

Short-range solvent-solvent and ion-solvent correlations at metal-electrolyte interfaces: Parametrization and benchmarking

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Short-range correlations in electrolyte solutions lead to oscillatory profiles of water polarization and ionic concentration at electrode-electrolyte interfaces. The recently developed density-potential-polarization functional theory (DPPFT) provides a comprehensive framework to incorporate these short-range correlation effects. In the present work, the parameters describing short-range solvent-solvent and ion-solvent correlations in DPPFT are determined from the wave-number-dependent dielectric susceptibility spectrum of pure water and ion solvation energies, respectively. The experimental trends in the ionic-radius-dependent hydration energies of alkali metal cations and halide anions are reproduced by the solvation model. Within this model, the charge hydration asymmetry is phenomenologically rationalized by a stronger short-range repulsion between cations and water molecules than between anions and water molecules. Using these parameters, DPPFT is then applied to describe short-range correlation effects at the Ag(111)-NaF aqueous electrolyte interface. The water polarization profiles obtained from DPPFT calculations agree with *ab initio* molecular dynamics simulations. Furthermore, as the strength of short-range ion-solvent repulsion increases, the peaks of anionic and cationic layers shift from regions near centers of positive and negative polarization charges, respectively, toward those of opposite sign, thereby preserving solvation configurations similar to those in bulk solution. This work develops a procedure for parametrizing short-range correlation effects within the DPPFT framework, thereby enabling a more quantitative and computationally efficient description of atomic-scale phenomena at electrochemical interfaces.

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I. INTRODUCTION

Understanding the interfacial structure between electrode materials and aqueous electrolyte solutions is of great relevance to the advancement of electrochemical devices such as fuel cells, batteries, and electrolyzers. Short-range correlations within electrolyte solutions are closely linked to atomic-scale interfacial phenomena, such as spatial oscillations in electrostatic potential and ion density over a wide

range of electrolyte concentrations [1–4]. While molecular dynamics (MD) simulations can accurately capture atomistic details, a continuum theory incorporating short-range correlation effects is needed for large-scale modeling.

The effects of short-range correlations between solvent molecules can be taken into account through nonlocal electrostatics [5–9], wherein the dielectric susceptibility becomes wave vector dependent in Fourier space, giving rise to its spatial dispersion spectrum (unless otherwise specified, polarization and dielectric response throughout refer to their longitudinal components). A commonly used form of the susceptibility spectrum is the Lorentzian, which in real space corresponds to a Yukawa-type susceptibility that decays over the correlation length. The Lorentzian form of the susceptibility spectrum is equivalent to the second-order Landau-Ginzburg (LG) functional of the corresponding polarization mode, as used in the Marčelja-Radič model [10]. An oscillatory

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susceptibility has also been considered to describe ion solvation [11]. The inclusion of the nonlocal electrostatic effect within the continuum theory leads to substantially improved agreement between the predicted solvation energies of alkali metal and halide ions and experimental values [8,12,13].

Recently, an extended fourth-order LG functional, with the orientational polarization as the functional variable, has been adopted to describe the short-range correlation energy between water molecules, with particular focus on the structure of water in nanoconfinement [14] and in the vicinity of ions [15]. The wave-number-dependent dielectric susceptibility derived from this extended LG functional captures the primary peak in the spatial dispersion spectrum of pure water at $k \approx 3 \text{ \AA}^{-1}$, as observed in inelastic neutron scattering experiments and MD simulations [14,16–19]. Based on the LG functional description for short-range correlations between water molecules in the electrical double layer (EDL), Hedley *et al.* [20] introduced polarization as a separate order parameter, in addition to the charge density. This two-order-parameter EDL model delineates spatial oscillations in electric potential and ionic concentration, which arise from the polarized water layering induced by short-range correlations between water molecules [20].

Meanwhile, a field-theoretic model has been developed by Blossey and Podgornik for structured electrolyte solutions [21,22]. Beyond the LG-based description for solvent correlations in the EDL model by Hedley *et al.* [20], further physical aspects such as ion-solvent short-range correlations, nonlinear dielectric response, and constituent polarizability have also been accounted for in this field-theoretic approach. The Blossey-Podgornik model was later combined by us with an orbital-free density functional theory (DFT) of electrons on the metal side within a grand canonical framework [23], referred to as the density-potential-polarization functional theory (DPPFT) approach. DPPFT incorporates the electron spillover effects and eliminates the need to specify boundary conditions for the polarization at the metal surface. The double-layer capacitance (C_{dl}) simulated using this semiclassical EDL model shows improved agreement with experimental data at the Ag-aqueous KPF_6 solution interface compared to previous work [24], particularly in the enhanced capacitance magnitude at the potential of zero charge (PZC). This improvement is attributed to short-range solvent-solvent correlations that give rise to a layered solvent structure, leading to a reduced effective dielectric constant near the surface, as verified by experiments [25] and MD simulations [26–29].

In the field-theoretic approach to structured electrolyte solutions [21–23], the solvent orientational polarization $\mathbf{P}$ is influenced by both the electrostatic field and an auxiliary field $\mathcal{E}$, as described by a modified Langevin polarization equation, i.e.,

$$\mathbf{P} = -\frac{pn_s\mathcal{L}(\beta p|\mathcal{E} + \nabla\phi|)}{|\mathcal{E} + \nabla\phi|}(\mathcal{E} + \nabla\phi), \quad (1)$$

where $\beta = 1/(k_B T)$ is the thermal factor, ϕ is the electrostatic potential, n_s is the number density of solvent molecules, and $\mathcal{L}(x) = \coth(x) - 1/x$ denotes the Langevin function. The solvent dipole moment has a magnitude of p , and here, its direction is conventionally defined from the negative to the positive charge center, in contrast to the definition adopted in the previous work [21–23,30]. The auxiliary field $\mathcal{E}$ is expressed as [23]

$$\begin{aligned} \mathcal{E} = & \frac{1}{\epsilon_0} (K_s \mathbf{P} - K_\alpha \nabla^2 \mathbf{P} + K_\beta \nabla^4 \mathbf{P}) + \alpha_c e_0 \nabla n_c \\ & - \alpha_a e_0 \nabla n_a, \end{aligned} \quad (2)$$

where ϵ_0 is the vacuum permittivity, e_0 is the elementary charge, and n_a and n_c are the number densities of anions and cations, respectively. K_s , K_α , and K_β are expansion coefficients in the LG functional. The K_s term represents a local short-range correlation mode, while the K_α and K_β terms correspond to two nonlocal modes characterized by the characteristic lengths $|K_\alpha|^{1/2}$ and $|K_\beta|^{1/4}$, respectively. α_c and α_a are the leading-order expansion coefficients of the short-range correlation energy between ions and solvent molecules, characterizing the strength of short-range cation-solvent and anion-solvent correlations, respectively. The corresponding correlation lengths measured from the cationic and anionic charges are given by $|\alpha_c \epsilon_{\text{ir}}|^{1/2}$ and $|\alpha_a \epsilon_{\text{ir}}|^{1/2}$, respectively. Here, the infrared dielectric permittivity ϵ_{ir} accounts for the nonorientational polarization modes of the medium, including electronic and atomic polarizations.

The description of solvent dielectric polarization behavior is a central aspect of continuum dielectric theory. As seen in Eq. (1), the auxiliary field $\mathcal{E}$ is a nonelectrostatic field that represents the averaged influence of short-range correlations on the solvent orientational polarization. In the limiting case where all short-range correlation parameters vanish, $\mathcal{E} = 0$, and Eq. (1) reduces to the classical Langevin polarization model [31,32], which describes the orientations of noninteracting permanent dipoles in response to a local electrostatic field. Therefore, determining the short-range correlation parameters in Eq. (2) is a necessary first step toward quantifying this short-range correlation effect. Once this is done, combining Eqs. (1) and (2) with the Poisson equation enables us to quantitatively describe short-range correlation effects in the electrolyte solution or, in the DPPFT approach, to consider the short-range correlation effect on the interfacial structure and properties of the whole interface. To this end, in the following, we consider the nonlocal electrostatics of pure water and ion solvation, respectively, to determine the short-range correlation parameters between water

molecules and between ions and water and finally examine the short-range correlation effects on the interfacial structure between the metal and the aqueous electrolyte solution in a DPPFT framework.

II. PURE WATER

The effect of short-range correlations between water molecules, which are associated with hydrogen-bonding networks [20,33], is reflected, as noted above, in the wave number dependence of the dielectric susceptibility. The dielectric susceptibility is related to the structure factor, the correlation function of the solvent's longitudinal polarization, through the fluctuation-dissipation theorem [17]. For water, the structure factor can be decomposed into partial HH, OH, and OO structure factors, which can be obtained through neutron scattering techniques [16] or MD simulations [17], assuming a localized charge distribution on the atoms. In the linear response regime relevant to the spectrum, Eq. (1) reduces to its linearized form:

$$\mathbf{P} \approx -\frac{1}{3}\beta p^2 n_s^b (\mathcal{E} + \nabla\phi). \quad (3)$$

Combining the above equation and Eq. (2), with α_c and α_a being zero (pure water system), the relationship between the electric displacement $\mathbf{D}$ and the orientational polarization of water $\mathbf{P}$ is given by

$$\begin{aligned} \mathbf{D} &= \epsilon_{\text{ir}} \mathbf{E} + \mathbf{P} \\ &= \left(1 + \epsilon_{\text{ir}} K_s + \frac{3\epsilon_{\text{ir}}\epsilon_0}{\beta p^2 n_s}\right) \mathbf{P} - \epsilon_{\text{ir}} K_\alpha \nabla^2 \mathbf{P} + \epsilon_{\text{ir}} K_\beta \nabla^4 \mathbf{P}, \end{aligned} \quad (4)$$

where $\epsilon_{\text{ir}} = \epsilon_{\text{ir}}/\epsilon_0$ denotes the infrared dielectric constant. Performing a Fourier transform on both sides of the above equation, the spectrum of the longitudinal dielectric susceptibility of orientational polarization is obtained as [14]

$$\chi(k) = \frac{1}{\chi_0^{-1} + \epsilon_{\text{ir}} K_\alpha k^2 + \epsilon_{\text{ir}} K_\beta k^4}, \quad (5)$$

with the reciprocal of $\chi(k)$ at $k = 0$,

$$\chi_0^{-1} = 1 + \epsilon_{\text{ir}} K_s + \frac{3\epsilon_{\text{ir}}\epsilon_0}{\beta p^2 n_s}, \quad (6)$$

where χ_0 is the static dielectric susceptibility of the orientational polarization, which is related to the static dielectric constant of water ϵ_s and ϵ_{ir} by $\chi_0 = 1 - \epsilon_{\text{ir}}/\epsilon_s$. For water, based on its vibrational dispersion spectrum [34,35], the values of 4.9 and 78.5 are used for ϵ_{ir} and ϵ_s , respectively, which gives a value of 0.9376 for χ_0 .

From Eq. (6), the parameter K_s can be determined from bulk properties of the solvent, such as the dipole moment,

number density, and static dielectric constant, as follows:

$$K_s = \frac{1}{\epsilon_s - \epsilon_{\text{ir}}} - \frac{3\epsilon_0}{\beta p^2 n_s}. \quad (7)$$

The magnitude of K_s reflects the extent to which short-range correlations contribute to the local dielectric response. The larger effective dipole moment estimated from the classical Langevin polarization model can be attributed to this contribution. Another factor contributing to the enhanced effective dipole moment is the cavity field effect. Because of dielectric screening, a water molecule experiences a local electric field stronger than the macroscopic field, which can notably modify the effective dipole moment at highly charged surfaces [36].

For a negative K_α and a positive K_β , corresponding to attractive and repulsive short-range correlation modes between solvent molecules, Eq. (5) attains its maximum at the wave number $k_{\text{max}} = (-K_\alpha/(2K_\beta))^{1/2}$ with the corresponding maximum value χ_{max} . Conversely, K_α and K_β can be determined from k_{max} and χ_{max} :

$$K_\beta = \frac{\chi_0^{-1} - \chi_{\text{max}}^{-1}}{\epsilon_{\text{ir}} k_{\text{max}}^4}, \quad K_\alpha = -2K_\beta k_{\text{max}}^2. \quad (8)$$

The dielectric susceptibility spectrum, whether measured experimentally or simulated using MD, may arise not only from orientational polarization but also from atomic polarization χ_{atomic} and electronic polarization χ_{el} of the solvent. We assume that only the dielectric susceptibility associated with solvent orientations is wave number dependent. The total dielectric susceptibility χ_{tot} is then the sum of contributions from different polarization modes,

$$\chi_{\text{tot}}(k) = \chi_{\text{el}} + \chi_{\text{atomic}} + \chi(k) = \frac{\epsilon_{\text{ir}} - 1}{\epsilon_s} + \chi(k). \quad (9)$$

The experimentally measured spectrum of electric susceptibility exhibits a broad overscreening zone, peaking at $k_{\text{max}} = 3 \text{ \AA}^{-1}$ with a maximum value of approximately 40 [14]. As shown in Eq. (9), $\chi(k)$ differs from χ_{tot} by only 0.05 for $\epsilon_{\text{ir}} = 4.9$ and $\epsilon_s = 78.5$. This discrepancy is negligible compared with the dielectric susceptibility in the overscreening region, where $\chi_{\text{tot}} > 1$ and can be neglected in this regime. In this case, K_α and K_β in Eq. (8) are determined using the values of k_{max} and χ_{max} as $-0.047 \text{ \AA}^2$ and $0.0026 \text{ \AA}^4$, respectively.

These short-range correlation parameters can be related to the structural properties of water through its static structure factor, which corresponds to the real-space correlation function of the longitudinal component of the polarization. Assuming purely classical orientations of solvent molecules at constant temperature, this correlation function is proportional to the orientational

dielectric susceptibility by a constant factor [14]. The orientational dielectric susceptibility $\chi(r)$ is obtained by performing an inverse Fourier transform on Eq. (5) as [37]:

$$\chi(r) = \frac{\sin(ar)e^{-br}}{2\pi\epsilon_{\text{ir}}Xr}, \quad (10)$$

provided that the following inequality is satisfied:

$$X^2 = K_\beta\gamma_0 - K_\alpha^2 > 0, \quad \text{with} \quad \gamma_0 = 4(\chi_0\epsilon_{\text{ir}})^{-1}. \quad (11)$$

Accordingly, the correlation function of the orientational polarization exhibits a periodic length λ_p and a decay length λ_d , which can be derived as [14,37]:

$$\lambda_p = \frac{2\pi}{a} = 2\pi\sqrt{\frac{4K_\beta}{-K_\alpha + \sqrt{K_\beta\gamma_0}}} = 2\pi k_{\text{max}}^{-1} \sqrt{\frac{2}{1 + \sqrt{\frac{1}{1 - \chi_0\epsilon_{\text{ir}}^{-1}}}}}, \quad (12)$$

$$\lambda_d = \frac{1}{b} = \sqrt{\frac{4K_\beta}{K_\alpha + \sqrt{K_\beta\gamma_0}}} = k_{\text{max}}^{-1} \sqrt{\frac{2}{-1 + \sqrt{\frac{1}{1 - \chi_0\epsilon_{\text{ir}}^{-1}}}}}. \quad (13)$$

Given the values of $k_{\text{max}} = 3 \text{ \AA}^{-1}$, $\chi_0 = 0.9376$, and $\chi_{\text{max}} = 40$, the characteristic lengths λ_p and λ_d are calculated using the above equations as $\lambda_p = 2.1 \text{ \AA}$ and $\lambda_d = 4.3 \text{ \AA}$. The dielectric susceptibility underlying the LG approach in Eq. (10) takes a Yukawa-type form modified by an oscillatory term, which accounts for the emergence of oscillations in the polarization and electric potential in relevant models [20,23]. At small wave numbers, corresponding to the wavelength $\lambda \gg \lambda_p$, the structural oscillations of water molecules cannot be resolved. Accordingly, the limit $a \rightarrow 0$ is taken, which gives $K_\alpha = \gamma_0/(2b^2)$ and $K_\beta = \gamma_0/(4b^4)$ (see Eq. S9 in Supplemental Material [37]). The longitudinal dielectric susceptibility in Eq. (5) is reduced to the Lorentzian form:

$$\begin{aligned} \chi(k) &= \frac{1}{\chi_0^{-1} + \frac{\epsilon_{\text{ir}}\gamma_0}{2b^2}k^2(1 + \frac{k^2}{2b^2})} \xrightarrow{\text{small } k} \chi_{\text{Lorentz}}(k) \\ &= \frac{\chi_0}{1 + 2\lambda_d^2k^2}. \end{aligned} \quad (14)$$

III. ION SOLVATION

The short-range correlation parameters of water, K_s , K_α , and K_β , can be determined using Eqs. (7) and (8). When a single ion is immersed in water, its electric field polarizes nearby water molecules, leading to ion solvation. The short-range correlations between the ion and the solvent exert a nonelectrostatic field effect on the surrounding

medium, as described in Eq. (2), and consequently influence the dielectric response of water. In the field-theoretic approach [22,23], these ion-solvent short-range correlations are effectively described by a constant kernel, α_c or α_a , which couples the ionic charge density and solvent polarization charge. Let $\rho(\mathbf{r})$ denote the ion charge density distribution; then Eq. (2) takes the form:

$$\mathcal{E} = \frac{1}{\epsilon_0}(K_s\mathbf{P} - K_\alpha\nabla^2\mathbf{P} + K_\beta\nabla^4\mathbf{P}) + \alpha\nabla\rho(\mathbf{r}), \quad (15)$$

where the subscript on α is omitted. In principle, the ionic charge density distribution can be obtained from quantum mechanical calculations [38]. Combining Eqs. (15) and (1) with the Poisson equation, one can solve for the electric potential distribution of an ion in the solvent medium, $\phi(\mathbf{r})$, and in vacuum, $\phi_{\text{vac}}(\mathbf{r})$. The ion solvation energy, ΔG_{solv} , is then given by the difference between the electrostatic energies in the solvent medium and in vacuum, i.e.,

$$\Delta G_{\text{solv}} = \frac{1}{2} \int d\mathbf{r} \rho(\mathbf{r})[\phi(\mathbf{r}) - \phi_{\text{vac}}(\mathbf{r})]. \quad (16)$$

Thus, the only unknown parameter in ΔG_{solv} is α , whose value can therefore be determined from the experimental value of the solvation energy.

As a simplified case, we examine the solvation of a spherical ion in the linear response regime of the solvent polarization, such that Eq. (3) holds. In this case, by combining Eqs. (3) and (15) with the fundamental electrostatic relationship, $\nabla \cdot \mathbf{D} = \rho$, we have the following:

$$\mathbf{D} = \chi_0^{-1}\mathbf{P} - \epsilon_{\text{ir}}K_\alpha\nabla^2\mathbf{P} + \epsilon_{\text{ir}}K_\beta\nabla^4\mathbf{P} + \alpha\epsilon_{\text{ir}}\epsilon_0\nabla^2\mathbf{D}. \quad (17)$$

Performing a Fourier transform on both sides of the above equation, we obtain the corresponding dielectric susceptibility spectrum, which is modified by short-range correlations between the ion and the orientational polarization of the solvent,

$$\chi_\alpha(k) = \frac{1 + \alpha\epsilon_{\text{ir}}\epsilon_0k^2}{\chi_0^{-1} + \epsilon_{\text{ir}}K_\alpha k^2 + \epsilon_{\text{ir}}K_\beta k^4}. \quad (18)$$

The ion solvation energy in the nonlocal dielectric medium is then given by the Dogonadze-Kornyshev solvation equation [12,37],

$$\Delta G_{\text{solv}} = -\frac{1}{4\pi^2\epsilon_0} \int_0^\infty dk \rho^2(k) \left(\frac{\epsilon_{\text{ir}} - 1}{\epsilon_s} + \chi_\alpha(k) \right), \quad (19)$$

where $\rho(k)$ is the Fourier transform of the ionic charge density. The above equation clearly separates the solvation energy into contributions from fast polarization and slow orientational polarization modes. The solvation energy

often reaches several electron volts and therefore has a significant impact on electron transfer reactions. First, the difference in the total solvation energy between the reactant and product states contributes to the thermodynamic driving force of the reaction. Second, only the slow orientational part of the solvation contributes to the reorganization energy, which modulates the activation barrier for electron transfer [39].

To calculate the solvation energy, one must first prescribe the ionic charge density. The simplest representation is given by the Born sphere model, where the ionic charge ze_0 is taken to be uniformly distributed over the surface of a sphere of radius R , with z denoting the ion valency. In this case, the ionic charge density in Fourier space is given by

$$\rho(k) = ze_0 \frac{\sin(kR)}{kR}. \quad (20)$$

When short-range correlation effects are neglected, i.e., $K_\alpha, K_\beta, \alpha = 0$, so that $\chi_\alpha(k) = \chi_0$, Eq. (19) simplifies to the Born solvation formula. However, the Born sphere model is incompatible with quantum mechanical calculations, where the ionic charge distribution is radially smeared rather than confined to a spherical surface. To account for the smeared charge effect, a convenient model for the ionic charge density is the stretched Gaussian of order n (SGn), which in real space is given by [40]

$$\rho_{\text{SGn}}(r) = ze_0 \frac{2^n n^{\frac{2n+3}{2}}}{\pi^{\frac{3}{2}} (2n+1)!! R^{2n+3}} r^{2n} e^{-\frac{nr^2}{R^2}}, \quad (21)$$

while its Fourier transform reads

$$\rho_{\text{SGn}}(k) = ze_0 \frac{(-1)^n 2^n n^{\frac{2n+3}{2}}}{(2n+1)!! R^{2n+3}} \frac{\partial^n}{\partial y^n} \left(\frac{e^{-\frac{k^2}{4y}}}{y^{\frac{3}{2}}} \right), \quad (22)$$

where $y = n/(R^2)$. A smaller n in the SGn model corresponds to a broader charge distribution around the spherical surface of radius R . For very large n , e.g., $n = 50$, the distribution becomes sharply localized and approaches the Born sphere model.

Comparisons between the experimental hydration energies of alkali metal cations (circles) and halide anions (squares) and those calculated from Eq. (19) using the SGn model [Eq. (21)] for the ionic charge distribution are shown in Fig. 1. Ionic crystal radii are used for R , and their values, together with the corresponding hydration energies, are taken from Ref. [41]. Experimental data show that both anions and cations exhibit stronger hydration at smaller ionic radii, a behavior attributed to the enhanced polarization of water by the more intense electric fields of the smaller ions. Moreover, anions are found to be more strongly hydrated than cations at comparable ionic radii, e.g., K^+ compared with F^- , a phenomenon referred to as

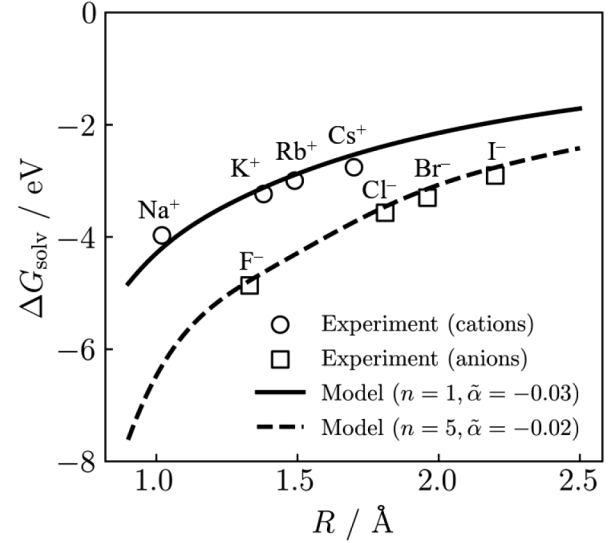


FIG. 1. Comparisons of experimental hydration energies of alkali metal cations (circles) and halide anions (squares) with those calculated from Eq. (19) using the SGn model for the ionic charge distribution. The dimensionless short-range ion-solvent correlation parameter is defined as $\tilde{\alpha} = \alpha \epsilon_0 / a_0^2$, with the reference distance $a_0 = 1 \text{ \AA}$. Other parameters used are: $K_\alpha = -0.047 \text{ \AA}^2$ [determined from Eq. (8)], $K_\beta = 0.0026 \text{ \AA}^4$ [determined from Eq. (8)], $\epsilon_{\text{ir}} = 4.9$ (Ref. [35]), $\epsilon_s = 78.5$ (Ref. [35]). Ionic crystal radii are used for R , and their values together with the corresponding hydration energies are taken from Ref. [41].

charge hydration asymmetry [42,43]. As seen in Fig. 1, the monotonic dependence of hydration energies on ionic radius, observed experimentally for alkali metal cations and halide anions, can be reproduced by the solvation model in Eq. (19), provided that different sets of α and n are used for the two ion classes. However, if either the smeared charge effect (e.g., $n = 50$) or the short-range ion-solvent correlation effect ($\alpha = 0$) is neglected, the charge hydration asymmetry cannot be accounted for, as shown in Figs. S1 and S2 in Supplemental Material [37]. As shown in Fig. S1 in Supplemental Material [37], the solvation energy exhibits pronounced oscillatory behavior with the ion radius when the charge distribution is localized near the ion surface. In the present model, this oscillation is smoothed by the smeared charge distribution, whereas it can also be smoothed by allowing fluctuations in the ionic (or cavity) radius [11].

The contribution of short-range ion-solvent correlations to the solvation energy is given by $\int d\mathbf{r} \alpha \rho(\mathbf{r}) \rho_{\text{pol}}(\mathbf{r})$ [23], where ρ_{pol} denotes the solvent polarization charge density. Negative values of α imply that short-range ion-solvent correlations partially cancel the electrostatic interactions between the ionic charge and the solvent polarization charge. This partial cancellation destabilizes the electrostatically ordered solvation structure, thereby weakening solvation. Consequently, a negative α corresponds to a net short-range repulsive interaction between the ion and

solvent, whereas a positive α corresponds to a net short-range attractive interaction. A more negative value of α , as used for alkali metal cations in Fig. 1, indicates a stronger net repulsion between the cation and water molecules. In addition, a smaller value of n corresponds to a more broadly distributed ionic charge for cations. Together, these two factors keep water molecules farther away from the cationic surface than from the anionic surface. This can be seen from the ion-water radial distribution functions (RDFs). For example, although Na^+ has a smaller ionic crystal radius than Cl^- , the first peak of the Na^+-O RDF occurs at a larger distance from the ion center than the first peak of the Cl^--H RDF [44]. This observation indicates that, relative to its ionic crystal size, water molecules remain farther from the cationic surface. Therefore, the stronger cation-water repulsion combined with the more smeared charge distribution in our solvation model leads to a larger Born radius for alkali metal cations relative to halide anions, thereby giving rise to charge hydration asymmetry. The present model provides a phenomenological rationalization of this effect based on a simple solvation formula in Eq. (19) rather than a detailed microscopic explanation. More specific microscopic origins proposed in the literature include stronger dispersion interactions of the highly polarizable halide anions [45], solvent orientation effects [46], asymmetry in the charge distribution of water molecules [47], and differences in the water density within the hydration shells of anions and cations [48].

IV. INTERFACIAL SOLVATION

The solvent structure at electrochemical interfaces is strongly influenced by intricate interactions between the solvent and the electrode surface, encompassing electrostatic forces, van der Waals interactions, and even covalent contributions such as partial charge transfer of water molecules at the Pt(111)-water interface [49]. Moreover, free electrons spill out from the electrode surface by approximately 1–2 Å, which induces a substantial surface potential and markedly affects the electrostatic field sensed by the solvent. Therefore, accurate modeling of the interfacial solvent structure necessitates careful consideration of near-surface physics. The DPPFT approach incorporates these effects within a grand-canonical framework. Specifically, the free electrons of the electrode are treated as an inhomogeneous gas using orbital-free DFT, while the short-range interactions between electrolyte solution particles and the electrode surface are semiempirically described by Lennard-Jones or Morse potentials [23,24,50]. The gradient coefficient in the kinetic energy functional and the parameters of the short-range interaction potentials are electrode-specific. They can be calibrated using the recently developed Kohn-Sham-Poisson-Boltzmann model [51] and DFT-computed binding energies of

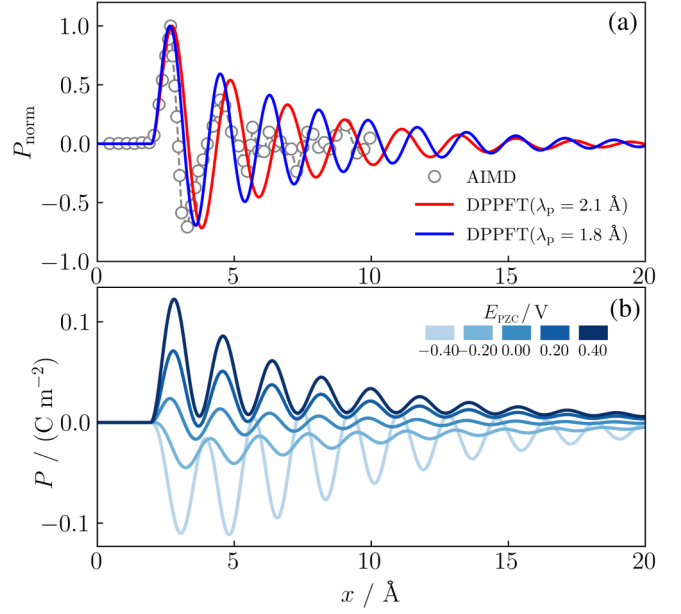


FIG. 2. (a) Water polarization at the PZC of the Ag(111)-water interface from AIMD simulations (circles) and from the DPPFT model for the Ag(111)-100 mM NaF aqueous solution interface. In the DPPFT calculations, K_α and K_β are obtained using $\lambda_p = 2.1$ Å for pure water and an adjusted $\lambda_p = 1.8$ Å for interfacial water, while the same decay length $\lambda_d = 4.3$ Å is used in both cases. All other parameters are as listed in Table S1 in Supplemental Material [37] (see also Refs. [56,57] therein). The water polarization is normalized to its maximum value. (b) Water polarization simulated by the DPPFT model with $\lambda_p = 1.8$ Å at different electrode potentials relative to the PZC, as indicated in the figure. In both panels, the metal surface is located at $x = 0$ Å.

electrolyte components [52], respectively. In addition, the Anderson-Newns-Schmickler chemisorption model can be employed to explicitly account for partial charge transfer [53]. By solving the closed set of equations derived within DPPFT, one can obtain the spatial distributions of particle densities (including both classical electrolyte solution particles and quantum electrons), the electrostatic potential, and the solvent polarization (see Ref. [23] or Supplemental Material [37] for details).

Figure 2(a) compares the water polarization profiles simulated by *ab initio* molecular dynamics (AIMD) [54] and by the DPPFT model. AIMD simulations are performed at the Ag(111)-water interface [54], while the DPPFT calculations are carried out at the PZC for the Ag(111)-100 mM NaF aqueous solution interface, corresponding to an electrochemical potential of -3.98 eV inferred from experimental C_{dl} profiles [55]. For the blue curve in Fig. 2(a), we use the short-range ion-solvent correlation parameters determined from the ion solvation energies in Sec. III, i.e., $\tilde{\alpha}_c = -0.03$ and $\tilde{\alpha}_a = -0.02$, as well as K_α and K_β obtained from the dielectric susceptibility spectrum in Sec. II, corresponding to a periodic

length of 2.1 Å and a decay length of 4.3 Å, as defined in Eqs. (12) and (13). Other parameters used in the DPPFT model are listed in Table S1 in Supplemental Material [37]. As shown in Fig. 2(a), the DPPFT model can reproduce the key features of the water profile observed in AIMD simulations, namely its oscillatory decay toward the bulk solution. The first water layer adopts an oxygen-down configuration (i.e., an average orientation in which the oxygen atoms of water molecules point toward the electrode surface), which is attributed to the positive electric field induced by electron spillover. Subsequent layers exhibit alternating orientations due to hydrogen bonding. The AIMD-predicted water layers are more compact than those obtained from DPPFT using K_α and K_β determined from the dielectric response of pure water. This suggests that the periodic length at the Ag(111)-water interface is smaller than that in pure water. From the AIMD results, the interfacial water periodic length can be identified as the separation between the first two polarization peaks, i.e., 1.8 Å. Assuming the same decay length as in pure water, the short-range correlation parameters K_α and K_β for interfacial water can be determined by inverting Eqs. (12) and (13) as follows:

$$K_\alpha = -\frac{(a^2 - b^2)\gamma_0}{2(a^2 + b^2)^2}, \quad (23)$$

$$K_\beta = \frac{\gamma_0}{4(a^2 + b^2)^2}, \quad \text{with} \quad a = \frac{2\pi}{\lambda_p}, \quad b = \frac{1}{\lambda_d}.$$

With K_α and K_β tuned for interfacial water, while all other parameters are kept fixed as listed in Table S1 in Supplemental Material [37], the DPPFT model (red curve in Fig. 2) achieves improved agreement with the water polarization profile from AIMD simulations. Thus, Eq. (23) provides an alternative and more appropriate method for determining K_α and K_β at the interface from AIMD simulations. Accordingly, the bulk-water susceptibility spectrum discussed in Sec. II is used as a reference for the initial parametrization of short-range solvent-solvent correlations, rather than as an assumption of bulk-like interfacial dielectric response. Interfacial effects on these correlations are phenomenologically incorporated into the tuned parameters K_α and K_β , as reflected by the change in λ_p from 2.1 Å for pure water to 1.8 Å for interfacial water.

Figure 2(b) shows the water polarization profiles near the Ag(111) surface, simulated using the DPPFT model with $\lambda_p = 1.8$ Å at varying electrode potentials relative to the PZC, denoted as E_{PZC} . At positive potentials, the first and subsequent water layers adopt an oxygen-down configuration due to the presence of a positive electric field acting on the solvent. As the electrode potential decreases toward negative values, the water layers

gradually transition to a hydrogen-down configuration (i.e., an average orientation in which the hydrogen atoms of water molecules point toward the electrode surface). We also observe that the first water layer shifts closer to the metal surface at more negative potentials, consistent with AIMD simulations for the Ag(111)-aqueous solution interface [58]. However, the shift of the water polarization peak toward the metal surface at more positive potentials reported in AIMD studies [58] is not captured by the present DPPFT model. This discrepancy is likely due to the omission of water chemisorption in the current DPPFT model. In our previous work [23], the orientational transition of the water layer was found to be insensitive to changes in electrode potential; specifically, the first water layer adopted an oxygen-down configuration even at -0.2 V relative to the PZC. This is attributed to an overestimation of the electron spillover effect in the earlier model, which produced an excessively strong positive electric field acting on solvent molecules near the surface. To mitigate this issue, in the present work we introduce a vacuum region between the metal surface and the first water layer, where the dielectric constant is set to unity. The spatial distribution of the infrared dielectric constant implemented in the DPPFT model is depicted in Fig. S3 in Supplemental Material [37]. The presence of the vacuum region leads to reduced screening of the surface potential, thereby pushing electrons back into the metal and weakening the electron spillover effect. As a natural consequence, introducing this vacuum region is expected to decrease the magnitude of C_{dl} compared with the previous model [23]. At a more fundamental level, avoiding the overestimation of the electron spillover effect requires a more accurate electronic energy functional.

V. INTERFACIAL IONIC STRUCTURE

A characteristic feature of ion distribution near a charged electrode surface is the excess of ions in the diffuse layer, which gradually diminishes toward the bulk solution over a distance characterized by the Debye length. This behavior originates from the electrostatic interactions between the free charges on the electrode surface and ionic charges, as described by Poisson–Boltzmann-type theories. Surface phenomena such as electron spillover and partial charge transfer can, however, alter the surface potential and thereby modulate these electrostatic interactions. Figures 3(b) and 3(c) present the concentration profiles of anions and cations obtained from DPPFT simulations. It is evident that counterions form layered structures at the interface, with their concentrations exhibiting an oscillatory decay toward the bulk solution. The ionic layering has also been reported in AIMD simulations of the Ag(111)-NaF aqueous solution interface [58]. The emergence of such ionic layering is related to the interactions between ions and interfacial water layers, as shown in Fig. 2. On the one hand, oscillatory water polarization

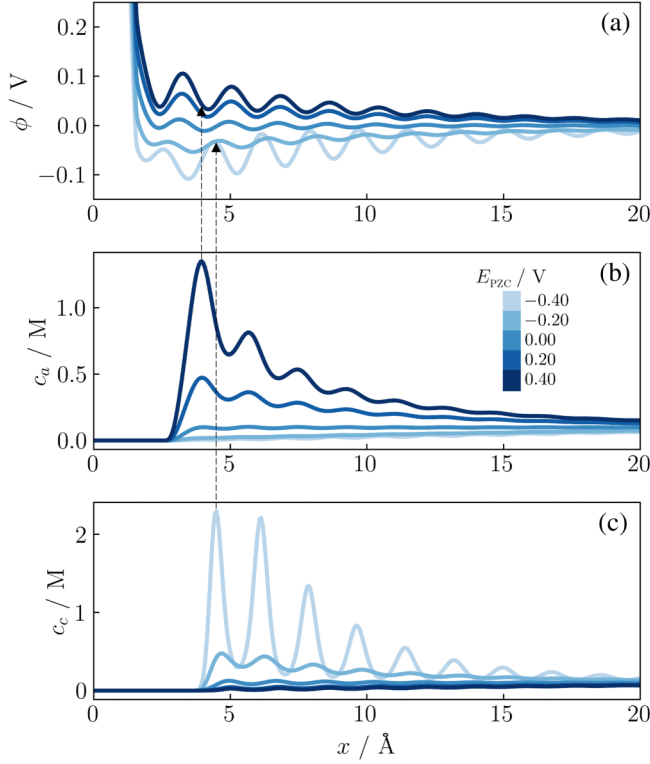


FIG. 3. Spatial profiles of (a) water polarization, (b) anionic concentration, and (c) cationic concentration obtained from DPPFT simulations using the parameters in Table S1 in Supplemental Material [37], at different electrode potentials relative to the PZC [as indicated in Fig. 3(b)]. The metal surface is located at $x = 0$ Å in all panels.

gives rise to alternating distributions of polarization charge with opposite signs, i.e., $\rho_{\text{pol}} = -\nabla \cdot \mathbf{P}$, which in turn generate local minima and maxima in the electrostatic potential on the solution side [Fig. 3(a)]. These potential extrema, corresponding to centers of positive and negative polarization charges, tend to attract anions and cations, respectively, leading to their accumulation near corresponding regions. However, as shown in Figs. 3(b) and 3(c), the peak positions of the anionic and cationic layers do not coincide with the potential minima or maxima. For instance, the first anionic peak at 0.4 V relative to the PZC approximately coincides with a potential minimum, whereas the first cationic peak at -0.4 V relative to the PZC corresponds to a potential maximum, as indicated by the dashed arrows in Fig. 3. This finding indicates that electrostatic interactions between ions and polarized water layers cannot fully account for the ionic layering observed in the present results.

On the other hand, ions exhibit repulsive short-range correlations with the solvent, characterized by the parameters α_c and α_a . As discussed in Sec. III, a more negative value of α_c or α_a corresponds to a stronger repulsive effect. Figure 4 shows the profiles of water polarization and anionic concentration at an electrode potential of 0.4 V

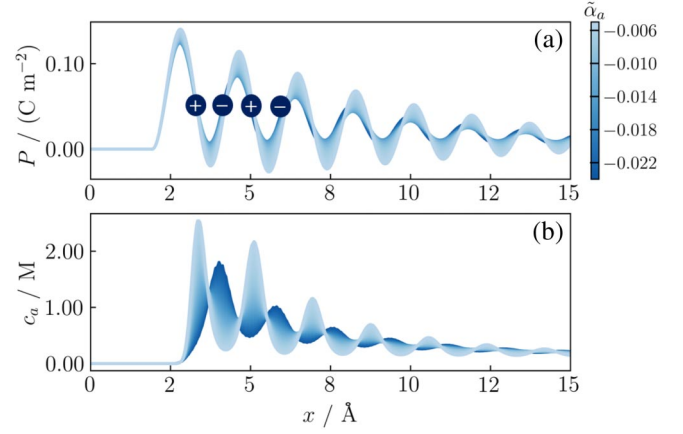


FIG. 4. Spatial profiles of (a) water polarization and (b) anionic concentration obtained from DPPFT simulations at an electrode potential of 0.4 V relative to the PZC, for different α_a values as indicated, with all other parameters fixed (Table S1 in Supplemental Material [37]). The metal surface is located at $x = 0$ Å in both panels. The polarization charge centers are indicated in Fig. 4(a).

relative to the PZC, for different α_a values, with all other parameters kept fixed, as listed in Table S1 in Supplemental Material [37]. When $\alpha_a \approx 0$, i.e., in the absence of short-range ion-solvent correlations, anions are attracted to regions near the centers of positive polarization charges, as shown in Fig. 4(b). As α_a becomes more negative, the dielectric susceptibility of water decreases [Eq. (18)], reflecting a reduced polarization response of each water layer [Fig. 4(a)]. Consequently, the magnitude of the positive polarization charge decreases, weakening its attraction to anions. In addition, a more negative α_a implies a stronger repulsive interaction between the anionic charge and the positive polarization charges, i.e., the hydrogen ends of water molecules. This repulsion pushes the anions into the regions between adjacent layers of positive polarization charges, corresponding to the centers of negative polarization charges [Fig. 4(b)]. This behavior suggests that anions tend to reside within water layers in order to preserve a solvation configuration similar to that in bulk solution, namely with the hydrogen ends (positive polarization charges) of water molecules oriented toward the anion. Moreover, a more negative α for cations indicates that cations experience a stronger repulsive effect from water molecules, thereby forming more distinct interfacial layering. Such behavior is also observed in AIMD simulations [58].

Ionic layering has often been observed at highly concentrated electrolyte interfaces [3,4,59,60], the limiting case of which corresponds to ionic liquid interfaces. However, the physical origin of ionic layering at highly concentrated electrolyte interfaces is fundamentally different from that at the dilute electrolyte interfaces considered in the present work. At dilute electrolyte interfaces, the

solvent is the dominant component and forms a layered structure due to short-range solvent-solvent correlations, as discussed above. Ionic layering then arises from the interactions of ions with these solvent layers. In particular, short-range ion-solvent correlations influence how the ions fit within the solvent layers, as shown in Fig. 4. In contrast, at highly concentrated electrolyte interfaces, ions become the dominant component, and the ionic layering originates from short-range ion-ion correlations. At moderately concentrated electrolyte interfaces, the interfacial structure is expected to transition from being governed by short-range solvent-solvent correlations to short-range ion-ion correlations as the concentration increases. Consequently, at moderately concentrated electrolyte interfaces, short-range solvent-solvent, ion-solvent, and ion-ion correlations all play significant roles in determining the interfacial structure.

The short-range ion-ion correlations are not accounted for in the present DPPFT model. Therefore, the applicability of the present DPPFT model is limited to electrolyte concentrations below a certain threshold. Recent molecular dynamics simulations by Chen *et al.* [61] show that the peak positions in the oscillatory part of the ion-ion correlation functions remain largely independent of concentration up to 1.9 M, indicating that the electrolyte structure is primarily governed by water. This observation suggests that the present DPPFT model may remain applicable for electrolyte concentrations up to approximately 1.9 M. A natural direction for future development of the DPPFT model is to overcome this limitation and extend its applicability across the full range of electrolyte concentrations. This can be achieved by incorporating short-range ion-ion correlations into the field theory of electrolyte solutions, with appropriate choices of nonlocal correlation kernels. Some theoretical models that reproduce interfacial layering at ionic liquid interfaces [62–65] have been developed in this regard. Furthermore, the correlation functions or structure factors can be obtained within the random phase (one-loop) approximation from the field-theoretic formulation [19,66,67]. By comparing them with those computed from molecular dynamics simulations, the short-range correlation parameters can be self-consistently determined.

It would also be of considerable interest to combine the DPPFT model with electron transfer theory to describe reactive electrochemical interfaces. One of the authors of the present work has previously developed a unified theoretical framework that integrates continuum EDL models with the Anderson-Newns-Schmickler theory of chemisorption [68]. This framework enables the calculation of key electron-transfer parameters, such as the solvent reorganization energy, reaction free energy, and activation free energy, while also providing access to local reaction conditions, including the local electrostatic potential, reactant concentration, and dielectric response.

A promising direction for future work is to refine this framework by employing the DPPFT model to describe the EDL. An interesting question is how short-range correlations and interfacial layering influence key electron-transfer parameters and local reaction conditions and thereby affect electron transfer kinetics.

VI. CONCLUSIONS

In this work, we discussed a scheme to determine the short-range correlation parameters in the recently developed field-theoretic approach [21,22] for structured electrolyte solutions. Within this framework, solvent-solvent correlations are described by a fourth-order Landau-Ginzburg (LG) functional, which reproduces the primary peak in the wave-number-dependent dielectric susceptibility spectrum of pure water. The relevant parameters can therefore be determined from the peak position. The dielectric susceptibility associated with the LG functional takes a Yukawa-type form with a decay length, multiplied by an oscillatory term characterized by a periodic length. On this basis, the ion solvation energy in the linear response regime is derived from nonlocal electrostatics. The short-range ion-solvent correlation parameters for alkali metal cations and halide anions are then obtained by fitting the experimental trends in the ionic-radius-dependent hydration energies. The more negative value found for cation-solvent interactions indicates stronger short-range repulsion, thereby phenomenologically rationalizing the observed charge hydration asymmetry.

With the short-range correlation parameters determined from pure water and ion solvation, the interfacial structure of the Ag(111)-NaF aqueous electrolyte system was investigated within the DPPFT. Water polarization profiles from AIMD simulations are more compact than those from the initial DPPFT calculations, suggesting a shorter periodic length for interfacial water. When solvent-solvent correlation parameters corresponding to this reduced periodic length are adopted, the DPPFT model shows improved agreement with AIMD results. Furthermore, the interactions between ions and interfacial water layers result in the formation of oscillatory ionic layering. As the strength of short-range ion-solvent repulsion increases, the peaks of anionic and cationic layers shift from regions near the centers of positive and negative polarization charges toward those of negative and positive polarization charges in order to preserve solvation configurations similar to those in bulk solution. In conclusion, we have established a practical methodology for determining short-range correlation parameters within the DPPFT framework. This semiclassical and computationally efficient approach enables a quantitative description of short-range correlation effects and provides a refined understanding of the interfacial structure of macroscopic electrochemical systems.

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DATA AVAILABILITY

The data are available from the authors upon reasonable request.

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