^{*})\right)^{N_{a}} \left(\frac{\lambda_{s}}{\Lambda_{s}^{3}} \frac{\sin(\beta p |\boldsymbol{\mathcal{E}}^{*} - \nabla \phi^{*}|)}{\beta p |\boldsymbol{\mathcal{E}}^{*} - \nabla \phi^{*}|}\right)^{N_{s}}}$$
(30)

It can be found that W is exactly the series expansion of an exponential function, *i.e.*,

$$W = \exp\left(\frac{\lambda_{\rm c}}{\Lambda_{\rm c}^3}\int_r \exp(i\beta e_0\phi^* + i\beta e_0\phi_{\rm c}^*)\right)\exp\left(\frac{\lambda_{\rm a}}{\Lambda_{\rm a}^3}\int_r \exp(-i\beta e_0\phi^*) - i\beta e_0\phi_{\rm a}^*)\right)\exp\left(\frac{\lambda_{\rm s}}{\Lambda_{\rm s}^3}\int_r \frac{\sin(\beta p|\boldsymbol{\mathcal{E}}^* - \nabla\phi^*|)}{\beta p|\boldsymbol{\mathcal{E}}^* - \nabla\phi^*|}\right)$$
(31)

 $Z_{\rm gc}$ is then reformulated as,

$$Z_{\rm gc} = \int_{\mathbb{F}} \exp\left(-\beta \left(H + i \int_{r} \boldsymbol{\mathcal{E}}^{*} \cdot \boldsymbol{P} + i \int_{r} \phi^{*} \rho + i \int_{r} \phi^{*}_{c} \rho_{\rm c} + i \int_{r} \phi^{*}_{\rm a} \rho_{\rm a} - i \int_{r} \phi^{*} \rho^{\rm ex} - V\right)\right)$$
(32)

with

$$V = \frac{1}{\beta} \int_{r} \left(\frac{\lambda_{c}}{\Lambda_{c}^{3}} \exp(i\beta e_{0}\phi^{*} + i\beta e_{0}\phi_{c}^{*}) + \frac{\lambda_{a}}{\Lambda_{a}^{3}} \exp(-i\beta e_{0}\phi^{*} - i\beta e_{0}\phi_{a}^{*}) + \frac{\lambda_{s}}{\Lambda_{s}^{3}} \frac{\sin(\beta p |\boldsymbol{\mathcal{E}}^{*} - \nabla \phi^{*}|)}{\beta p |\boldsymbol{\mathcal{E}}^{*} - \nabla \phi^{*}|} \right)$$
(33)

2.4 Saddle-point approximation

Within the saddle point approximation, the auxiliary fields are purely imaginary, i.e., $\mathcal{E}^* = i\mathcal{E}, \phi^* = i\phi, \phi^*_c = i\phi_c, \phi^*_a = i\phi_a$, with $\mathcal{E}, \phi, \phi_c, \phi_a$ being real-valued quantities [50]. In this scenario, the fluctuations around the average are completely omitted, which can be treated using the one-loop expansion as in our previous work [62], and the grand partition function is approximated as,

$$Z_{\rm gc} \approx \exp\left(-\beta\left(H - \int_r \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P} - \int_r \phi \rho - \int_r \phi_a \rho_a - \int_r \phi_c \rho_c + \int_r \phi \rho^{\rm ex} - V\right)\right)$$
(34)

with

$$V = \frac{1}{\beta} \int_{r} \left(\frac{\lambda_{\rm c}}{\Lambda_{\rm c}^3} \exp(-\beta e_0 \phi - \beta e_0 \phi_{\rm c}) + \frac{\lambda_{\rm a}}{\Lambda_{\rm a}^3} \exp(\beta e_0 \phi + \beta e_0 \phi_{\rm a}) + \frac{\lambda_{\rm s}}{\Lambda_{\rm s}^3} \frac{\sinh(\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|)}{\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|} \right)$$
(35)

where we use the identity, $\sin(ix) = i \sinh x$. Here, an integration constant should be present in Eq. 34; however, it does not affect the results, and thus, we omit it hereinafter. The grand potential of the classical part $\Omega_{\rm C}$ can be obtained by its definition,

$$\Omega_{\rm C} = -\frac{1}{\beta} \log Z_{\rm gc} = H - \int_r \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P} - \int_r \phi \rho - \int_r \phi_{\rm a} \rho_{\rm a} - \int_r \phi_{\rm c} \rho_{\rm c} + \int_r \phi \rho^{\rm ex} - V$$
(36)

To obtain $F_{\mathbb{C}}$, we perform a Legendre transformation to convert the grand potential back to the Helmholtz free energy, *i.e.*,

$$F_{\mathbb{C}} = \Omega_{\mathrm{C}} + \sum_{i=\mathrm{a,c,s}} \int_{r} n_{i} \tilde{\mu}_{i}^{c}$$
(37)

where $\tilde{\mu}_i^c$ is the electrochemical potential of the electrolyte component *i* in the classical part. The difference between $\tilde{\mu}_i^c$ and $\tilde{\mu}_i$ in Eq. 1 should be noted. The latter also accounts for short-range interactions between electrolyte component *i* and the metal. The variables ρ_a and ρ_c in Eq. 36 are the charge densities of anions and cations. They are given by $\rho_a = -e_0 n_a$ and $\rho_c = e_0 n_c$. With the definition of particle number $N_i = \int_r n_i = -\frac{\partial \Omega_c}{\partial \tilde{\mu}_i^c}$, we have,

$$\tilde{\mu}_{\rm c}^c = \frac{1}{\beta} \log(n_{\rm c} \Lambda_{\rm c}^3) + e_0(\phi + \phi_{\rm c}) \tag{38}$$

$$\tilde{\mu}_{a}^{c} = \frac{1}{\beta} \log(n_{a} \Lambda_{a}^{3}) - e_{0}(\phi + \phi_{a})$$
⁽³⁹⁾

$$\tilde{\mu}_{s}^{c} = \frac{1}{\beta} \log(n_{s} \Lambda_{s}^{3}) - \frac{1}{\beta} \log \frac{\sinh(\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|)}{\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|}$$

$$\tag{40}$$

When the classical system reaches the equilibrium, $\Omega_{\rm C}$ reaches its extremal value. At equilibrium, $\frac{\delta \Omega_{\rm C}}{\delta \rho_{\rm c}} = \frac{\delta \Omega_{\rm C}}{\delta \rho_{\rm a}} = 0$, which gives

$$\phi_{\rm c} = \alpha_{\rm c} \nabla \cdot \boldsymbol{P}$$
, $\phi_{\rm a} = \alpha_{\rm a} \nabla \cdot \boldsymbol{P}$

Substituting Eq. 36 and Eq. 38-40 into Eq. 37, we obtain,

$$F_{\mathbb{C}} = \frac{1}{2} \int_{rr'} \rho(r) G(r, r') \rho(r') + \frac{1}{2\epsilon_0} \int_r (K_{\mathrm{s}} \mathbf{P}^2 + K_\alpha (\nabla \cdot \mathbf{P})^2 + K_\beta (\nabla^2 \mathbf{P})^2) - \int_r \mathbf{\mathcal{E}} \cdot \mathbf{P}$$

$$- \int_r \phi \rho + \int_r \phi \rho^{\mathrm{ex}} + \int_r n_{\mathrm{c}} e_0 (\phi + \alpha_{\mathrm{c}} \nabla \cdot \mathbf{P}) - \int_r n_{\mathrm{a}} e_0 (\phi + \alpha_{\mathrm{a}} \nabla \cdot \mathbf{P})$$

$$- \int_r \frac{n_{\mathrm{s}}}{\beta} \log \frac{\sinh(\beta p | \mathbf{\mathcal{E}} - \nabla \phi|)}{\beta p | \mathbf{\mathcal{E}} - \nabla \phi|} + \sum_{i=\mathrm{a,c,s}} \int_r \frac{1}{\beta} (n_i \log(n_i \Lambda_i^3) - n_i)$$
(42)

To account for excluded volume effects, which distinguish the real system from the ideal gas system, a so-called volumetric excess free energy $\Phi_{ex}(\{n_i\})$ is added into the Helmholtz free energy density $f_{\mathbb{C}}$, defined as the kernel of the free energy functional $F_{\mathbb{C}} = \int_r f_{\mathbb{C}}$. Budkov [63] and Lue *et al.* [64] attempted to incorporate excluded volume effects self-consistently into the grand partition function of the system. The derivative of the volumetric excess free energy is defined as the excess chemical potential, which is expressed in the Bikerman model as [65],

$$\mu_i^{\text{ex}} = \frac{\partial \Phi_{\text{ex}}}{\partial n_i} = \frac{1}{\beta} \log \frac{1}{1 - \sum_{i=\text{a,c,s}} n_i \gamma_i \Lambda_B^3}$$
(43)

where $\Lambda_{\rm B}$ is the characteristic length of referenced lattice, and the maximum number density of referenced lattices is $n_{\rm max} = \Lambda_{\rm B}^{-3}$. $\gamma_i = \left(\frac{d_i^3}{\Lambda_{\rm B}^3}\right)$ is the relative size of electrolyte component *i* referenced to the size of lattice. d_i is the characteristic length of electrolyte component *i*. Then $f_{\mathbb{C}}$ has the form

$$f_{\mathbb{C}} = \frac{1}{2}\rho(r)G(r,r')\rho(r') + \frac{1}{2\epsilon_0} \left(K_{\mathrm{s}}\boldsymbol{P}^2 + K_{\alpha}(\nabla \cdot \boldsymbol{P})^2 + K_{\beta}(\nabla^2 \boldsymbol{P})^2\right) - \boldsymbol{\mathcal{E}} \cdot \boldsymbol{P} - \phi\rho + \phi\rho^{\mathrm{ex}} + n_{\mathrm{c}}e_0(\phi + \alpha_{\mathrm{c}}\nabla \cdot \boldsymbol{P}) - n_{\mathrm{a}}e_0(\phi + \alpha_{\mathrm{a}}\nabla \cdot \boldsymbol{P}) - \frac{n_{\mathrm{s}}}{\beta}\log\frac{\sinh(\beta p|\boldsymbol{\mathcal{E}} - \nabla\phi|)}{\beta p|\boldsymbol{\mathcal{E}} - \nabla\phi|} + \sum_{i=\mathrm{a,c,s}}\frac{1}{\beta}\left(n_i\log(n_i\Lambda_i^3) - n_i\right) + \Phi_{\mathrm{ex}}$$

$$(44)$$

As for short-range interactions between electrolyte component i and the metal, we use the repulsive part of the Morse potential w_i to prevent electrolyte particles from penetrating into the metal, *i.e.*,

$$F_{\otimes} = \sum_{i=a,c,s} \int_{r} n_i w_i \tag{45}$$

with

$$w_i = D_i \exp\left(-2\beta_i (d - d_i)\right) \tag{46}$$

Here, D_i represents the depth of the Morse potential well, β_i is the coefficient controlling the

width of the potential well, and d, d_i denote the distances from the position and the equilibrium position of electrolyte particle i to the metal surface, respectively.

2.5 Variational analysis

Combining the above sections, the grand potential density g, which is the kernel of the grand potential functional, *i.e.*, $\Omega = \int_r g$, is formulated as

$$g = e_{au}a_{0}^{-3}t_{TF}(1 + \theta_{T}s^{2}) + e_{au}a_{0}^{-3}u_{X}^{0}(1 + \theta_{X}s^{2}) + e_{au}a_{0}^{-3}(u_{C}^{0} + (n_{e}a_{0}^{3})\theta_{C}t^{2}) + \frac{1}{2}\rho(r)G(r,r')\rho(r') + \frac{1}{2\epsilon_{0}}(K_{s}P^{2} + K_{\alpha}(\nabla \cdot P)^{2} + K_{\beta}(\nabla^{2}P)^{2}) - \mathcal{E} \cdot P - \phi\rho + \phi\rho^{ex} + n_{c}e_{0}(\phi + \alpha_{c}\nabla \cdot P) - n_{a}e_{0}(\phi + \alpha_{a}\nabla \cdot P) - \frac{n_{s}}{\beta}\log\frac{\sinh(\beta p|\mathcal{E} - \nabla\phi|)}{\beta p|\mathcal{E} - \nabla\phi|} + \sum_{i=a,c,s}\frac{1}{\beta}(n_{i}\log(n_{i}\Lambda_{i}^{3}) - n_{i}) + \Phi_{ex} + \sum_{i=a,c,s}n_{i}w_{i} - \left(n_{e}\tilde{\mu}_{e} + \sum_{i=a,c,s}n_{i}\tilde{\mu}_{i}\right)$$
(47)

where g and Ω are the functional of the field variables ρ , ϕ , \mathcal{E} , P and particle number density n_e , n_c , n_a , n_s . The grand potential has its minimum under equilibrium, where its variation with respect to the field variables and particle number density will be zero, *i.e.*,

$$\frac{\delta\Omega}{\delta X} = 0 \left(X = \rho, \phi, \mathcal{E}, \mathcal{P}, n_{\rm e}, n_{\rm c}, n_{\rm a}, n_{\rm s} \right)$$
(48)

For $X = n_e$, Eq. 48 transforms into an Euler-Lagrange equation for n_e , *i.e.*,

$$\frac{\partial g}{\partial n_{\rm e}} - \nabla \left(\frac{\partial f}{\partial (\nabla n_{\rm e})} \right) = 0 \tag{49}$$

which gives,

$$\overline{\nabla}\overline{\nabla}\overline{n}_{e} = \frac{20}{3}\overline{n}_{e}\frac{\omega}{(\theta_{T}\omega - \theta_{XC})} \left(\frac{\partial t_{TF}}{\partial \overline{n}_{e}} + \frac{\partial u_{X}^{0}}{\partial \overline{n}_{e}} + \frac{\partial u_{C}^{0}}{\partial \overline{n}_{e}} - \frac{(\tilde{\mu}_{e} + e_{0}\phi)}{e_{au}}\right) + \frac{\left(\theta_{T}\omega - \frac{4}{3}\theta_{XC}\right)}{2\overline{n}_{e}(\theta_{T}\omega - \theta_{XC})}(\overline{\nabla}\overline{n}_{e})^{2}$$

$$(50)$$

with dimensionless electron density $\bar{n}_{\rm e} = n_{\rm e}a_0^3$, dimensionless gradient operator $\bar{\nabla} = a_0\nabla$, $\omega = \frac{2}{5}(3\pi^5)^{\frac{1}{3}}(\bar{n}_{\rm e})^{\frac{1}{3}}$, the constant $\theta_{\rm XC} = \theta_{\rm X} - \frac{\pi^2}{3}\theta_{\rm C}$. A detailed derivation was given in Ref. [54].

For $X = \rho$, Eq. 48 leads to,

$$\phi = \int_{r'} G(r, r') \rho(r') = \int_{r'} \frac{\rho(r')}{4\pi\epsilon_{\infty} |r - r'|}$$
(51)

i.e., the electric potential. Inversely, we have,

$$\rho = -\nabla(\epsilon_{\infty}\nabla\phi) \tag{52}$$

where ϵ_{∞} varies spatially in the metal-solution interfacial region.

For $X = \mathcal{E}$, Eq. 48 is transformed to the constitutive relation,

$$\boldsymbol{P} = -\frac{pn_{s}\mathcal{L}(\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|)}{|\boldsymbol{\mathcal{E}} - \nabla \phi|} (\boldsymbol{\mathcal{E}} - \nabla \phi)$$
(53)

where $\mathcal{L}(u) = \coth u - \frac{1}{u} = \frac{\partial \log(\sinh u/u)}{\partial u}$ is the Langevin function.

For $X = \phi$, Eq. 48 gives

$$\frac{\partial g}{\partial \phi} - \nabla \left(\frac{\partial g}{\partial (\nabla \phi)} \right) = 0 \tag{54}$$

which combined with Eq. 52 and 53 gives the modified Poisson-Boltzmann equation,

$$\nabla \cdot (\epsilon_{\infty} \nabla \phi + \mathbf{P}) = -(n_c - n_a)e_0 - \rho^{\text{ex}}$$
(55)

with external charge density $\rho^{\text{ex}} = (n_{\text{cc}} - n_{\text{e}})e_0$. n_{cc} is the background charge density contributed by metal cationic cores.

For X = P, Eq. 48 is transformed to,

$$\frac{\partial g}{\partial \mathbf{P}} - \nabla \left(\frac{\partial g}{\partial (\nabla \cdot \mathbf{P})} \right) + \nabla^2 \left(\frac{\partial g}{\partial \nabla^2 \mathbf{P}} \right) = 0$$
(56)

which gives,

$$\epsilon_0^{-1} \left(K_{\rm s} \boldsymbol{P} - K_\alpha \nabla^2 \boldsymbol{P} + K_\beta \nabla^4 \boldsymbol{P} \right) - \alpha_{\rm c} e_0 \nabla n_{\rm c} + \alpha_{\rm a} e_0 \nabla n_{\rm a} = \boldsymbol{\mathcal{E}}$$
(57)

For $X = n_c$, n_a , n_s , Eq. 48 gives the electrochemical potentials of ions and solvent,

$$\tilde{\mu}_{\rm c} = \frac{1}{\beta} \log \frac{n_{\rm c} \Lambda_{\rm c}^3}{1 - \sum_i n_i \gamma_i \Lambda_{\rm B}^3} + e_0(\phi + \alpha_{\rm c} \nabla \cdot \boldsymbol{P}) + w_{\rm c}$$
(58)

$$\tilde{\mu}_{a} = \frac{1}{\beta} \log \frac{n_{a} \Lambda_{a}^{3}}{1 - \sum_{i} n_{i} \gamma_{i} \Lambda_{B}^{3}} - e_{0} (\phi + \alpha_{a} \nabla \cdot \boldsymbol{P}) + w_{a}$$
⁽⁵⁹⁾

$$\tilde{\mu}_{\rm s} = \frac{1}{\beta} \log \frac{n_{\rm s} \Lambda_{\rm s}^3}{1 - \sum_i n_i \gamma_i \Lambda_{\rm B}^3} - \frac{1}{\beta} \log \frac{\sinh(\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|)}{\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|} + w_{\rm s}$$
(60)

which leads to the distributions of electrolyte component *i*,

$$n_i = n_{\max} \frac{\chi_i \Theta_i}{1 + \sum_i \gamma_i \chi_i (\Theta_i - 1)}$$
(61)

with thermodynamic factors Θ_i

$$\Theta_{\rm c} = \exp(-\beta e_0(\phi + \alpha_{\rm c} \nabla \cdot \boldsymbol{P}) - \beta w_{\rm c}) \tag{62}$$

$$\Theta_{a} = \exp(\beta e_{0}(\phi + \alpha_{a}\nabla \cdot \boldsymbol{P}) - \beta w_{a})$$
(63)

$$\Theta_{\rm s} = \frac{\sinh(\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|)}{\beta p |\boldsymbol{\mathcal{E}} - \nabla \phi|} \exp(-\beta w_{\rm s}) \tag{64}$$

where $\chi_i = \frac{n_i^b}{n_{\text{max}}}$, and n_i^b is the bulk number density of electrolyte component *i*.

We can comprehend the physical significance of the introduced auxiliary fields from Eq. 62-64. $\phi_c = \alpha_c \nabla \cdot P$ and $\phi_a = \alpha_a \nabla \cdot P$ represent the impact of short-range correlations with solvent molecules on ionic distributions. \mathcal{E} represents the impact of short-range correlations among solvent molecules and between ions and solvent molecules on the solvent distribution.

Considering the possible presence of vacancies number density n_v^b in bulk solution, we have $\sum_i \gamma_i \chi_i + \chi_v = 1$ with $\chi_v = n_v^b/n_{max}$. Eq. 61 then becomes,

$$n_i = n_{\max} \frac{\chi_i \Theta_i}{\chi_v + \sum_i \gamma_i \chi_i \Theta_i}$$
(65)

where $n_{\text{max}} = \Lambda_{\text{B}}^{-3} = (\sum_{i} n_{i}^{\text{b}} \gamma_{i})/(1 - \chi_{\text{v}})$. Substituting Eq. 65 into Eq. 55 and Eq. 57 results in a second-order ordinary differential equation (ODE) in ϕ , a fourth-order ODE in P, respectively. Combined, Eq. 50, 55, 57 constitute a closed set of equations that can be solved for the distributions of electron density, electric field, and polarization field in the EDL.

2.6 Boundary conditions

We consider a metal-solution interface. The boundary conditions (BCs) in solution bulk, *i.e.*, the right boundary conditions (RBCs), are,

$$n_e = 0, \phi = 0, P = 0, \nabla^2 P = 0 \tag{66}$$

where the first identity reflects the fact that metal electrons are absent in solution bulk, the second identity corresponds to defining the electric potential in solution bulk as the potential reference, the third identity means that solvent molecules are distributed homogenously and orientated isotropically in solution bulk. The fourth identity serves as an additional boundary condition required for solving the fourth-order ODE of the polarization field. Here we choose the second-order gradient of the polarization field to be zero, as a consequence of zero polarization charge in the solution bulk. This imposes an RBC for the variable introduced below for the reduction of the fourth-order ODE in P.

The BCs in metal bulk, i.e., the left boundary conditions (LBCs), are,

$$\nabla n_e = 0, \nabla \phi = 0, \mathbf{P} = 0, \nabla^2 \mathbf{P} = 0 \tag{67}$$

In the simplest scenario, the metal cationic cores are treated as a uniform background of positive charge density. In this case, the first and second equations imply that electron density and electric

potential remain constant in the metal bulk, *viz.*, at distances far from the metal surface. The distance to the left boundary from the metal surface should be large enough, say >10 Å, to ensure accessibility to the metal bulk. For the case where size and arrangement of metal cationic cores are explicitly considered, we can take the left boundary at the central plane of metal cationic cores. The third identity reflects the absence of solvent molecules in the metal phase. The fourth identity is obvious.

In this model, constant-potential conditions are implemented by varying the electrochemical potential $\tilde{\mu}_e$ in Eq. 50 [66]. The electrochemical potential of metal electrons is related to the chemical potential μ_e , and the inner potential of the metal, ϕ_M , by,

$$\tilde{\mu}_{\rm e} = -e_0 \phi_{\rm M} + \mu_{\rm e} \tag{68}$$

Eq. 52 represents a nonlinear relation that coupling the auxiliary field \mathcal{E} with the polarization field P and the electric field $-\nabla \phi$. In numerical implementations, it can be treated as a zeroth order differential equation in \mathcal{E} . In the absence of solvent molecules in the metal bulk, \mathcal{E} equals zero, while in the solution bulk, \mathcal{E} also equals zero due to isotropic short-range interactions.

2.7 Numerical implementation

In this work, differential equations are solved in the one-dimensional case with the coordinate x. In 1D, P and \mathcal{E} can be treated as scalar quantities P, \mathcal{E} , with positive values indicating that the fields are directed towards the solution bulk. We define dimensionless variables, marked with an overbar, as follows,

$$\bar{n}_{i} = a_{0}^{3} n_{i}, \bar{x} = \frac{x}{a_{0}}, \bar{\phi} = \frac{e_{0}\phi}{k_{B}T}, \bar{p} = \frac{p}{e_{0}a_{0}}, \bar{e}_{\infty} = \frac{\epsilon_{\infty}}{\epsilon_{0}}, \bar{P} = \frac{\kappa a_{0}^{2}P}{e_{0}}, \bar{\mathcal{E}} = \frac{e_{0}a_{0}\bar{\mathcal{E}}}{k_{B}T}, \bar{K}_{\alpha} = \frac{K_{\alpha}}{a_{0}^{2}}, \bar{K}_{\beta}$$

$$= \frac{K_{\beta}}{a_{0}^{4}}, \bar{\alpha}_{i} = \frac{\epsilon_{0}\alpha_{i}}{a_{0}^{2}}, \bar{\beta}_{i} = \beta_{i}a_{0}$$
(69)

where $\kappa = \frac{e_0^2}{k_B T a_0 \epsilon_0}$ is a constant. The modified Poisson-Boltzmann equation in Eq. 53 is rewritten in dimensionless variables as,

$$\overline{\nabla}(\bar{\epsilon}_{\infty}\overline{\nabla}\bar{\phi}+\bar{P}) = -\kappa(\bar{n}_{\rm cc}-\bar{n}_{\rm e}+\bar{n}_{\rm c}-\bar{n}_{\rm a}) \tag{70}$$

where the dimensionless number density of ions and solvent molecules are given as,

$$\bar{n}_{i} = \bar{n}_{\max} \frac{\chi_{i} \Theta_{i}}{\chi_{v} + \sum_{i=a,c,s} \gamma_{i} \chi_{i} \Theta_{i}}$$
(71)

with Θ_i expressed in dimensionless variables,

$$\Theta_{\rm c} = \exp(-\bar{\phi} - \bar{\alpha}_{\rm c} \overline{\nabla} \bar{P} - \beta w_{\rm c}) \tag{72}$$

$$\Theta_{a} = \exp(\bar{\phi} + \bar{\alpha}_{a}\overline{\nabla}\bar{P} - \beta w_{a}) \tag{73}$$

$$\Theta_{\rm s} = \frac{\sinh(\bar{p}|\bar{\mathcal{E}} - \bar{\nabla}\bar{\phi}|)}{\bar{p}|\bar{\mathcal{E}} - \bar{\nabla}\bar{\phi}|} \exp(-\beta w_{\rm s}) \tag{74}$$

By introducing the second-order derivative field $Q = \nabla^2 P$, the fourth-order ODE Eq. 57 is transformed to two second-order ODEs in Q and in P, respectively. In their dimensionless 1D form, they are written as,

$$K_{\rm s}\bar{P} - \bar{K}_{\alpha}\bar{Q} + \bar{K}_{\beta}\bar{\nabla}^2\bar{Q} - \kappa\bar{\alpha}_{\rm c}\bar{\nabla}\bar{n}_{\rm c} + \kappa\bar{\alpha}_{\rm a}\bar{\nabla}\bar{n}_{\rm a} = \bar{\mathcal{E}}$$

$$\tag{75}$$

$$\overline{\nabla}^2 \overline{P} = \overline{Q} \tag{76}$$

where $\bar{Q} = (\kappa a_0^4/e_0)Q$ is the dimensionless derivative field. Eq. 66 and 67 impose the boundary conditions $\bar{Q} = 0$ at both the left boundary and right boundary for Eq. 75. The constitutive relation Eq. 53 can be rewritten in dimensionless variables as,

$$\bar{P} = -\frac{\kappa \bar{p} \bar{n}_{s} \mathcal{L} \left(\bar{p} | \bar{\mathcal{E}} - \bar{\nabla} \bar{\phi} | \right)}{\left| \bar{\mathcal{E}} - \bar{\nabla} \bar{\phi} \right|} (\bar{\mathcal{E}} - \bar{\nabla} \bar{\phi})$$
(77)

We substitute $\psi = (\bar{n}_e)^{\frac{1}{3}}$ to get rid of fractional exponents of \bar{n}_e [54]. In this scheme, Eq. 50 can then be rewritten as,

$$\overline{\nabla}\overline{\nabla}\psi + \frac{\theta_{\rm T}\omega}{2(\theta_{\rm T}\omega - \theta_{\rm XC})\psi}(\overline{\nabla}\psi)^2 = \frac{20}{9}\psi\frac{\omega}{(\theta_{\rm T}\omega - \theta_{\rm XC})}\left(\frac{\partial t_{\rm TF}^0}{\partial\overline{n}_{\rm e}} + \frac{\partial u_{\rm X}^0}{\partial\overline{n}_{\rm e}} + \frac{\partial u_{\rm C}^0}{\partial\overline{n}_{\rm e}} - \frac{(\widetilde{\mu}_{\rm e} + e\phi)}{e_{\rm au}}\right)$$
(78)

Eq. 70, and 75-78 are solved in COMSOL. Technical details on the numerical implementation are provided in Supporting Information (SI).

3. Results and discussions

3.1 Model parameterization and calibration

The model parameters used in the base case are listed in Tables 1 to 4, respectively. Most parameters are adapted from the literature, with the remaining parameters calibrated by fitting the experimental double-layer capacitance at the Ag(110)-KPF₆ aqueous interface [18]. Specific adsorption of ions is very weak at this interface, eliminating the need for considering specific adsorption, which were treated with the Newns-Anderson Hamiltonian in a previous work [67].

Table 1. General parameters of the base case

Symbol	Item	Value	
k _B	Boltzmann constant	$1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$	
Т	temperature	298 K	
e_0	elementary charge	$1.6 \times 10^{-19} \text{ C}$	
a_0	Bohr radius	$5.29 \times 10^{-11} \text{ m}$	
ϵ_{0}	vacuum permittivity	$8.85 \times 10^{-12} \mathrm{F} \cdot \mathrm{m}^{-1}$	

N _A	Avogadro constant	$6.02 \times 10^{23} \text{ mol}^{-1}$
e _{au}	energy constant from a.u. to SI	$e_0^2/(4\pi\epsilon_0a_0)$
κ	dimensionless constant	$e_0^2/(k_{\rm B}T\epsilon_0a_0)$

Metal cationic cores are described in the simplest case using a uniform background with a dimensionless positive charge density \bar{n}_{cc}^{0} , namely,

$$\bar{n}_{\rm cc} = \bar{n}_{\rm cc}^0 \theta(\bar{x}_{\rm M} - \bar{x}) \tag{79}$$

where $\theta(x)$ is the Heaviside step function, with \bar{x}_{M} denoting the dimensionless position of the metal surface, and $n_{cc}^{0} = 4N_{Ag} \left(\frac{a_{0}}{a_{Ag}}\right)^{3} = 0.408$ with $N_{Ag} = 47$ representing the number of electrons of a silver atom. Moreover, $a_{Ag} = 4.08$ Å is the length of the cubic closed-packed cell of Ag, which contains four silver atoms. We consider all electrons, and we use the vacuum permittivity ϵ_{0} as the high-frequency dielectric permittivity in the metal bulk, implying $\bar{\epsilon}_{\infty,M} = 1$. We use the PBE functional with $\theta_{X} = 0.1235$ and $\theta_{C} = 0.046$ [59]. The only free parameter in electronic functionals is the coefficient in the kinetic energy, θ_{T} , which is calibrated according to the experimental potential of zero charge. This is a simplified treatment that lumps interactions between electrons in different orbitals into a single parameter θ_{T} . However, this simple treatment is sufficient for our purpose because there is no formation or cleavage of chemical bonds at this interface.

Table 2. Metal parameters of the base case
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Symbol	Item	Value
<i>a</i> ₁	coefficient in the PBE functional	0.0310907
<i>a</i> ₂	coefficient in the PBE functional	0.2137
<i>a</i> ₃	coefficient in the PBE functional	7.5957
<i>a</i> ₄	coefficient in the PBE functional	3.5876
<i>a</i> ₅	coefficient in the PBE functional	1.6382
<i>a</i> ₆	coefficient in the PBE functional	0.49294
$\theta_{\rm X}$	gradient coefficient in the exchange functional	0.1235
$\theta_{\rm C}$	gradient coefficient in the correlation functional	0.046
θ_{T}	gradient coefficient in the kinetic energy functional	1.663
$\epsilon_{\infty,\mathrm{M}}$	high-frequency dielectric permittivity in the metal bulk	ϵ_0
$ar{n}_{ m cc}^0$	dimensionless charge density of metal cationic cores	0.408

On the solution side, we use $R_{sol} = 2.75$ Å as the diameter of water molecules [68], which is taken as the reference size, *i.e.*, $\Lambda_{\rm B} = R_{sol}$. For K⁺ cations, its solvation shell comprises first-layer water molecules that are tightly bound and outer water molecules that are loosely bound.

Therefore, we consider the cation with its first solvation shell as a whole, and introduce α_c to account for the short-range interactions between the solvated cation and outer water molecules. Molecular dynamics (MD) simulations have determined the distance between K⁺ and the oxygen in its first solvation shell to be within the range of 2.6 – 3.6 Å [69], and we use the upper limit, 3.6 Å, as the radius of solvated cations. PF₆⁻ anions bind surrounding water molecules weaker than the cations. Hence, the radius of anions correspond to bare anions, and we introduce α_a to describe the short-range interactions between the bare anions and the solvating water molecules. The radius of a solvated PF₆⁻ is determined to be within 4 - 6 Å [70], and we use an effective radius of PF₆⁻ to be around 2.7 Å by subtracting the water diameter. The fraction of vacancy lattice sites in the solution bulk is then calculated as $\chi_v = 1 - \Lambda_B^3 \sum_i n_i^b \gamma_i$, with $n_s^b = 55.6 \text{ mol} \cdot \text{m}^{-3}$.

Under quasi-static conditions, when the frequency of the electric field tends to zero, the polarization field responds linearly to the electric field. This implies that in Eq. 52, $\boldsymbol{\mathcal{E}}$ is linear with \boldsymbol{P} . The linear relationship is given by Eq. 56, $\boldsymbol{\mathcal{E}} = \epsilon_0^{-1} K_s \boldsymbol{P}$. Substituting this relationship into Eq. 53 and taking the case into the solution bulk, we obtain the static dielectric permittivity ϵ_s in the solution bulk,

$$\epsilon_{\rm s} = \epsilon_{\infty,\rm S} + \frac{\beta p^2 n_{\rm s}^{\rm b}}{3\epsilon_0 + \beta p^2 n_{\rm s}^{\rm b} K_{\rm s}} \epsilon_0 \tag{80}$$

where p, $\epsilon_{\infty,S}$ and K_s describe the contribution of low-frequency orientational polarization, highfrequency polarization, and short-range correlations of solvent molecules to the static dielectric permittivity, respectively. $\epsilon_{\infty,S}$ and ϵ_s are 4.5 and 78.5, respectively, based on the dielectric dispersion spectrum of water [71]. Setting K_s to zero in Eq. 80, we obtain an effective dipole moment $\sqrt{\frac{3(\epsilon_s - \epsilon_{\infty,S})}{\beta n_s^b}}$ as 4.66 Debye, into which the short-range correlation effects of solvent molecules have been incorporated. The continuous transition of the high-frequency dielectric constant at the metal surface is described as [54],

$$\bar{\epsilon}_{\infty}(\bar{x}) = \bar{\epsilon}_{\infty,\mathrm{M}} + \frac{\bar{\epsilon}_{\infty,\mathrm{S}} - \bar{\epsilon}_{\infty,\mathrm{M}}}{2} \left(1 - \mathrm{erf}\left(-\bar{\beta}_{\infty}(\bar{x} - \bar{x}_{\mathrm{M}})\right) \right)$$
(81)

with the error function $\operatorname{erf}(\bar{x})$. $\bar{\beta}_{\infty}$ is a dimensionless coefficient controlling the width of the transition region, and we use the value of 1 inherited from Ref. [54]. In principle, the coefficients K_{α} and K_{β} can be obtained by fitting the response function of the static longitudinal dielectric property to spatial dielectric dispersion spectrum of water as in Refs. [39,48]. The fundamental formalism of the dielectric response function and its comparison to experimental and simulated results will be addressed in future works. Here, K_{α} , K_{β} , together with α_c , α_a , are determined by calibrating with experimental C_{dl} data. As shown in Table 3, the calibrated α_c and α_a are negative values, suggesting that short-range correlations between ions and solvent molecules make the solvation energies less negative. In other words, negative α_c and α_a mean that the solvation energies are overestimated on the mean-field level. We note that the solvation energy predicted by

Born model, based on the mean-field electrostatic interactions, is more negative than the experimental value especially for small ions. Another reason for this discrepancy is that spatial correlations between solvent molecules reduce the effective dielectric permittivity in regions within characteristic correlation distances from the ion, known as dielectric saturation [72], which is also considered in our present model.

Symbol	Item	Value	
$c_{\rm s}^{\rm b}$	bulk solvent concentration	$55600 \text{ mol} \cdot \text{m}^{-3}$	
r _c	radius of solvated cations	3.6 Å	
r _a	radius of bare anions	2.7 Å	
R _{sol}	diameter of solvent molecules	2.75 Å	
$\epsilon_{\infty,\mathrm{S}}$	high-frequency dielectric permittivity in the solution bulk	$4.53 \epsilon_0$	
$\epsilon_{\rm s}$	static dielectric permittivity of solution bulk	78.5 ϵ_0	
K _α	coefficient in the short-interaction functional of solvent molecules	$-0.35 a_0^2$	
K _β	coefficient in the short-interaction functional of solvent molecules	$0.145 a_0^4$	
α _c	strength of short-range interactions between solvated cations and surrounding water molecules	$-0.05 a_0^2/\epsilon_0$	
α _a	strength of short-range interactions between bare anions and surrounding water molecules	$-0.081 a_0^2/\epsilon_0$	

Table 3. Solution parameters of the base case

Parameters of the Morse potentials describing metal solution interactions can be acquired from Kohn-Sham DFT calculations [73]. In the present model, we simply use the repulsive part of the Morse potential to prevent ions and solvent molecules from penetrating into the metal phase. In this case, Eq. 46 can be equivalently recast into,

$$w_i = \beta^{-1} \exp\left(-2\beta_i \left(d - d_i^{\mathrm{M}}\right)\right) \tag{82}$$

with,

$$d_i^{\rm M} = d_i + \frac{\ln(\beta D_i)}{2\beta_i} \tag{83}$$

where d_i^{M} represents an effective equilibrium distance of electrolyte component *i* from the metal surface. The parameters D_i and d_i are combined into the single effective parameter d_i^{M} , with smaller values indicating that the electrolyte component *i* can be drawn closer to the metal surface due to stronger short-range interactions with the metal surface. The values of d_i^{M} and β_i in Eq. 82 are calibrated with experimental C_{dl} data, as shown in Table 4. The calibrated values of d_i^{M}

capture the phenomenon that ions are farther from the metal surface compared to water molecules.

Symbol	Item	Value
$ar{eta_{s}}$	dimensionless coefficient in the Morse potential of solvent molecules	0.95
$ar{eta_{ m c}}$	dimensionless coefficient in the Morse potential of cations	0.19
$ar{eta}_{a}$	dimensionless coefficient in the Morse potential anions	4.5
$d_{ m s}^{ m M}$	effective equilibrium distance of solvent molecules	6.6 a ₀
$d_{ m c}^{ m M}$	effective equilibrium distance of cations	13.3 a ₀
$d_{\mathrm{a}}^{\mathrm{M}}$	effective equilibrium distance of anions	11.6 a ₀

Table 4. Metal-Solution interaction parameters of the base case

As discussed above, unknown parameters, including θ_T , K_α , K_β , α_i , d_i^M , β_i , are estimated by fitting C_{dl} curves at three concentrations measured by Valette [18]. The impact of these parameters on the model results will be gauged in a parametric analysis in section 3.3. In the model, C_{dl} is calculated by differentiating the surface free charge σ_{free} with respect to ϕ_M ,

$$C_{\rm dl} = \frac{\partial \sigma_{\rm free}}{\partial \phi_{\rm M}} = -e_0 \frac{\partial \sigma_{\rm free}}{\partial \tilde{\mu}_{\rm e}} = \frac{e_0^2}{a_0^2} \frac{\partial}{\partial \tilde{\mu}_{\rm e}} \int d\bar{x} (\bar{n}_{\rm c} - \bar{n}_{\rm a}) = \frac{e_0^2}{a_0^2} \frac{\partial}{\partial \tilde{\mu}_{\rm e}} \int d\bar{x} (\bar{n}_{\rm e} - \bar{n}_{\rm cc})$$
(84)

with the surface free charge $\sigma_{\text{free}} = \frac{e_0}{a_0^2} \int d\bar{x} (\bar{n}_c - \bar{n}_a) = \frac{e_0}{a_0^2} \int d\bar{x} (\bar{n}_e - \bar{n}_{cc})$. The electrode potential measured in experiments [18], which is on the saturated calomel electrode (SCE) scale and denoted as E_{SCE} , can be converted with $\tilde{\mu}_e$ through the following relation,

$$-\tilde{\mu}_{\rm e} = e_0 (E_{\rm SCE} + E_{\rm SHE}^* + 0.2415 \,\rm V) - e_0 \chi_{\rm s} \tag{85}$$

where 0.2415 V is used to transform the electrode potential from SCE scale to standard hydrogen electrode (SHE) scale. E_{SHE}^* represents the absolute electrode potential of SHE, for which we use the value of 4.44 V [74]. The last term arises from the consideration that we take the inner potential of the electrolyte solution as the potential reference [75]. χ_s is the surface potential of the solution-vacuum interface, and we adopt the recommended value of 0.17 V for the water-vacuum interface [74].

Figure 1 compares the model-based and experimental C_{dl} at the Ag(110)-KPF₆ aqueous interface at KPF₆ concentrations of 20, 40, and 100 mM. The electrode potential is rescaled with reference to the potential of zero charge (PZC), where the Gouy Chapman minimum is located. At the Gouy Chapman minimum, $\tilde{\mu}_e = -3.53 \text{ eV}$, corresponding to a potential of zero charge (PZC) of -0.98 V vs saturated calomel electrode (SCE), is reproduced by the model. It's worth noting that the PZC is taken directly as an EDL parameter in classical models, while the present model is able to derive it from an orbital-free description of metal electrons. The model results at three concentrations are calculated using the same set of model parameters in Tables 1-4. The model can well reproduce the camel shape of the C_{dl} curves, as well as the trend of the C_{dl} curve with concentration, namely the decrease in the Gouy-Chapman minimum and the larger distance between two camel peaks as the concentration decreases. The agreement between model and experiment has been greatly improved compared to a previous work [54]. The improvement is discernable in the magnitude of C_{dl} and the distance between the two peaks in C_{dl} curves. The microscopic structure of the EDL behind the C_{dl} curves, as well as the influence of model parameters on the interfacial structure and consequently on the profiles of C_{dl} curves, will be discussed in sections 3.2 and 3.3.



Figure 1. Model (lines) and experimental results (circles) of the differential double layer capacitance (C_{dl}) at the Ag(110)-KPF₆ aqueous interface, at KPF₆ concentrations of 20, 40, and 100 mM, respectively. E_{pzc} is the electrode potential referenced to the potential of zero charge (PZC). The experimental data, measured by Valette, are corrected using a roughness factor of 1.15 as suggested [18]. The same set of parameters is used across all three concentrations.

3.2 Interfacial structure

The model can delineate a spatially-resolved, atomistic scale picture of the EDL. Toward a more realistic description of the metal-solution interface, we consider a one-dimensional, discrete, periodic arrangement of metal cationic cores. The charge distribution of metal cationic cores in this case is written as [67],

$$\frac{\bar{n}_{cc}(x)}{\bar{n}_{cc}^{0}} = \theta(x) - \theta\left(x - \frac{a_{cc}}{2}\right) + \theta\left(x - \frac{a_{cc}}{2} - t\right) - \theta\left(x - \frac{3a_{cc}}{2} - t\right) + \theta\left(x - \frac{3a_{cc}}{2} - 2t\right) \\
- \theta\left(x - \frac{5a_{cc}}{2} - t\right) + \theta\left(x - \frac{5a_{cc}}{2} - 3t\right) - \theta\left(x - \frac{7a_{cc}}{2} - 3t\right) \\
+ \theta\left(x - \frac{7a_{cc}}{2} - 4t\right) - \theta\left(x - \frac{9a_{cc}}{2} - 4t\right)$$
(86)

where a_{cc} is the diameter of metal cationic cores, t the separation distance between two metal cationic cores, \bar{n}_{cc}^{0} the dimensionless charge density of metal cationic cores. In this scheme, only valency electrons are considered, while core electrons are embedded into metal cationic cores. The atomic and electronic polarization of metal cationic cores results in a high-frequency dielectric

permittivity larger than the vacuum permittivity. These parameters can be obtained using DFT calculations. Here, we use $a_{cc} = 1.1$ Å, t = 1.25 Å, $\bar{n}_{cc}^0 = 0.2042$ and $\bar{\epsilon}_{\infty,M} = 2$ as in ref. [67]. Other parameters remain the same as in Tables 1-4. Figure 2 and Figure 3 displays the model results of distributions of electron density, polarization field, electric potential, and number density of solution components for the Ag(110)-0.1 M KPF₆ aqueous interface at five electrode potentials referenced to the PZC. In these plots, the metal edge is located to x = 0.

3.2.1 Oscillation

In Figure 2a, due to the discreteness of metal cationic cores, the electron density and electric potential oscillate in the metal phase. The electrons spill out of the metal edge by approximately 2 Å, with the extent of spillover increasing at more negative electrode potentials. This is because the electrochemical potential of electrons is more positive at more negative electrode potentials, enabling electrons spill out further into the solution compartment. Figure 2b illustrates the oscillatory distribution of the polarization field. The amplitude of the oscillation decreases gradually as it moves away from the metal surface and eventually vanishes in the solution bulk. The oscillatory polarization field results in an oscillatory distribution of the polarization charge. Therefore, an oscillatory electric potential is generated on the solution side, as depicted in the inset of Figure 2c. The formation of the oscillatory polarization field stabilizes the interface through the term $K_{\alpha}(\nabla \cdot \mathbf{P})^2 = K_{\alpha}\rho_b^2$ in the grand potential with a negative K_{α} . In the presence of a negative polarization field near the metal surface, the oxygen atoms of water molecules direct towards the metal surface, forming the oxygen-down configuration [76], whereas a positive polarization field means the hydrogen-down configuration. The valleys and peaks in Figure 2b represent water molecules in opposite orientations, with an alternating distribution. The water molecules closest to the metal surface exhibits a preference for the oxygen-down configuration, as observed in molecular dynamics (MD) simulations [30,77]. This is attributed to the metal electronic effects. The electron spillover from the metal surface generates a strong positive electric field within a ~ 2 Å region adjacent to the metal surface. This built-in positive electric field tends to orient the oxygen atom of water molecules in the first layer towards the metal surface. Compared to the AIMD results [30,77,78], the water layers are slightly farther way from the metal surface in our model. This is due to our simplified consideration of the repulsive interactions between water molecules and the metal surface. As the electrode potential gradually becomes more negative, the overall polarization field becomes more positive, as shown in Figure 2b. This implies that the hydrogen-down configuration is more favored in a more negative electric field, as reported in computational [30,79] and experimental studies [76,80-82].



Figure 2. Model results for the Ag(110)-0.1 M KPF₆ aqueous interface at five electrode potentials, referenced to the PZC, as indicated in the legends of (b): (a) distribution of the dimensionless electron density, with the inset presenting an enlarged view near the metal surface, (b) distribution of the polarization field, (c) distribution of the electric potential, with the inset presenting an enlarged view on the solution side. In all these plots, the metal edge is located at x = 0. The top figure shows a schematic illustration of the EDL structure, with periodically arranged metal cationic cores, and layered distributions of ions and solvent molecules near the metal surface.

3.2.2 Layering

An oscillatory water polarization indicates water layering, which has recently been observed at the Ag(hkl)-NaOH aqueous interfaces using *in situ* surface X-ray diffraction measurements [83]. Figure 3a depicts the layered distribution of water molecules at the interface. As the electrode potential becomes more negative, the concentration of the oxygen-down water increases, while that of the hydrogen-down water decreases. These changes depict reorientation of water molecules in response to the varying electric field at the interface. The alternating layers of water molecules with different net orientations generate local minima and maxima in electric potential, as shown in

Figure 2c. The oscillatory electric field, along with short-range correlations with water molecules, leads to a layered pattern of ion distributions, as shown in Figure 3b and 3c. Both anions and cations are distributed in an alternating layered structure, with their peak concentrations rapidly decaying to bulk concentrations as they move away from the metal surface. Furthermore, due to weaker interactions with the metal surface, ions are unable to penetrate the water layers closest to the metal surface.

The layering phenomenon of ions determines the position of the reaction plane of electrochemical reactions, usually referred to as the position of the peak concentration of ions in the first layer. Interestingly, despite with larger sizes and effective equilibrium distances, cations are noticeably closer to the metal surface compared to anions, as shown in Figure 3b and 3c. This highlights the significant impact of interfacial oscillations on the EDL structure. We also observe that as the potential becomes more negative, the anion concentration in the first layer gradually decreases. However, as shown in the inset of Figure 3b, even at a potential as negative as -0.2 V vs PZC, the concentration of anions in the first layer remains ca. one-third compared to the bulk solution. In fact, at a potential at -0.1 V vs PZC, the concentration of anions in the first layer is even slightly higher than the bulk concentration. The situation is opposite for cations, as shown in Figure 3c. This contrasts with classical double layer theory, where ions near the metal surface carrying excess charge with the same sign would exhibit lower concentrations compared to those in the bulk solution. The anomalous anion accumulation near a negatively charged surface is due to the structured solvent stabilizing the ions near the metal surface. Recently, Lukatskaya et al. have observed the apparent anion effect in the electrochemical CO_2 reduction reaction (eCO₂RR) [84]. Their experiments show that inorganic anions, *i.e.*, perchlorate, sulfate, chloride, lead to higher overpotentials of eCO₂RR. This observation could be attributed to the non-negligible concentration of anions near the metal surface that remains even at negative surface charge. Anions near the metal surface may destabilize the negatively charged transition and final state of the first elementary step in eCO₂RR [85], namely the formation of partially charged $CO_2^{\delta-}$ from CO₂ adsorption, which is generally accepted to be the rate-determining step (RDS) of eCO₂RR [86,87].



Figure 3. Model results for the Ag(110)-0.1 M KPF₆ aqueous interface at five electrode potentials, referenced to the PZC, as indicated in the legend of (a): (a) distribution of the solvent concentration, (b) distribution of the anion concentration, with the inset presenting an enlarged view at negative potentials, (c) distribution of the cation concentration, with the inset presenting an enlarged view at positive potentials. In all of these plots, the metal edge is located at x = 0.

In summary, our theory depicts a microstructure of the EDL that differs dramatically from classical EDL theories. The periodic arrangement of metal cation cores within the metal phase leads to a periodic distribution of electron density and potential within the metal phase, as illustrated in the top schematic figure of Figure 2. Interfacial solvent molecules, due to short-range correlations, form a layered structure with alternating orientations, resulting in an oscillatory distribution of the electric potential on the solution side. Anions and cations also exhibit layered distributions, sandwiched between the solvent layers. Moving towards the bulk electrolyte solution, the layered distributions gradually vanish.

3.3 Parametric analysis

In this section, we use the calibrated model to explore the influence of model parameters on capacitance curves and EDL structure. The parametric analysis will be conducted in three groups. The first group contains parameters related to metal electronic structure, including the gradient coefficient in electronic kinetic functional, $\theta_{\rm T}$, and the metal cationic charge density $\bar{n}_{\rm cc}^0$. The second group focuses on the influence of ionic properties, including the radii of anions and cations,

 $r_{\rm a}$ and $r_{\rm c}$, the strengths of their short-range correlations with solvent molecules, $\alpha_{\rm a}$ and $\alpha_{\rm c}$, the parameters describing the short-range interactions between ions and the metal surface, $d_{\rm a}^{\rm M}$, $d_{\rm c}^{\rm M}$, $\beta_{\rm a}$ and $\beta_{\rm c}$. The third group consists of parameters related to the solvent, including the static dielectric permittivity $\epsilon_{\rm s}$, the optical permittivity $\epsilon_{\infty,\rm S}$, the correlation coefficients, K_{α} and K_{β} , and the parameter describing the short-range interactions between solvent molecules and the metal surface, $d_{\rm s}^{\rm M}$ and $\beta_{\rm s}$.

3.3.1 Electronic structure parameters



Figure 4. Differential double layer capacitance (C_{dl}) curves as a function of the electrochemical potential of electrons, $-\tilde{\mu}_e$, which can be transformed to the electrode potential up to a constant. The (a) gradient coefficient θ_T , (b) dimensionless n_{cc}^0 , are varied at three levels. respectively. In this one-factor-at-a-time study, other parameters except the one under evaluation have their base values.

Figure 4a and 4b shows the C_{dl} curve as a function of $-\tilde{\mu}_e$ at three values of θ_T and n_{cc}^0 , respectively. Other parameters except the one under evaluation have their base values listed in Tables 1-4. According to Eq. 68, $-\tilde{\mu}_e$ is proportional to ϕ_M . As θ_T varies toward more positive values, the C_{dl} curves shift to the right along the $-\tilde{\mu}_e$ axis. The value of $-\tilde{\mu}_e$ corresponding to the PZC, denoted as $-\tilde{\mu}_{e,pzc}$, becomes more positive with a larger value of θ_T . $-\tilde{\mu}_{e,pzc}$ is decomposed as,

$$-\tilde{\mu}_{e,pzc} = -\mu_e + e_0 \phi_{M,pzc} \tag{87}$$

where $\phi_{M,pzc}$ is the inner potential of the bulk metal at PZC, which is mainly influenced by the surface dipoles, formed by spillover of electrons and orientational polarization of solvent molecules [88,89]. The chemical potential of metal electrons in the bulk metal can be expressed as

$$\mu_{e} = \frac{\partial t_{\mathrm{ni}}}{\partial n_{e}} + \frac{\partial u_{\mathrm{X}}}{\partial n_{e}} + \frac{\partial u_{\mathrm{C}}}{\partial n_{e}}$$

$$= e_{\mathrm{au}} \left(\frac{\partial t_{\mathrm{TF}}}{\partial \bar{n}_{e}} + (1 + \theta_{\mathrm{X}} s^{2}) \frac{\partial u_{\mathrm{X}}^{0}}{\partial \bar{n}_{e}} + \frac{\partial u_{\mathrm{C}}^{0}}{\partial \bar{n}_{e}} + u_{\mathrm{X}}^{0} \theta_{\mathrm{XC}} \frac{\partial s^{2}}{\partial \bar{n}_{e}} \right) - \frac{3}{10} e_{\mathrm{au}} (3\pi^{2})^{\frac{2}{3}} s^{2} (\bar{n}_{e})^{\frac{2}{3}} \theta_{\mathrm{T}}$$
(88)

As shown in Eq. 88, μ_e is independent on θ_T due to uniform electron density in the jellium metal. However, the electrons at the metal surface possess higher kinetic energy, which enables electrons spillover farther from the metal surface. Greater spillover leads to a larger surface dipole potential at the metal surface, shifting the PZC positively, as shown in Figure 4a.

Different metals have different values of n_{cc}^0 , which exerts a significant impact on C_{dl} , especially the Helmholtz layer capacitance [31]. As shown in Figure 4b, the C_{dl} curve is elevated at larger n_{cc}^0 because more electrons are presented to screen the electric field in the EDL. A nonmonotonic dependence of $-\tilde{\mu}_{e,pzc}$ on n_{cc}^0 is observed. In the examined range, $-\mu_e$ decreases with increasing n_{cc}^0 in Eq. 87 [54]. However, $\phi_{M,pzc}$ increases since more electrons spillover from the metal surface, resulting in larger surface dipole potential and, consequently, larger $\phi_{M,pzc}$. This is supported by the calculated dipole potential using a jellium-hard-sphere-electrolyte model [31], which exhibits a monotonically increasing trend of dipole potential with n_{cc}^0 , aligning closely with the experimentally estimated dipole potential at different metals [90]. The opposing trends in $-\mu_e$ and $\phi_{M,pzc}$ with respect to n_{cc}^0 lead to the non-monotonic variation of the PZC.

The same metal but with different crystal faces should have the same values of n_{cc}^0 , but different values of θ_T are expected. Figure 5 compares the experimentally measured C_{dl} profiles of Ag(110) and Ag(100) in a 0.1 M KPF₆ aqueous solution, exhibiting a positive shift of 0.11 V in the PZC from Ag(110) to Ag(100) interface. By solely tuning the values of θ_T from 1.663 at the Ag(110) interface to 1.777 at the Ag(100) interface, while keeping all other parameters at their base values, the simulated results agree well with the experimental C_{dl} profile at the Ag(100) interface. This implies that electrons at the Ag(100) surface possess higher kinetic energy and exhibit greater spillover. This metal electronic effect contributes to the observed positive shift in the PZC.



Figure 5. Model (lines) and experimental results (circles) of the differential double layer capacitance (C_{dl}) at Ag(110) and Ag(100) in 0.1 M KPF6 aqueous solution as a function of the electrochemical potential of electrons, $-\tilde{\mu}_e$, which can be transformed to the electrode potential up to a constant. The experimental data at Ag(110) and Ag(100), measured by Valette, are corrected using a suggested roughness factor of 1.15 [18] and 1.07 [16], respectively. In the modelling of

Ag(100)-0.1 M KPF₆, only θ_{T} is tuned to 1.777 while all other parameters are maintained at their base values.

3.3.2 Ion properties

Figure 6a and 6b shows the influence of anion and cation size on the C_{dl} profile, respectively. The anionic peak of the C_{dl} curve, corresponding to anion crowding, is smaller and appears at less positive potential for larger anions. Similar behaviors are observed for the cationic peak corresponding to cation crowding. The size behaviors are similar to classical EDL theories [91]. However, as shown in Figure 9, Valette's experiments reveal that the electrode potential at the anionic peak remains nearly the same at both the Ag(110)-KPF₆ and Ag(110)-NaClO₄ aqueous interfaces. Nevertheless, the anionic peak is more pronounced at the Ag(110)-NaClO₄ aqueous interface. Additionally, the capacitance at PZC is higher at the Ag(110)-NaClO₄ aqueous interface to the Ag(110)-KPF₆ aqueous interface. These indicate that the parameter of ionic size alone is insufficient to fully explain the effects of ion properties on the C_{dl} curve. As a refinement beyond the classical EDL theory, our model considers not only the size of ions but also their short-range correlations with solvent molecules and their short-range interactions with the metal.



Figure 6. Differential double layer capacitance (C_{dl}) curves as a function of the electrochemical potential of electrons, $-\tilde{\mu}_{e}$, which can be transformed to the electrode potential up to a constant. The (a) anion radius, (b) cation radius, (c) dimensionless α_{a} , (d) dimensionless α_{c} , are varied at three levels. respectively. In this one-factor-at-a-time study, other parameters except the one under

evaluation have their base values.

Figure 6c shows the C_{dl} curves at three different values of α_a . As α_a becomes less negative, the anionic peak of C_{dl} curve narrows. Similarly, Figure 6d shows that the cationic peak of C_{dl} curve narrows as the magnitude of negative α_c decreases. To elucidate the origin of this behavior, we will focus on the effect of α_a on C_{dl} curve as an example. The distributions of the electric potential at the PZC for various values of α_a are shown in Figure 7a. It can be seen that α_a has a negligible effect on the oscillations of the electric potential, which also implies a negligible impact on the interfacial solvent structure. However, as discussed in Eq. 17, a less negative α_a indicates that the short-range correlations between anions and solvent molecules screen the electrostatic forces of solvent molecules on anions to a less extent. Consequently, the influence of the local maximum electric potential on anions, which originates from the electrostatic potential of structured solvent dipoles, augments as α_a becomes less negative. As a result, a less negative α_a strengthens the anionic layering and leads to a preferable distribution of anions between solvent layers, as shown in Figure 7b.



Figure 7. The distributions of (a) the electric potential and (b) the anion concentration at the PZC of the C_{dl} curves in Figure 6c, at different values of $\bar{\alpha}_a$, as indicated in Figure 7a. The metal edge is located at x = 0.

Therefore, as α_a becomes less negative, more anions can be accommodated within anion layers, reducing the effective thickness of the EDL. This results in an increase in C_{dl} in the potential region just above the PZC, and a less positive potential of the anionic peak due to a promoted anion crowding. Additionally, anions are drawn closer to the metal surface, especially the first anion layer, where the solvent screening effects become more pronounced. This leads to a lower effective dielectric permittivity at less negative α_a , which in turn causes a steeper decrease in the C_{dl} curve at more positive potentials. Overall, the enhanced anion layering accounts for the narrower anionic peak observed in the C_{dl} profile at less negative values of α_a . The impact of α_c on the cationic peak of the C_{dl} profile is the same.

Different ions exhibit varying strengths of short-range interactions with the metal. Figure 8 shows the impact of related parameters on the C_{dl} profiles, including previously defined effective equilibrium distances and coefficients from Morse potentials. A smaller value of d_a^M indicates a weaker repulsive force between anions the metal surface, allowing anions to approach closer to the metal surface at potentials positive to the PZC. As discussed, this reduces the effective thickness and dielectric permittivity of the EDL, leading to a narrower anionic peak in the C_{dl} profile at smaller d_a^M values, as shown in Figure 8a. The impact of d_c^M on the cationic peak of the C_{dl} profile, as shown in Figure 8b follows a similar pattern. As for the coefficients in the Morse potentials of ions (β_a and β_c), they have negligible impact on the C_{dl} profile, as shown in Figure 8c and 8d.



Figure 8. Differential double layer capacitance (C_{dl}) curves as a function of the electrochemical potential of electrons, $-\tilde{\mu}_{e}$, which can be transformed to the electrode potential up to a constant. The (a) effective equilibrium distance of anions d_{a}^{M} , (b) effective equilibrium distance of cations d_{c}^{M} , (c) dimensionless β_{a} , (d) dimensionless β_{c} , are varied at three levels. respectively. In this one-factor-at-a-time study, other parameters except the one under evaluation have their base values.

The ion parameters r_i , α_i and d_i^{M} significantly impact the position and shape of the ionic peaks in the C_{dl} curves. Additionally, a smaller d_i^{M} or a less negative α_i can yield a larger capacitance at PZC. This is because reducing d_i^{M} and decreasing the negativity of α_i respectively increase the thickness of the diffuse layer and the capacity of the solvent layers to accommodate ions, both of which inherently enhance EDL's ability to store ionic charges. Naturally, these two parameters are not only related to the type of ions but also to the types of metals and solvents. Through the combined influence of these ion properties, the C_{dl} curve at the Ag(110)-NaClO₄ aqueous interface can be reproduced, as shown in Figure 9. We emphasize that only the ion parameters are altered, while all other parameters are maintained at their base values, in this case. The ion parameters for KPF₆ and NaClO₄ electrolytes are listed in Table 5. The solvated Na⁺ cations are smaller than the solvated K⁺ cations [69], while the sizes of PF₆⁻ and ClO₄⁻ anions are comparable. Compared to the KPF₆ electrolyte solution, the NaClO₄ electrolyte solution possesses less negative α_i values for Na⁺ and ClO₄⁻, resulting in increased capacitance at both the ionic peaks and PZC. Additionally, ClO₄⁻ can approach the Ag(110) surface more closely than PF₆⁻, consistent with Valette's findings that ClO₄⁻ has a stronger strength of specific adsorption compared to PF₆⁻ [18].



Figure 9. Model (lines) and experimental results (circles) of the differential double layer capacitance (C_{dl}) at Ag(110) in 0.1 M KPF₆ and 0.1 M NaClO₄ aqueous solution as a function of the electrochemical potential of electrons, $-\tilde{\mu}_e$, which can be transformed to the electrode potential up to a constant. The experimental data at Ag(110), measured by Valette, are corrected using a suggested roughness factor of 1.15 [18]. In the simulation of Ag(110)-0.1 M NaClO₄ aqueous interface, only the ion properties, as shown in Table 5, are tuned while all other parameters are maintained at their base values obtained for the Ag(110)-KPF₆ aqueous solution interface.

Table 5. Parameters of ion properties

Ion parameters	r₁/Å	$\bar{\alpha}_i$	$d_i^{\rm M}/a_0$	$ar{eta_i}$
Solvated K ⁺	3.6	-0.05	13.3	0.19
Solvated Na ⁺	3.25	-0.022	13.3	0.15
Bare PF_6^-	2.7	-0.081	11.6	4.5
Bare ClO ₄	2.75	-0.04	9.4	1

3.3.3 Solvent properties

The solvent significantly influences the Helmholtz layer [23,92] and the diffuse layer [93] of the EDL structure. In the present context, these solvent properties include basic static dielectric properties, short-range correlations between solvent molecules, and short-range interactions between the solvent and the metal surface. The solvent dependence of C_{dl} is determined by all solvent properties, rendering it difficult to decouple the influence of a single property without the aid of a model [73,94].



Figure 10. Differential double layer capacitance (C_{dl}) curves as a function of the electrochemical potential of electrons, $-\tilde{\mu}_{e}$, which can be transformed to the electrode potential up to a constant. The (a) effective dipole moment p, (b) high-frequency dielectric permittivity $\epsilon_{\infty,S}$, are varied at three levels. respectively. In this one-factor-at-a-time study, other parameters except the one under evaluation have their base values.

In our theoretical model, the static dielectric properties of the solvent, which dictate its ability to screen the electric field, are delineated by two key parameters: the high-frequency dielectric permittivity ($\epsilon_{\infty,S}$) and the effective dipole moment (p) of solvent. Their influences on C_{dl} curves are displayed in Figure 10a and 10b. As expected, an elevated C_{dl} profile is obtained at larger $\epsilon_{\infty,S}$ and p. When p increases, the solvent can better screen the electric field generated by electron spillover near the metal surface. This leads to a decrease in $\phi_{M,pzc}$ and, as a result, a negative shift in the PZC. Similarly, increasing $\epsilon_{\infty,S}$ also improves the solvent's screening capability, but its primary impact on the PZC arises from the enhancement of local screening within the region ~2 Å above the metal edge, as shown in Eq. 81. In a recent work, we have discussed the influence of static dielectric properties on the PZC at the Au(111)-KPF₆ interface [73]. The static dielectric properties primarily influence the overall magnitude and the PZC of C_{dl} curves but have little impact on their shapes.



Figure 11. Differential double layer capacitance (C_{dl}) curves as a function of the electrochemical potential of electrons, $-\tilde{\mu}_{e}$, which can be transformed to the electrode potential up to a constant. The (a) dimensionless K_{α} , (b) dimensionless K_{β} , are varied at three levels. respectively. In this one-factor-at-a-time study, other parameters except the one under evaluation have their base values.

In addition to the static dielectric properties, our theory also incorporates short-range correlations between solvent molecules, controlled by K_{α} and K_{β} , into the description of the solvent. Their influences on C_{dl} are shown in Figure 11a and 11b. When K_{α} becomes more negative or when K_{β} decreases, the C_{dl} at PZC is elevated, the anionic and cationic peaks are closer, and the PZC shifts to more negative potentials. It is observed that a more negative value of K_{α} leads to a more oscillatory solvent polarization, as shown in Figure 12a. As K_{α} approaches zero, the oscillations gradually diminish. A more oscillatory polarization field implies that solvent molecules near the metal surface more effectively screen the electric field generated from metal electron spillover, thereby lowering $\phi_{M,pzc}$ and shifting PZC to a more negative value. The increased oscillation at more negative K_{α} generate a more oscillatory distribution of the electric potential on the solution side, facilitating a more layered structure of ions, as shown in Figure 12b. The more layered structure allows more ions to be present within the solvent layers, causing an increase in C_{dl} at PZC. As discussed, a more layered structure of ions narrows the ionic peak in the C_{dl} profile. Additionally, at a more negative K_{α} , Figure 12a shows that solvent molecules exhibit a more ordered orientation within each layer. This implies a lower dielectric permittivity at the interface, which in turn leads to a steeper decrease in C_{dl} at potentials far from PZC. The mechanism of how K_{β} affects the C_{dl} curve is similar, as Figure S1 shows a more oscillatory solvent polarization and a more layered interface at smaller K_{β} , akin to the situation observed with a more negative K_{α} . The consideration of short-range correlations among solvent molecules, which lead to a layered structure at the interface, contributes to the increase in capacitance at PZC and narrowing of ionic peaks. This is primary reason why the model results of DPPFT better align with experimental observations.



Figure 12. The distributions of (a) the polarization field and (b) anion concentration at PZC of the $C_{\rm dl}$ curve in Figure 11a, at different value of dimensionless K_{α} , as indicated in Figure 12a. The metal edge is located at x = 0.

The DPPFT inherently accounts for the effects of short-range interactions between solvent molecules and the metal surface on the interfacial structure and properties. This consideration is not explicitly considered in the theory proposed by Berthoumieux and Kornyshev [39], as well as in that by Blossey and Podgornik [50,51]. Figure 13 highlights the significant impact of the short-range interaction parameters d_s^M and β_s on the C_{dl} profile. At a smaller d_s^M , we observe a more negative PZC, a higher C_{dl} at PZC, and a reduced distance between anionic peak and cationic peak of the C_{dl} curve. A similar trend is evident for β_s at a smaller value, as shown in Figure 13b.



Figure 13. Differential double layer capacitance (C_{dl}) curves as a function of the electrochemical potential of electrons, $-\tilde{\mu}_{e}$, which can be transformed to the electrode potential up to a constant. The (a) effective equilibrium distance of solvent molecules d_{s}^{M} , (b) dimensionless β_{s} , are varied at three levels. respectively. In this one-factor-at-a-time study, other parameters except the one under evaluation have their base values.

Figure 14 shows the distributions of the polarization field for various values of d_s^M and β_s . The EDL becomes more oscillatory and, therefore, more layered at smaller values of d_s^M or β_s . A more layered interface, as previously discussed, accounts for the observed trends in the C_{dl} profile with decreasing d_s^M and β_s in Figure 13. We also notice that the oscillatory distribution of the polarization field shifts closer to the metal surface at smaller d_s^M and β_s . This promotes ionic layering nearer to the metal surface, thereby facilitating the electron transfer between ions and the metal surface. The effects of d_s^M and β_s on the interfacial structure can be attributed to the impact of metal electronic effect on solvent molecules. Smaller values of d_s^M and β_s allow solvent molecules to approach the metal surface more closely, where they experience a stronger electric field generated by electron spillover. This induces a greater extent of oxygen-down orientation in the first solvent layer to screen the stronger electric field. The electrostatic interactions between solvent layers lead to more ordered orientations of solvent molecules in the subsequent layers. The more ordered orientation of solvent molecules in each layer contributes to a more oscillatory distribution of the polarization field.



Figure 14. The distributions of the polarization field of the $C_{\rm dl}$ curve in Figure 13, at different value of (a) $d_{\rm s}^{\rm M}$ and (b) $\bar{\beta}_{\rm s}$, as indicated. The metal edge is located at x = 0.

4 Conclusions

We have developed a computationally-efficient density-potential-polarization functional theory (DPPFT) for the modeling of electric double layers (EDLs) under constant-potential conditions. Compared to the previous density-potential functional theory (DPFT) [54,67,95], the DPPFT model provides a more realistic and refined description of the electrolyte solution within the EDL. In addition to electrostatic interactions, DPPFT incorporates short-range correlations among classical particles in the electrolyte solution. In comparison with the theories of Berthoumieux and Kornyshev [39], as well as Blossey and Podgornik [50,51], we incorporate a quantum mechanical treatment of metal electrons. Therefore, the DPPFT model provides a holistic approach to the EDL.

The DPPFT approach captures major phenomena at electrified interfaces, including metal

electronic effects, oscillatory electric and polarization fields, and the layered distributions of ions. Calibrated with existing capacitance data of the Ag(110)-KPF₆ aqueous interface [18], the model unveils details of the microscopic interfacial structure associated with profiles of double layer capacitance. Specifically, solvent molecules form layers with alternating orientation near the metal surface, that induces a layering of anions and cations within these solvent layers. The layered structure allows explain why excess co-ions do exist in the EDL, a phenomenon that is absent in the classical EDL theories. This novel finding opens avenues to understand anion adsorption at negatively charged surfaces and their leap effects on electrocatalytic reactions.

We conducted a parametric analysis on the calibrated model to explore how model parameters, including metal electronic parameters, ion properties, solvent properties, influence the microscopic interfacial structure and double layer capacitance. Thanks to an explicit account for metal electronic effects and combined effects of ion properties, the model well reproduces and explains the experimental capacitance observed across different crystal faces and in various electrolyte solutions. The coefficient in the gradient term of electronic kinetic energy affects the PZC monotonically via altering the surface potential, while the charge density of metal cationic cores exhibits a nonmonotonic relation with the PZC by simultaneously tuning the surface potential and the electron chemical potential in the bulk metal. The model delineates static dielectric properties of the solvent as effects of two key parameters: the solvent's high-frequency dielectric permittivity and effective dipole moment. The solvent with larger values of those parameters can more effectively screens the interface electric field, resulting in an increase in capacitance and a negatively shift in PZC.

We revealed that intensified ion layering results in an elevated capacitance at PZC and narrowed ionic peaks in the double layer capacitance profile. Ion layering is influenced strongly by short-range correlations/interactions between ions and solvent molecules, between solvent molecules, and between solvent molecules and the metal surface. Weaker short-range correlations between ions and solvent molecules result in less effective screening of the electrostatic potential between solvent layers, enabling more ions to be accommodated within these layers. The interfacial oscillations are enhanced in the presence of stronger short-range correlations between solvent molecules, and stronger short-range interactions between solvent molecules and the metal surface. The latter is attributed to enhanced metal electronic effects on the interfacial solvent molecules. A more oscillatory interface causes a negative shift in PZC and promotes a more layered ion structure.

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References

[1] J. Wu, Understanding the Electric Double-Layer Structure, Capacitance, and Charging Dynamics, Chem. Rev. **122**, 10821 (2022).

[2] L. D. Chen, M. Urushihara, K. Chan, and J. K. Nørskov, *Electric Field Effects in Electrochemical CO₂ Reduction*, ACS Catal. 6, 7133 (2016).

[3] X. Zhu, J. Huang, and M. Eikerling, *pH Effects in a Model Electrocatalytic Reaction Disentangled*, JACS Au **3**, 1052 (2023).

[4] S. Kondrat, G. Feng, F. Bresme, M. Urbakh, and A. A. Kornyshev, *Theory and Simulations of Ionic Liquids in Nanoconfinement*, Chem. Rev. **123**, 6668 (2023).

[5] P. M. Biesheuvel and M. Z. Bazant, *Analysis of Ionic Conductance of Carbon Nanotubes*, Phys. Rev. E **94**, 050601 (2016).

[6] A. Levy, J. P. de Souza, and M. Z. Bazant, *Breakdown of Electroneutrality in Nanopores*, J. Colloid Interface Sci. **579**, 162 (2020).

[7] E. Secchi, A. Niguès, L. Jubin, A. Siria, and L. Bocquet, *Scaling Behavior for Ionic Transport and Its Fluctuations in Individual Carbon Nanotubes*, Phys. Rev. Lett. **116**, 154501 (2016).

[8] R. T. Mathias, G. J. Baldo, K. Manivannan, and S. Mclaughlin, *Discrete Charges on Biological Membranes*, in *Electrified Interfaces in Physics, Chemistry and Biology*, edited by R. Guidelli (Springer Netherlands, Dordrecht, 1992), pp. 473–490.

[9] B. Roux, T. Allen, S. Bernèche, and W. Im, *Theoretical and Computational Models of Biological Ion Channels*, Q. Rev. Biophys. **37**, 15 (2004).

[10] K. Kristiansen, M. Valtiner, G. W. Greene, J. R. Boles, and J. N. Israelachvili, *Pressure Solution – The Importance of the Electrochemical Surface Potentials*, Geochim. Cosmochim. Acta **75**, 6882 (2011).

[11] W. Schmickler and E. Santos, *Interfacial Electrochemistry* (Springer Science & Business Media, 2010).

[12] A. J. Bard, L. R. Faulkner, and H. S. White, *Electrochemical Methods: Fundamentals and Applications* (John Wiley & Sons, 2022).

[13] D. C. Grahame and R. Parsons, *Components of Charge and Potential in the Inner Region of the Electrical Double Layer: Aqueous Potassium Chloride Solutions in Contact with Mercury at 25°*, J. Am. Chem. Soc. **83**, 1291 (1961).

[14] D. C. Grahame, *The Electrical Double Layer and the Theory of Electrocapillarity.*, Chem. Rev. **41**, 441 (1947).

[15] R. Parsons and N. F. Mott, *The Structure of the Mercury-Electrolyte Interphase in the Presence of Thiourea*, Proc. R. Soc. Lond. Ser. Math. Phys. Sci. **261**, 79 (1997).

[16] G. Valette, Double Layer on Silver Single Crystal Electrodes in Contact with Electrolytes Having Anions Which Are Slightly Specifically Adsorbed: Part III. The (111) Face, J. Electroanal. Chem. Interfacial Electrochem. **269**, 191 (1989).

[17] G. Valette, Double Layer on Silver Single Crystal Electrodes in Contact with Electrolytes

Having Anions Which Are Slightly Specifically Adsorbed: Part II. The (100) Face, J. Electroanal. Chem. Interfacial Electrochem. **138**, 37 (1982).

[18] G. Valette, Double Layer on Silver Single-Crystal Electrodes in Contact with Electrolytes Having Anions Which Present a Slight Specific Adsorption: Part I. The (110) Face, J. Electroanal. Chem. Interfacial Electrochem. **122**, 285 (1981).

[19] A. Hamelin, T. Vitanov, E. Sevastyanov, and A. Popov, *The Electrochemical Double Layer on Sp Metal Single Crystals*, J. Electroanal. Chem. Interfacial Electrochem. **145**, 225 (1983).

[20] S. Trasatti and L. M. Doubova, *Crystal-Face Specificity of Electrical Double-Layer Parameters at Metal/Solution Interfaces*, J. Chem. Soc. Faraday Trans. **91**, 3311 (1995).

[21] S. Trasatti, *Structure of the Metal/Electrolyte Solution Interface: New Data for Theory*, Electrochimica Acta **36**, 1659 (1991).

[22] Ojha, Kasinath and Doblhoff-Dier, Katharina and Koper, Marc TM, *Double-Layer Structure of the Pt(111)–Aqueous Electrolyte Interface*, Proc. Natl. Acad. Sci. **119**, e2116016119 (2022).

[23] J. Huang, Zooming into the Inner Helmholtz Plane of Pt(111)–Aqueous Solution Interfaces: Chemisorbed Water and Partially Charged Ions, JACS Au 3, 550 (2023).

[24] L. Zhang and J. Huang, *Measurement and Interpretation of the Double Layer Capacitance of Pt(111)/Aqueous Solution Interfaces*, Curr. Opin. Electrochem. **42**, 101419 (2023).

[25] K. Doblhoff-Dier and M. T. M. Koper, *Electric Double Layer of Pt(111): Known Unknowns and Unknown Knowns*, Curr. Opin. Electrochem. **39**, 101258 (2023).

[26] A. A. Kornyshev, *Metal Electrons in the Double Layer Theory*, Electrochimica Acta **34**, 1829 (1989).

[27] W. Schmickler, Electronic Effects in the Electric Double Layer, Chem. Rev. 96, 3177 (1996).

[28] J. Huang, Y. Zhang, M. Li, A. Groß, and S. Sakong, *Comparing Ab Initio Molecular Dynamics and a Semiclassical Grand Canonical Scheme for the Electric Double Layer of the Pt(111)/Water Interface*, J. Phys. Chem. Lett. **14**, 2354 (2023).

[29] J. Le, M. Iannuzzi, A. Cuesta, and J. Cheng, *Determining Potentials of Zero Charge of Metal Electrodes versus the Standard Hydrogen Electrode from Density-Functional-Theory-Based Molecular Dynamics*, Phys. Rev. Lett. **119**, 016801 (2017).

[30] L. Li, Y.-P. Liu, J.-B. Le, and J. Cheng, Unraveling Molecular Structures and Ion Effects of Electric Double Layers at Metal Water Interfaces, Cell Rep. Phys. Sci. **3**, 100759 (2022).

[31] W. Schmickler and D. Henderson, *The Interphase between Jellium and a Hard Sphere Electrolyte. A Model for the Electric Double Layer*, J. Chem. Phys. **80**, 3381 (1984).

[32] J. P. Badiali, M. L. Rosinberg, F. Vericat, and L. Blum, *A Microscopic Model for the Liquid Metal-Ionic Solution Interface*, J. Electroanal. Chem. Interfacial Electrochem. **158**, 253 (1983).

[33] W. Schmickler, *A Jellium-Dipole Model for the Double Layer*, J. Electroanal. Chem. Interfacial Electrochem. **150**, 19 (1983).

[34] J. N. Israelachvili and R. M. Pashley, *Molecular Layering of Water at Surfaces and Origin of Repulsive Hydration Forces*, Nature **306**, 249 (1983).

[35] R. M. Pashley and J. N. Israelachvili, *Molecular Layering of Water in Thin Films between Mica Surfaces and Its Relation to Hydration Forces*, J. Colloid Interface Sci. **101**, 511 (1984).

[36] R. M. Pashley, *DLVO and Hydration Forces between Mica Surfaces in Li⁺*, *Na⁺*, *K⁺*, and *Cs⁺ Electrolyte Solutions: A Correlation of Double-Layer and Hydration Forces with Surface Cation Exchange Properties*, J. Colloid Interface Sci. **83**, 531 (1981).

[37] Klaassen, Aram and Liu, Fei and Mugele, Frieder and Siretanu, Igor, *Correlation between Electrostatic and Hydration Forces on Silica and Gibbsite Surfaces: An Atomic Force Microscopy Study*, Langmuir Langmuir, 914 (2022).

[38] I. Siretanu, S. R. van Lin, and F. Mugele, *Ion Adsorption and Hydration Forces: A Comparison of Crystalline Mica vs. Amorphous Silica Surfaces*, Faraday Discuss. 246, 274 (2023).
[39] J. G. Hedley, H. Berthoumieux, and A. A. Kornyshev, *The Dramatic Effect of Water Structure on Hydration Forces and the Electrical Double Layer*, J. Phys. Chem. C 127, 18 (2023).

[40] A. Frumkin, *Wasserstoffüberspannung Und Struktur Der Doppelschicht*, Z. Für Phys. Chem. **164A**, 121 (1933).

[41] X. Zhu, J. Huang, and M. Eikerling, *Electrochemical CO₂ Reduction at Silver from a Local Perspective*, ACS Catal. **11**, 14521 (2021).

[42] J. Huang, J. Zhang, and M. Eikerling, *Unifying Theoretical Framework for Deciphering the Oxygen Reduction Reaction on Platinum*, Phys. Chem. Chem. Phys. **20**, 11776 (2018).

[43] L. Zhang, J. Cai, Y. Chen, and J. Huang, *Modelling Electrocatalytic Reactions with a Concerted Treatment of Multistep Electron Transfer Kinetics and Local Reaction Conditions*, J. Phys. Condens. Matter **33**, 504002 (2021).

[44] S. Ringe, E. L. Clark, J. Resasco, A. Walton, B. Seger, A. T. Bell, and K. Chan, *Understanding Cation Effects in Electrochemical CO₂ Reduction*, Energy Environ. Sci. **12**, 3001 (2019).

[45] L. B. T. de Kam, T. L. Maier, and K. Krischer, *Electrolyte Effects on the Alkaline Hydrogen Evolution Reaction: A Mean-Field Approach*, (2024).

[46] D. J. Gavaghan and S. W. Feldberg, *Extended Electron Transfer and the Frumkin Correction*,J. Electroanal. Chem. **491**, 103 (2000).

[47] S. W. Feldberg and N. Sutin, *Distance Dependence of Heterogeneous Electron Transfer through the Nonadiabatic and Adiabatic Regimes*, Chem. Phys. **324**, 216 (2006).

[48] G. Monet, F. Bresme, A. Kornyshev, and H. Berthoumieux, *Nonlocal Dielectric Response of Water in Nanoconfinement*, Phys. Rev. Lett. **126**, 21 (2021).

[49] M. Vatin, A. Porro, N. Sator, J.-F. Dufrêche, and H. Berthoumieux, *Electrostatic Interactions in Water: A Nonlocal Electrostatic Approach*, Mol. Phys. **119**, e1825849 (2021).

[50] R. Blossey and R. Podgornik, *Field Theory of Structured Liquid Dielectrics*, Phys Rev Res 4, 2 (2022).

[51] R. Blossey and R. Podgornik, *A Comprehensive Continuum Theory of Structured Liquids*, J. Phys. Math. Theor. **56**, 2 (2023).

[52] R. Blossey and R. Podgornik, *Continuum Theories of Structured Dielectrics*, Europhys. Lett. **139**, 2 (2022).

[53] J. Huang, *Hybrid Density-Potential Functional Theory of Electric Double Layers*, Electrochimica Acta **389**, 138720 (2021).

[54] J. Huang, Density-Potential Functional Theory of Electrochemical Double Layers: Calibration on the Ag (111)-KPF₆ System and Parametric Analysis, J. Chem. Theory Comput. **19**, 3 (2023).

[55] S. Lundqvist and N. H. March, *Theory of the Inhomogeneous Electron Gas* (Springer Science & Business Media, 2013).

[56] L. H. Thomas, *The Calculation of Atomic Fields*, Math. Proc. Camb. Philos. Soc. 23, 542 (1927).

[57] E. Fermi, Eine statistische Methode zur Bestimmung einiger Eigenschaften des Atoms und ihre Anwendung auf die Theorie des periodischen Systems der Elemente, Z. Für Phys. 48, 73 (1928).

[58] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple*, Phys. Rev. Lett. **77**, 3865 (1996).

[59] J. P. Perdew and S. Kurth, *Density Functionals for Non-Relativistic Coulomb Systems in the New Century*, in *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. A. L. Marques (Springer, Berlin, Heidelberg, 2003), pp. 1–55.

[60] Valentin V. Karasiev, Lázaro Calderín, and S. B. Trickey, *Importance of Finite-Temperature Exchange Correlation for Warm Dense Matter Calculations*, Phys Rev E **93**, 063207 (2016).

[61] J.-M. Caillol, O. Patsahan, and I. Mryglod, *Statistical Field Theory for Simple Fluids: The Collective Variables Representation*, Phys. Stat. Mech. Its Appl. **368**, 2 (2006).

[62] N. Bruch, T. Binninger, J. Huang, and M. Eikerling, *Incorporating Electrolyte Correlation Effects into Variational Models of Electrochemical Interfaces*, J. Phys. Chem. Lett. **15**, 2015 (2024).

[63] Y. A. Budkov and A. L. Kolesnikov, *Modified Poisson–Boltzmann Equations and Macroscopic Forces in Inhomogeneous Ionic Fluids*, J. Stat. Mech. Theory Exp. **2022**, 053205 (2022).

[64] L. Lue, *A Variational Field Theory for Solutions of Charged, Rigid Particles*, Fluid Phase Equilibria **241**, 236 (2006).

[65] J. J. Bikerman, XXXIX. Structure and Capacity of Electrical Double Layer, Lond. Edinb. Dublin Philos. Mag. J. Sci. **33**, 384 (1942).

[66] M. M. Melander, T. Wu, T. Weckman, and K. Honkala, *Constant Inner Potential DFT for Modelling Electrochemical Systems under Constant Potential and Bias*, Npj Comput. Mater. **10**, 5 (2024).

[67] J. Huang, S. Chen, and M. Eikerling, *Grand-Canonical Model of Electrochemical Double Layers from a Hybrid Density–Potential Functional*, J. Chem. Theory Comput. **17**, 4 (2021).

[68] K. Amann-Winkel, M.-C. Bellissent-Funel, L. E. Bove, T. Loerting, A. Nilsson, A. Paciaroni, D. Schlesinger, and L. Skinner, *X-Ray and Neutron Scattering of Water*, Chem. Rev. 116, 7570 (2016).

[69] C. N. Rowley and B. Roux, *The Solvation Structure of Na*⁺ and K^+ in Liquid Water Determined from High Level Ab Initio Molecular Dynamics Simulations, J. Chem. Theory Comput. **8**, 3526 (2012).

[70] S. G. Raju and S. Balasubramanian, Aqueous Solution of [Bmim][PF₆]: Ion and Solvent Effects on Structure and Dynamics, J. Phys. Chem. B **113**, 4799 (2009).

[71] A. M. Kuznetsov and J. Ulstrup, *Elements of Dielectric Theory*, in *Electron Transfer in Chemistry and Biology: An Introduction to the Theory* (John Wiley & Sons Ltd, Chichester, UK, 1999).

[72] J. Ulstrup, *Multiphonon Representation of Continuous Media*, in *Charge Transfer Processes in Condensed Media*, edited by J. Ulstrup (Springer, Berlin, Heidelberg, 1979), pp. 40–70.

[73] W. Tang, S. Zhao, and J. Huang, Origin of Solvent Dependency of the Potential of Zero Charge, JACS Au **3**, 3381 (2023).

[74] J. Cheng and M. Sprik, *Alignment of Electronic Energy Levels at Electrochemical Interfaces*, Phys. Chem. Chem. Phys. **14**, 11245 (2012).

[75] L. Andersson and C. Zhang, *Molecular Dynamics Simulations of Metal-Electrolyte Interfaces under Potential Control*, Curr. Opin. Electrochem. **42**, 101407 (2023).

[76] M. F. Toney, J. N. Howard, J. Richer, G. L. Borges, J. G. Gordon, O. R. Melroy, D. G. Wiesler, D. Yee, and L. B. Sorensen, *Voltage-Dependent Ordering of Water Molecules at an Electrode–Electrolyte Interface*, Nature **368**, 444 (1994).

[77] J. Le, A. Cuesta, and J. Cheng, *The Structure of Metal-Water Interface at the Potential of Zero Charge from Density Functional Theory-Based Molecular Dynamics*, J. Electroanal. Chem. **819**, 87 (2018).

[78] S. Schnur and A. Groß, *Properties of Metal–Water Interfaces Studied from First Principles*, New J. Phys. **11**, 12 (2009).

[79] A. Roudgar and A. Groß, *Water Bilayer on the Pd/Au(111) Overlayer System: Coadsorption and Electric Field Effects*, Chem. Phys. Lett. **409**, 157 (2005).

[80] J.-J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J. Guo, D. Prendergast, and M. Salmeron, *The Structure of Interfacial Water on Gold Electrodes Studied by X-Ray Absorption Spectroscopy*, Science **346**, 831 (2014).

[81] Y. Tong, F. Lapointe, M. Thämer, M. Wolf, and R. K. Campen, *Hydrophobic Water Probed Experimentally at the Gold Electrode/Aqueous Interface*, Angew. Chem. Int. Ed. **56**, 4211 (2017).

[82] N. García-Aráez, V. Climent, and J. M. Feliu, *Evidence of Water Reorientation on Model Electrocatalytic Surfaces from Nanosecond-Laser-Pulsed Experiments*, J. Am. Chem. Soc. **130**, 3824 (2008).

[83] A. Kasina, E. Cocklin, S. Horswell, Y. Grunder, and C. A. Lucas, *Structure of the Electrochemical Interface: Ag(Hkl) in an Alkaline Electrolyte*, J. Phys. Chem. C **128**, 13318 (2024).

[84] J. M. Yoo, J. Ingenmey, M. Salanne, and M. R. Lukatskaya, *Anion Effect in Electrochemical CO*₂ *Reduction: From Spectators to Orchestrators*.

[85] M. Koper, *Theory and Kinetic Modeling of Electrochemical Cation-Coupled Electron Transfer Reactions*, J. Solid State Electrochem. 1 (2023).

[86] X. Qin, H. A. Hansen, K. Honkala, and M. M. Melander, *Cation-Induced Changes in the Inner- and Outer-Sphere Mechanisms of Electrocatalytic CO₂ Reduction*, Nat. Commun. **14**, 7607

(2023).

[87] S. Ringe, C. G. Morales-Guio, L. D. Chen, M. Fields, T. F. Jaramillo, C. Hahn, and K. Chan, *Double Layer Charging Driven Carbon Dioxide Adsorption Limits the Rate of Electrochemical Carbon Dioxide Reduction on Gold*, Nat. Commun. **11**, 1 (2020).

[88] W. Schmickler and R. Guidelli, *The Partial Charge Transfer*, Electrochimica Acta **127**, 489 (2014).

[89] S. Trasatti, *Work Function, Electronegativity, and Electrochemical Behaviour of Metals*, J. Electroanal. Chem. Interfacial Electrochem. **33**, 351 (1971).

[90] S. Trasatti, Potentials of Zero Charge. What They Suggest About the Structure of the Interfacial Region, in Trends in Interfacial Electrochemistry, edited by A. F. Silva (Springer Netherlands, Dordrecht, 1986), pp. 25–48.

[91] M. Z. Bazant, M. S. Kilic, B. D. Storey, and A. Ajdari, *Towards an Understanding of Induced-Charge Electrokinetics at Large Applied Voltages in Concentrated Solutions*, Adv. Colloid Interface Sci. **152**, 1–2 (2009).

[92] P. Li, J. Huang, Y. Hu, and S. Chen, *Establishment of the Potential of Zero Charge of Metals in Aqueous Solutions: Different Faces of Water Revealed by Ab Initio Molecular Dynamics Simulations*, J. Phys. Chem. C **125**, 3972 (2021).

[93] A. Iglič, E. Gongadze, and K. Bohinc, *Excluded Volume Effect and Orientational Ordering near Charged Surface in Solution of Ions and Langevin Dipoles*, Bioelectrochemistry **79**, 223 (2010).

[94] A. S. Shatla, M. Landstorfer, and H. Baltruschat, On the Differential Capacitance and Potential of Zero Charge of Au(111) in Some Aprotic Solvents, ChemElectroChem 8, 1817 (2021).
[95] M. S. Shibata, Y. Morimoto, I. V. Zenyuk, and A. Z. Weber, Parameter-Fitting-Free

Continuum Modeling of Electric Double Layer in Aqueous Electrolyte, J. Chem. Theory Comput. **20**, 6184 (2024).