

Classical Theory of Electron-Ion Correlations at Electrochemical Interfaces: Closing the Circuit from Double-Layer Charging to Ion Adsorption

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The electric double layer (EDL) that forms at the interface between metals and ionic solutions is at the heart of various energy technologies. Recent experimental data have challenged our traditional understanding of the EDL charging behavior, which is based on mean-field Gouy-Chapman-Stern-type (GCS) models. In this article, we present a classical theory for the EDL, derived from first-principles statistical mechanics, that accounts for electron-ion correlation effects using the method of image charges and systematically extends beyond the mean-field level. Such electron-ion correlations introduce an additional interaction between the metal surface and electrolyte ions, significantly altering the EDL structure. Our theory, valid in the limit of dilute electrolyte solutions and weakly charged metal surfaces, achieves quantitative agreement with experimental capacitance data across a wide range of electrode materials and electrolyte solvents, and thus resolves long-standing questions on the origin of discrepancies to GCS predictions. Thereby, the framework conceptually unifies the processes of double-layer charging and ion adsorption, which are typically considered as distinct phenomena, but are shown to be manifestations of the same fundamental electrostatic principles.

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I. INTRODUCTION

Understanding the structure and behavior of the electric double layer (EDL) at metal-electrolyte interfaces is of great importance for emerging electrochemical energy technologies, ranging from batteries to electrolyzers and fuel cells. The classical Gouy-Chapman-Stern (GCS) theory recently celebrated its 100th anniversary and remains a landmark description of the EDL [1]. In the GCS model, the electrolyte region is divided into two parts: an inner region called the Helmholtz layer that is considered inaccessible to ions, and an outer diffuse layer, where the electrostatic potential distribution is described by the mean-field (MF) Poisson-Boltzmann (PB) equation, as analytically solved by Gouy and Chapman. Due to the layer structure, the respective capacitance contributions are connected in series and sum up inversely to the total

inverse capacitance of the GCS model,

$$C_{\text{GCS}}^{-1} = C_H^{-1} + C_{\text{GC}}^{-1}, \quad (1)$$

where C_H is the Helmholtz capacitance and C_{GC} the Gouy-Chapman solution for the differential capacitance of the diffuse layer.

The GCS model is widely used to interpret experimental capacitance data, especially at the potential of zero charge (PZC), i.e., the potential where the electrode surface does not carry any excess charge. A convenient technique for such a comparison between experiment and theory consists in a Parsons-Zobel (PZ) plot, where the inverse of the measured differential capacitance is plotted against the inverse of the theoretical diffuse layer capacitance, C_{GC}^{-1} . According to Eq. (1), GCS theory predicts a linear relationship with unity slope in a PZ plot. Often-observed discrepancies to unity slope in experimental PZ plots are commonly attributed to surface roughness of the electrode [2] or pseudocapacitive contributions due to spurious ion adsorption. Recent electrochemical capacitance data for platinum (111) interfaces displayed striking discrepancies to GCS theory with close to zero PZ slopes [3], whereby surface roughness can be largely excluded for single-crystalline electrodes, and no specific adsorption of

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electrolyte species is assumed to occur within the “double-layer window” of the applied electrode potential [4]. These latest results triggered a vivid and controversial discussion on our fundamental understanding of electrochemical charging phenomena. Among various proposed explanations, one hypothesis attributes the discrepancies to weak anion adsorption at the interface [5], while another suggests an additional attractive interaction between ions and the metal surface, the origin of which however remains unclear [6]. A third hypothesis points to specific adsorption of hydroxide ions [7]. Despite different interpretations of the underlying electrochemical phenomena, these explanatory schemes agree in the postulation of a weak ion-surface interaction that is not captured by traditional GCS theory [8]. As an alternative explanation, a nonvanishing polarization of water molecules at the electrode surface has been suggested as a cause for the decreased PZ slopes [9].

These observations suggest that GCS theory is missing important physical phenomena and needs to be refined. Fundamentally, GCS theory is a mean-field approach, which means that particles interact only with the mean electric field generated by all other charge carriers, thereby neglecting direct correlations due to instantaneous interactions. Recently, we have developed a systematic approach to include ion-ion and ion-solvent correlations in beyond-MF electrolyte models to account for the effects of ionic screening and solvation, respectively, on the properties of the EDL. Thereby, electrolyte correlations were shown to enhance the characteristic features of capacitance curves around the PZC, improving agreement with experimental data [10]. An aspect that is critically missing in state-of-the-art EDL models are electron-ion correlation effects, i.e., interactions due to instantaneous inhomogeneities in the distribution of the electronic surface charge induced by localized ionic charges in the direct vicinity of the electrode surface. These are difficult to model, because the quantum mechanical nature of electrons generally requires the use of a fully quantum mechanical framework to describe the specific interactions between electronic orbitals of ions and the metallic band structure of the electrode [11,12]. Focusing on *unspecific* electrostatic interactions, in this article we present an approach based on the method of image charges for incorporating electron-ion correlation effects into a classical theory for the EDL. The method of image charges is a tool to describe metallic and dielectric interfaces where imaginary mirror charges are introduced to ensure that the electrostatic boundary conditions at the interface are satisfied [13]. In a perfect conductor model of a metal electrode, image charges can be interpreted as *the limit of maximally correlated ion-electron pairs*, whereby the electronic charge of the metal electrode instantaneously adjusts to the (localized) ionic charges in the electrolyte—a “classical variant” of the Born-Oppenheimer approximation.

Several previous theoretical studies have investigated the effects of dielectric and metallic image charges on the EDL structure. Wang’s Gaussian-renormalized fluctuation theory [14] provides a nonperturbative field-theoretical framework for electrolytes in dielectrically inhomogeneous media, including systems with dielectric discontinuities. In this approach, unlike commonly used point-charge models, ionic charges are described by a physically motivated smeared charge distribution that reproduces the correct Born solvation energy while eliminating the ultraviolet divergences that typically arise for point charges approaching each other at close distance. This theory was recently used to compare metallic and dielectric boundary conditions and to demonstrate how image-charge interactions modify ionic screening and interfacial capacitance as a function of boundary type and permittivity [15]. In close proximity to low-permittivity membranes dielectric image charges have a repulsive effect, resulting in a decreased ion density [16]. On the other hand, at metal electrodes, the image-charge effect causes an attractive interaction between the electrode surface and electrolyte ions that adds to the mean-field interactions mediated by the electrostatic potential. In the EDL model by Skinner *et al.* [17], ions and image electrons form stable dipoles at the electrode-electrolyte interface, leading to strongly enhanced capacitance in comparison to MF predictions. Kornyshev *et al.* developed image-charge models that account for finite Thomas-Fermi (TF) screening of the metal electrode, yielding an effective image-charge potential profile with a minimum located between an attractive and repulsive component [18], whose exact form depends on the TF length of the electrode material and the polarization response of the solvent [19]. Due to ionic screening in the electrolyte solution, the effects of image charges are strongest at weakly charged interfaces and low electrolyte ion concentrations [20]. Monte Carlo (MC) simulations have shown that accounting for image-charge effects, ion densities at the electrode–electrolyte interface are significantly elevated compared to traditional MF predictions [21,22]. Similar behavior was found in recent molecular dynamics (MD) simulations [23–25], as well as in integral-equation approaches [26–32].

In this article, we explore the role of electron-ion correlations at the interface between a perfect metallic electrode and an electrolyte solution in the maximally correlated limit. To this end, the method of image charges is incorporated into a statistical field theory of charged solid-liquid interfaces, building upon earlier approaches by Netz and Orland [33] and Lau [34]. In contrast to earlier models that were based on a similar description, e.g., by Wang and Wang [16] and more recently, by Zhou *et al.* [15], where image charges are implicitly included via dielectric boundary conditions, our formulation explicitly incorporates image charges in the charge density as a microscopic representation of correlated electron-ion pairs. With

a focus on the weak coupling limit, i.e., dilute electrolyte solutions and weakly charged interfaces around the PZC, we derive analytical expressions for the capacitance that capture these correlation effects concretely. The theory is thus well suited for describing recent experimental results on the electrochemical charging behavior of Pt(111) [3] that have raised questions on the validity of GCS theory in this limit. It should be noted that solvent-specific correlations, as described in a recent model by Hedley *et al.* [9], are not considered, as the solvent is treated by the primitive model of a constant dielectric background. Moreover, ionic layering effects, as suggested for concentrated solutions and strongly charged double layers [35,36], are neglected here. Thus, while the theory is not intended for treating concentrated electrolytes or highly charged interfaces, it systematically bridges the gap between traditional GCS theory and beyond-MF approaches.

In particular, we employ a Hubbard-Stratonovich (HS) transformation [37,38] to convert the statistical partition function of the charged interfacial system into a functional integral involving the electrostatic potential [33]. Such field theoretic approaches have been used to study dielectric interfaces for biological membrane systems [16,39–42] and recently also for metallic electrodes [15]. Here, for the first time, we demonstrate that electron-ion correlation effects consistently explain long-standing discrepancies between experimental capacitance data and GCS predictions across a wide range of electrode materials in both aqueous and nonaqueous electrolyte solutions, in a limit where classical GCS theory is typically assumed to be applicable. In our model, the strength of the electron-ion correlation effect is controlled by a single parameter that determines the effective minimum distance between an ion and its image charge. Tuning to zero corresponds to the limit of a maximally localized electron-ion pair, establishing a seamless transition from EDL charging to unspecific ion adsorption.

The article is organized as follows. In the theory section (Sec. II), we systematically derive analytical expressions for electrostatic potential, ion densities, and the differential capacitance, as a function of the electrode potential including the effect of electron-ion correlations. In the results section (Sec. III), predictions of our theoretical capacitance model are compared with experimental capacitance data for aqueous as well as nonaqueous electrolytes, demonstrating that the model quantitatively explains experimental data trends at the PZC, which the GCS model was found incapable of. The additional attractive interaction, previously postulated as the cause of the strongly suppressed Parsons-Zobel slope of Pt(111) capacitance data [6], is thus suggested to result from interfacial correlations between the metal electronic surface charge and electrolyte ions. In the discussion section (Sec. IV), we analyze the profound consequences of the developed theory for overcoming the traditional conceptual distinction between EDL

charging and ion-adsorption mechanisms, thus unifying the theoretical description of double-layer capacitance and pseudocapacitance.

II. THEORY

This section presents the derivation of a classical theory of a perfect metallic conductor in contact with an electrolyte solution, accounting for electron-ion correlations using the method of image charges. A schematic of the model is illustrated in Fig. 1. On the left-hand side is a metal electrode and on the right-hand side (rhs) an electrolyte solution. Symbols are provided in the list of symbols. In the image-charge method [13], for each charge in the electrolyte (e.g., the anion and two cations in the solution phase in Fig. 1), an image charge of opposite sign is placed on the opposite side at the same distance from the metal surface (indicated as dashed charges in Fig. 1). The image-charge method provides the correct *inhomogeneous* electronic surface-charge distribution σ_M at the metal electrode for any given ion configuration (gray-shaded curve in Fig. 1) [43]. In contrast, in classical theories, the electrode charge is typically described by a *homogeneous* surface-charge density at the metal surface that is constant in in-plane directions [33,34,39]. It will be shown that the present image-charge theory reduces to the constant-surface-charge model at the mean-field level, where ions interact only with mean charge distributions and the electronic surface charge gets smeared out to a constant in-plane averaged value. This means that, conceptually, the image charges already represent the entire

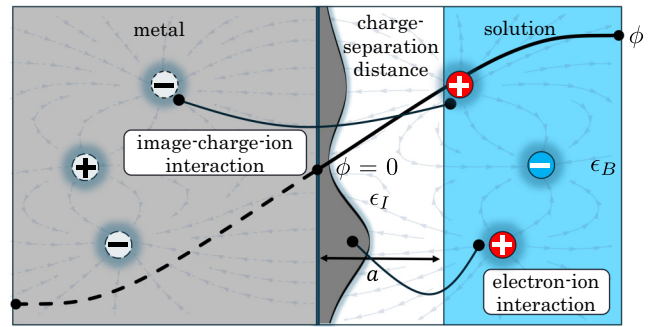


FIG. 1. Metal (left) in contact with electrolyte solution (right). Solution and metal region are separated by a charge-separation distance a with a residual dielectric permittivity ϵ_I . The solution is characterized by a solvent dielectric permittivity ϵ_B . Arrows are the physical electrostatic field vectors for the ionic configuration shown. Image charges in the metal (charges with dashed boundary) enforce the boundary condition at the metal surface and represent the physical electron charge density (dark gray). Due to the symmetry of the image charge method, the electrostatic potential ϕ is antisymmetric under reflection at the image-charge plane (black line in the solution, black-dashed in the metal).

electronic surface charge of the metal electrode, and no additional surface charge must be applied. Electrostatic correlations beyond the MF level captured by our framework are thus interpreted as a classical representation of fundamental electron-ion correlations at electrochemical interfaces [12].

To avoid the divergence of the electrostatic energy as ion and image charges get arbitrarily close to each other, a minimum distance a must be introduced to which ions can approach the image plane of the metal surface. While this appears as an effective “contact layer” akin to the Helmholtz layer in GCS theory, it is important to note that in the present theory, the parameter a must *not* be interpreted as the geometric minimum distance between electrode surface and the atomic centers of ions. Instead, the parameter a controls the minimum distance between electronic and ionic *charge centers*, which is not restricted in value to typical interatomic distances. In particular, a can assume values of subatomic scale due to electron spillover from the electrode surface into the electrolyte region [44,45]. Thereby, a is related to the effective charge screening length at the electrode-electrolyte interface, as described by the Thomas-Fermi length in another recent model [19]. However, the present theory even allows the parameter a to approach values close to zero to describe the limit of charge transfer during ion adsorption, corresponding to (partial) ion discharge as the electronic (image) charge gets fully contracted to the site of the adsorbing ion. We note that, besides our interpretation of the parameter a as a measure for interfacial electron-ion correlations, our model setup is equivalent to the one used by Zhou *et al.* [15].

As this work is focused on electron-ion correlations, the effect of the polarizable solvent medium is implicitly described by a dielectric background of permittivity ϵ_B in the electrolyte region. This approach allows studying the essential influence of electron-ion correlations without interference from other effects such as interfacial solvent structuring [46]. An explicit description of the dipolar solvent is intended to be included in future extensions of the theory. A residual dielectric permittivity ϵ_I is assumed in the interfacial region between the metal image plane (located at $z = 0$) and the electrolyte boundary separated by a charge-separation distance a . Therefore, the overall dielectric profile of the system in the region $z > 0$ is given by

$$\epsilon(r) = \begin{cases} \epsilon_I, & \text{for } 0 < z < a, \\ \epsilon_B, & \text{for } z > a, \end{cases} \quad (2)$$

where z is the coordinate perpendicular to the metal surface. For the purpose of clarity we will abbreviate the three-dimensional (3D) spatial coordinate as $r \equiv \vec{r}$.

The potential energy of the system of ion species and their image charges interacting by Coulomb interaction

$$V(r, r') = 1/(4\pi\epsilon|r - r'|) \text{ is}$$

$$U = \frac{1}{4} \int_{r, r'} \rho(r) V(r, r') \rho(r'), \quad (3)$$

where the integration domain comprises both the electrolyte and metal image-charge regions. For the sake of clarity, the differential of the integration variable is not always displayed and the integral sign is abbreviated as $\int_r$. The one-quarter prefactor (instead of the usual one-half [33]) is due to the fact that the electrostatic energy of the real system of electrolyte and metal surface charge (electrons) is equal to half of the coulombic energy of the system of ions and image charges [47]. The charge density, which comprises both ionic and image charges, is given by

$$\begin{aligned} \rho(r) &= \rho_{\text{ion}}(r) + \rho_{\text{image}}(r) \\ &= \sum_{i=a/c} \sum_{k=1}^{N_i} q_i (\delta(r - r_{i,k}) - \delta(r - r_{i,k}^{\text{im}})), \end{aligned} \quad (4)$$

where $i = a, c$ denote anions and cations, and q_i and $r_{i,k}$, respectively, are the charge and position of ion k of type i . Its image charge is located at $r_{i,k}^{\text{im}}$, which is given by $r_{i,k}$ but with the sign of the z coordinate reversed, $z_{i,k}^{\text{im}} = -z_{i,k}$. Unlike the canonical ensemble with fixed ionic particle numbers N_i , the grand-canonical ensemble fixes the ionic chemical potentials μ_i via external reservoirs, determining N_i and thus the metal charge due to electroneutrality. Here, the grand-canonical description is adopted to derive a theory for interface charging as a function of the applied electrode potential.

In order to calculate the thermodynamic quantities of a grand-canonical system, it is first necessary to determine the grand-canonical partition function $\mathcal{Z}_{\text{gc}}$. The grand-canonical partition function for a system comprising N_i ionic charges with thermal wavelength Λ_i , fugacity $\lambda_i = \exp(\beta\mu_i)$, and chemical potential μ_i is the configuration integral over all states,

$$\begin{aligned} \mathcal{Z}_{\text{gc}}(\{\lambda_i\}) &= \prod_{i=a/c} \sum_{N_i=0}^{\infty} \lambda_i^{N_i} \frac{1}{N_i! (\Lambda_i^3)^{N_i}} \prod_{k=1}^{N_i} \int d^3 r_{i,k} \\ &\quad \Theta(z_{i,k} - a) \exp(-\beta U). \end{aligned} \quad (5)$$

The ions are free to move in the region of the electrolyte solution but constrained by a minimal distance a to the metal image plane, as described by the Heaviside step function Θ . A Hubbard-Stratonovich (HS) transformation, as outlined in Refs. [37,46], introduces the HS field, ψ , which yields the field-theoretic formulation of the partition

function,

$$\mathcal{Z}_{\text{gc}}(\{\lambda_i\}) = \int D\psi \exp(-\beta S[\psi]), \quad (6)$$

as a functional over a nonlinear action,

$$S[\psi] = \int_r \epsilon(r) (\nabla \psi(r))^2 - \sum_{i=a/c} \beta^{-1} \lambda_i \Lambda_i^{-3} \int_r \Theta(z-a) e^{-i\beta q_i (\psi(r) - \psi(r^{\text{im}}))}. \quad (7)$$

Details are shown in Appendix A 1. Here, $D\psi$ is the functional measure originating from the HS transformation [33]. The action functional is nonlocal as ψ is evaluated both at r and r^{im} . The problem is significantly simplified by utilization of the mirror (anti)symmetry with respect to the image plane at $z = 0$, and restricting the integral measure to HS fields in the solution region,

$$D\psi = \Pi_{r \in (\text{Electrode} + \text{Solution})} d\psi(r) = \Pi_{r \in (\text{Solution})} d\psi(r) d\psi(r^{\text{im}}) \equiv D(\psi, \psi^{\text{im}}), \quad (8)$$

effectively doubling the functional degrees of freedom. This freedom allows us to define a linear field transformation to the symmetric, ψ_s , and antisymmetric, ψ_a , components of ψ ,

$$\psi_s(r) = \psi(r) + \psi(r^{\text{im}}), \quad (9)$$

$$\psi_a(r) = \psi(r) - \psi(r^{\text{im}}). \quad (10)$$

Inserting Eq. (8), and applying the variable transformations (9) and (10) in (6) one arrives at

$$\mathcal{Z}_{\text{gc}}(\{\lambda_i\}) = \int D(\psi_a, \psi_s) \exp(-\beta S[\psi_a, \psi_s]), \quad (11)$$

with

$$S[\psi_a, \psi_s] = \int_{r>0} \frac{\epsilon(r)}{2} (\nabla \psi_s(r))^2 + \int_{r>0} \frac{\epsilon(r)}{2} (\nabla \psi_a(r))^2 + (-1) \sum_{i=a/c} \beta^{-1} \lambda_i \Lambda_i^{-3} \int_{r>0} \Theta(z-a) e^{-i\beta q_i \psi_a(r)}, \quad (12)$$

where $\int_{r>0}$ stands symbolically for the integration over the electrolyte solution region ($z > 0$). The value of the Jacobian determinant of the linear transformation above has been absorbed into the measure $D(\psi_a, \psi_s)$. The integrals over ψ_s and ψ_a are fully decoupled. Performing the

Gaussian functional integral over ψ_s yields a simple multiplicative constant that can be absorbed into the functional measure [48]. What is left is the integral over ψ_a ,

$$\mathcal{Z}_{\text{gc}}(\{\lambda_i\}) = \int D\psi_a \exp(-\beta S[\psi_a]), \quad (13)$$

with an effective action

$$S[\psi_a] = S_{\text{free}}[\psi_a] + S_{\text{int}}[\psi_a, \{\lambda_i\}] = \underbrace{\int_{r>0} \frac{\epsilon(r)}{2} (\nabla \psi_a(r))^2}_{S_{\text{free}}} + \overbrace{(-1) \sum_{i=a/c} \beta^{-1} \lambda_i \Lambda_i^{-3} \int_{r>0} \Theta(z-a) e^{-i\beta q_i \psi_a(r)}}^{S_{\text{int}}}, \quad (14)$$

where S_{free} is the action of a field theory without interactions and S_{int} is the Coulomb interacting part of the theory, controlled by the ionic chemical potentials (fugacities λ_i). The image-charge contribution to the action is the restriction of the integral to the solution side along with the boundary condition for $\psi_a(z = 0) = 0$ (because ψ_a is antisymmetric).

From Eq. (13), thermodynamic quantities can be extracted utilizing functional averages,

$$\langle \dots \rangle = \frac{1}{\mathcal{Z}_{\text{gc}}} \int D\psi_a e^{-\beta S[\psi_a]} (\dots). \quad (15)$$

Adding a fictitious term to the potential energy [Eq. (3)] of the form $\int_r v_i^{\text{aux}}(r) n_i(r)$ that couples an auxiliary potential v_i^{aux} to the ion density $n_i(r) = \sum_k \delta(r - r_{i,k})$ allows us to compute the average ion density (cf. Ref. [46]) through

$$\begin{aligned} \langle n_i(r) \rangle &= -\frac{1}{\beta} \frac{1}{\mathcal{Z}_{\text{gc}}} \frac{\delta \mathcal{Z}_{\text{gc}}}{\delta v_i^{\text{aux}}(r)} \bigg|_{v_i^{\text{aux}}=0} \\ &= \lambda_i \Lambda_i^{-3} \Theta(z-a) \langle e^{-i\beta q_i \psi_a(r)} \rangle. \end{aligned} \quad (16)$$

The Schwinger-Dyson equation $\langle \delta S / \delta \psi \rangle = 0$ [34] for Eq. (14) is the Poisson equation,

$$-\nabla (\epsilon(r) \nabla \phi(r)) = \sum_{i=a/c} q_i \langle n_i(r) \rangle, \quad (17)$$

with the electrostatic potential given by

$$\phi(r) = i \langle \psi_a(r) \rangle, \quad (18)$$

where i is the imaginary unit. Through the electrostatic potential, the surface-charge density at the metal phase can

be obtained using Gauss's theorem,

$$\sigma_M = -\epsilon_B \left. \frac{\partial \phi(r)}{\partial z} \right|_{z=a}, \quad (19)$$

where ϵ_B is the bulk permittivity of the electrolyte solvent, cf. Eq. (2). As a primary objective, we aim to determine the contribution of electron-ion correlations, viz., the image-charge effect, to the interfacial capacitance, C_d . The latter is defined as the (partial) derivative of the metallic surface charge with respect to the electrode potential, $\mathcal{E}$,

$$C_d = \frac{\partial \sigma_M}{\partial \mathcal{E}}. \quad (20)$$

A. Definition of the electrode potential

Experimentally, the electrode potential is defined as the measurable voltage between the working and reference electrodes, which is essentially equal to the difference between the respective electronic chemical potentials. In classical modeling, the electrode potential is typically defined as the difference between the inner electrostatic potentials of the metal electrode and electrolyte, which is consistent with the experimental definition up to an unimportant additive constant. For the present image-charge model, however, the definition of the electrode potential requires clarification. In Eq. (18), the electrostatic potential is determined by the antisymmetric HS field, which is zero at the electrode surface (mirror plane) and approaches an inner bulk value that is equal in magnitude and opposite in sign to the inner potential in the electrolyte, see Fig. 1. The question thus arises whether the “real” inner potential of the electrode is given by the value of the antisymmetric electrostatic potential at the electrode surface or in the bulk electrode region. In other words, does the electrode potential correspond to the electrostatic potential difference between solution bulk and metal *surface*, or, due to the presence of the image charges, between solution bulk and metal *bulk*?

Fundamentally, the electrode potential is defined as the free-energy change for transferring a neutral pair of an electron and ion from a reference state to the working electrode [49]. Thermodynamically, the partial derivative of the grand potential Ω with respect to the electrode potential is equal to the negative excess charge of the metal surface, Q_M [12],

$$\frac{\partial \Omega}{\partial \mathcal{E}} = -Q_M. \quad (21)$$

Due to the required overall charge neutrality, the electrode surface charge equals the negative of the net ionic charge of the electrolyte, $Q_M = -q(N_c - N_a)$, where q is the charge number of cations and anions. For single-valent

ions, q is equal to the elementary charge, $q = e$. The grand potential is the Legendre transform of the free energy

$$\Omega(\mu_a, \mu_c) = \mathcal{F}(N_a, N_c) - \mu_a N_a - \mu_c N_c, \quad (22)$$

where μ_i and N_i are the chemical potential and particle number of anions and cations. It will turn out useful to perform a linear transformation of the ionic chemical potentials to define two new chemical potentials,

$$\mu_+ = \frac{\mu_c + \mu_a}{2}, \quad (23)$$

$$\mu_- = \frac{\mu_c - \mu_a}{2}. \quad (24)$$

Inserting Eqs. (23) and (24) into Eq. (22) leads to

$$\begin{aligned} \Omega(\mu_+, \mu_-) &= \mathcal{F}(N_a, N_c) - \mu_+ (N_c + N_a) - \mu_- (N_c - N_a), \\ &= \mathcal{F}(N_a, N_c) - \mu_+ N_{\text{tot}} - \mu_- N_{\text{diff}}, \end{aligned} \quad (25)$$

with the total number of ions, $N_{\text{tot}} = N_c + N_a$, and the number difference between cations and anions, $N_{\text{diff}} = N_c - N_a$, corresponding to the net charge $Q_{\text{sol}} = qN_{\text{diff}}$ of the electrolyte solution, which is the negative of the net metallic surface charge $Q_M = -Q_{\text{sol}}$. Computing the partial derivatives of Ω with respect to μ_+ and μ_- , shown in Appendix A 2,

$$\frac{\partial \Omega(\mu_+, \mu_-)}{\partial \mu_+} = -N_{\text{tot}}, \quad (26)$$

$$\frac{\partial \Omega(\mu_+, \mu_-)}{\partial \mu_-} = -N_{\text{diff}} = Q_M/q, \quad (27)$$

shows that μ_+ and μ_- correspond to the chemical potentials for N_{tot} and N_{diff} , respectively. Clearly, comparing Eq. (21) with Eq. (27) shows that the electrode potential is defined by

$$\mathcal{E} = -\frac{\mu_-}{q}. \quad (28)$$

This relation between the electrode potential and the chemical potential of ions enables a fully grand-canonical calculation of the differential capacitance, where the chemical potentials are free and independent parameters, which is a central advantage of our approach.

B. Perturbative expansion

Computing quantities such as the electrostatic potential [Eq. (18)] with the full functional average [Eq. (15)] is not possible to achieve analytically. The only functional averages that can be performed analytically are Gaussian averages, i.e., where the action is quadratic in ψ_a [50]. This work employs a perturbative expansion of the HS

field [33,51] using the loop parameter ℓ , corresponding to a mean-field theory in zeroth order, and then systematically incorporating coulombic correlation effects, including image-charge correlations, with increasing orders.

Here, ℓ is treated as a “bookkeeping parameter” that is set to unity after the loop expansion has been organized and evaluated order by order, so ℓ itself has no direct physical magnitude or limit. The physically relevant small parameter controlling the convergence of the loop expansion is instead deduced from a dimensional analysis of the field-theoretic action, as detailed in Appendix A3. There, it is shown that the inverse Debye length plays the role of the actual expansion parameter. The derivation follows the standard weak-coupling construction of Netz and Orland [33] and shows explicitly that this dimensionless coupling controls the loop (fluctuation) expansion and is, therefore, valid only in the weak-coupling regime of low electrolyte concentration, while the formal loop index ℓ is fixed to $\ell = 1$ throughout.

The perturbative expansion

$$\psi_a(r) = \psi_c(r) + \ell^{-1/2} \delta\psi(r) \quad (29)$$

is performed around a specific field configuration ψ_c that is specified later. In this context, the loop parameter ℓ serves the purpose of distinguishing between terms of different orders and is set to $\ell = 1$ at the end of the calculation. In addition ℓ must be multiplied in front of the action [Eq. (15)] to systematically organize corrections in even powers of that parameter [33]. Expanding the electrostatic potential [Eq. (18)] yields

$$\phi(r) = i \frac{1}{\mathcal{Z}_{\text{gc}}} \int D\delta\psi (\psi_c + \ell^{-1/2} \delta\psi) e^{-\beta \ell S[\psi_c + \ell^{-1/2} \delta\psi]}. \quad (30)$$

The action S , as defined in Eq. (14), expanded around ψ_c , takes the following form:

$$\begin{aligned} S[\psi_c + \ell^{-1/2} \delta\psi, \{\lambda_i\}] \\ = S[\psi_c, \{\lambda_i\}] + \ell^{-1/2} \int_{r,r'} \delta\psi(r) \frac{\delta S[\psi, \{\lambda_i\}]}{\delta\psi(r)} \Big|_{\psi=\psi_c} \\ + \frac{\ell^{-1}}{2} \int_{r,r'} \delta\psi(r) \frac{\delta^2 S[\psi, \{\lambda_i\}]}{\delta\psi(r) \delta\psi(r')} \Big|_{\psi=\psi_c} \delta\psi(r') \\ + \sum_{n=3}^{\infty} \ell^{-n/2} \Gamma^{(n)}[\{\lambda_i\}], \end{aligned} \quad (31)$$

with the so-called bare vertex

$$\begin{aligned} \Gamma^{(n)}[\{\lambda_i\}] &= \frac{1}{n!} \int_{r_1, \dots, r_n} \delta\psi(r_1) \dots \delta\psi(r_n) \\ &\times \Gamma^{(n)}(\{\lambda_i\}, r_1, \dots, r_n), \end{aligned} \quad (32)$$

and its corresponding vertex function,

$$\Gamma^{(n)}(\{\lambda_i\}, r_1, \dots, r_n) = \frac{\delta^n S[\psi, \{\lambda_i\}]}{\delta\psi(r_1) \dots \delta\psi(r_n)} \Big|_{\psi=\psi_c}. \quad (33)$$

Once the perturbative expansion exceeds the zeroth-order term, the chemical potentials must be adjusted in order to yield a well-defined theory without unphysical divergences [34,52]. We choose an appropriate gauge chemical potential μ_g for the ion chemical potentials $\mu_i \rightarrow \mu_i + \ell^{-1} \mu_g$, which is the same for both ion species. For the fugacities, this results in another expansion

$$\lambda_i = e^{\beta(\mu_i + \ell^{-1} \mu_g)} = \lambda_i^0 \left(1 + \ell^{-1} \omega + \frac{\ell^{-2}}{2} \omega^2 + \mathcal{O}(\ell^{-3}) \right), \quad (34)$$

where $\omega = \beta \mu_g$. Inserting Eq. (34) into Eq. (31) one arrives at

$$\begin{aligned} S[\psi, \{\lambda_i\}] &= S[\psi_c, \{\lambda_i^0\}] \\ &+ \ell^{-1} S_{\text{int}}[\psi_c, \{\lambda_i^0 \omega\}] + \ell^{-1/2} \int_r \delta\psi(r) \frac{\delta S[\psi, \{\lambda_i^0\}]}{\delta\psi(r)} \Big|_{\psi=\psi_c} \\ &+ \frac{\ell^{-1}}{2} \int_{r,r'} \delta\psi(r) \frac{\delta^2 S[\psi, \{\lambda_i^0\}]}{\delta\psi(r) \delta\psi(r')} \Big|_{\psi=\psi_c} \delta\psi(r') \\ &+ \ell^{-3/2} S_I^{(3)}[\psi_c] + \mathcal{O}(\ell^{-2}), \end{aligned} \quad (35)$$

with S_{int} as defined in Eq. (14) and a renormalized vertex function of order 3,

$$\begin{aligned} S_I^{(3)}[\psi_c] &= \int_{r,r'} \frac{\delta S_{\text{int}}[\psi, \{\lambda_i^0 \omega\}]}{\delta\psi(r)} \Big|_{\psi=\psi_c} \delta\psi(r) \\ &+ \frac{1}{3!} \int_{r,r',r''} \Gamma^{(3)}(\{\lambda_i^0\}, r, r', r'') \delta\psi(r) \delta\psi(r') \delta\psi(r''). \end{aligned} \quad (36)$$

The saddle-point configuration of the action functional of Eq. (14) is the field configuration with the largest statistical weight in the partition function of Eq. (13) [51]. Therefore, it is selected as the expansion point ψ_c in the loop expansion of the HS field, Eq. (29). The saddle-point field satisfies

$$\frac{\delta S[\psi, \{\lambda_i^0\}]}{\delta\psi(r)} \Big|_{\psi=\psi_c} = 0. \quad (37)$$

Inserting Eq. (35) along with Eq. (37) into the expansion for the electrostatic potential [Eq. (30)] yields

$$\phi(r) = i\psi_c(r) + i\ell^{-1/2} \left\langle \delta\psi(r) \exp \left(-\beta\ell^{-1/2} S_I^{(3)}[\psi_c] + \mathcal{O}(\ell^{-2}) \right) \right\rangle_G, \quad (38)$$

where

$$\langle \dots \rangle_G = \frac{1}{\mathcal{Z}_G} \int D\delta\psi(\dots) e^{-\frac{\beta}{2} \int_{r,r'} \delta\psi(r) G^{-1}(r,r') \delta\psi(r')}, \quad (39)$$

with $\mathcal{Z}_G = \int D\delta\psi \exp \left(-(\beta/2) \int_{r,r'} \delta\psi(r) G^{-1}(r,r') \delta\psi(r') \right)$, is a Gaussian functional average with respect to the second-order functional derivative of the action,

$$G^{-1}(r,r') = \left. \frac{\delta^2 S}{\delta\psi(r)\delta\psi(r')} \right|_{\psi=\psi_c}. \quad (40)$$

In particular, since the average of Eq. (39) is Gaussian, the average of a product of two HS field fluctuations is exactly given by

$$\langle \delta\psi(r)\delta\psi(r') \rangle_G = \beta^{-1} G(r,r'), \quad (41)$$

which is defined by

$$\int_{r''} G^{-1}(r,r'') G(r'',r') = \delta(r,r'). \quad (42)$$

The correlation function $G(r,r')$ [Eq. (41)] quantifies correlations in $\delta\psi$ by linking its amplitude at r to that at r' . In a similar fashion, inserting the perturbative expansion of ψ [Eq. (29)] into the formula for the ion densities [Eq. (16)] leads to

$$\langle n_i(r) \rangle = \lambda_i \Lambda_i^{-3} \Theta(z-a) e^{-i\beta q_i \psi_c(r)} \left\langle e^{-\ell^{-1/2} i\beta q_i \delta\psi(r)} e^{-\beta\ell^{-1/2} S_I^{(3)}[\psi_c] + \mathcal{O}(\ell^{-2})} \right\rangle_G. \quad (43)$$

The expansions of the electrostatic potential [Eq. (38)] and ion densities [Eq. (43)] are exact but also impossible to calculate analytically. The following sections present approximations corresponding to different orders in the perturbative expansion, i.e., truncating the expansions at different orders of ℓ .

C. Mean-field theory

At the MF level, only terms of zeroth order in ℓ are kept, i.e., $\delta\psi = 0$. At this level of theory, the field $\psi_a(r)$ is replaced in all functional averages by the saddle-point field $\psi_c(r)$. We will see at the end of this section, that this theory at MF level coincides with the traditional GCS theory with

a homogeneous surface-charge density, corresponding to an in-plane averaged (smeared-out) image-charge distribution. In physical terms, this means that the MF approach does not account for ion-ion and ion-electron correlations.

1. Electrostatic potential

The electrostatic potential [Eq. (38)] at the MF level is simply given by

$$\phi^{\text{MF}}(r) = i\psi_c(r). \quad (44)$$

The zero potential reference is set at the metal surface (image plane) rather than in the bulk electrolyte. This choice is required by the asymmetry of ψ_c upon reflection at the metal surface, which arises from the asymmetry of ψ_a in Eq. (10) and the inherent asymmetry of the action in Eq. (13). The saddle-point equation [Eq. (37)] of the action [Eq. (14)] defining $\psi_c(r)$ (and thus $\phi^{\text{MF}}(r)$) within the electrolyte solution region ($z > a$) is given by

$$-\epsilon_B \nabla^2 \phi^{\text{MF}}(r) - \sum_{i=a/c} q_i \lambda_i \Lambda_i^{-3} e^{-\beta q_i \phi^{\text{MF}}(r)} = 0 \quad (45)$$

and within ($0 < z < a$) by

$$-\epsilon_I \nabla^2 \phi^{\text{MF}}(r) = 0. \quad (46)$$

Far from the interface ($z \gg a$), where ϕ^{MF} is constant, the saddle-point equation is satisfied for

$$\phi^{\text{MF}}(\infty) \equiv \phi_0 = -\frac{1}{2\beta q} \log \left(\frac{\lambda_a \Lambda_a^{-3}}{\lambda_c \Lambda_c^{-3}} \right), \quad (47)$$

where a symmetric electrolyte with $q = q_c = -q_a$ was assumed. Inserting the redefined chemical potentials Eqs. (23) and (24) into Eq. (47), the electrolyte bulk value of ϕ^{MF} is determined by μ_- alone, $\phi_0 = \mu_-/q$. In other words, the electrolyte bulk value of ϕ^{MF} depends only on the difference between the ionic chemical potentials and thus directly corresponds to the electrode potential according to Eq. (28),

$$\phi_0 = \frac{\mu_-}{q} = -\mathcal{E}. \quad (48)$$

This relation resolves the ambivalence discussed in Sec. II A and shows that even in the presence of image charges, the common definition of the electrode potential in terms of the electrostatic potential difference between solution bulk and metal surface still holds [53]. Knowing that the saddle-point field ϕ^{MF} converges to a constant value ϕ_0 in the electrolyte bulk, we insert $\phi^{\text{MF}}(r) = \phi_0 + \Delta\phi^{\text{MF}}(r)$ into Eq. (45) and find the approximate solution for the MF electrostatic potential for a weakly charged surface (with details shown in Appendix A 4),

$$\phi^{\text{MF}}(r) = -\mathcal{E} + \frac{4}{\beta q} \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}(z-a)} \right), \quad (49)$$

which coincides with the GCS solution. The Debye length

$$\lambda_D = \sqrt{\frac{\epsilon_B}{2\beta q^2 n_{\text{ion}}^b}} \quad (50)$$

is determined by the bulk ion density n_{ion}^b discussed in the following.

2. Electroneutrality in the solution bulk

Ion densities [Eq. (43)] at the MF level are simply given by the Boltzmann-type relation

$$\langle n_i(r) \rangle^{\text{MF}} = \lambda_i \Lambda_i^{-3} \Theta(z-a) e^{-\beta q_i \phi^{\text{MF}}(r)}. \quad (51)$$

Inserting $\phi^{\text{MF}}(r) = \phi_0 + \Delta\phi^{\text{MF}}(r)$ yields the same relationship with the zero potential reference in the bulk electrolyte,

$$\langle n_i(r) \rangle^{\text{MF}} = \Theta(z-a) n_{\text{ion}}^b e^{-\beta q_i \Delta\phi(r)}, \quad (52)$$

with an identical bulk ion concentration for cations and anions,

$$\langle n_i(\infty) \rangle \equiv n_{\text{ion}}^b = \lambda_i \Lambda_i^{-3} e^{-\beta q_i \phi_0} = \Lambda_i^{-3} e^{\beta \mu_i}, \quad (53)$$

where

$$\mu_i - q_i \phi_0 = \frac{\mu_a + \mu_c}{2} = \mu_+ \quad (54)$$

was used in the last step. The equal bulk concentrations of anions and cations mean that electroneutrality in the solution bulk is automatically satisfied. Thus, regardless of the values of the individual ion chemical potentials μ_a and μ_c as defined by respective external reservoirs, the inner electrostatic potential in the electrolyte bulk will always adjust to a value such that electroneutrality is satisfied. This confirms the consistency of the present grand-canonical approach where both the cation and anion chemical potentials are free and independent parameters.

3. Capacitance

The metallic surface-charge density [Eq. (19)] is given by

$$\begin{aligned} \sigma_M^{\text{MF}} &= -\epsilon_B \frac{\partial \phi^{\text{MF}}}{\partial z} \Big|_{z=a} \\ &= \frac{2}{\beta q} \frac{\epsilon_B}{\lambda_D} \sinh \left(\frac{\lambda_D}{a(\epsilon_B/\epsilon_I) + \lambda_D} \frac{\beta q \mathcal{E}}{2} \right) \end{aligned} \quad (55)$$

and the (inverse) differential capacitance is calculated according to Eq. (20),

$$\begin{aligned} C_{\text{MF}}^{-1} &= \left(\frac{\partial \sigma_M^{\text{MF}}}{\partial \mathcal{E}} \right)^{-1} \\ &= \frac{\lambda_D}{\epsilon_B} \frac{1}{\cosh \left(\frac{q\beta}{2} \left(\mathcal{E} - \frac{a}{\epsilon_I} \sigma_M^{\text{MF}}(\mathcal{E}) \right) \right)} + \frac{a}{\epsilon_I} \\ &= C_{\text{GC}}^{-1} + C_H^{-1} = C_{\text{GCS}}^{-1}. \end{aligned} \quad (56)$$

This expression is precisely equal to the inverse GCS capacitance, which is the sum of inverse Gouy-Chapman and Helmholtz capacitances, the latter given by a/ϵ_I in the present model. This result proves that the image-charge theory reduces to GCS theory when restricted to the MF level. At this level, the instantaneous inhomogeneous distribution of image charges, and thus (electronic) surface charge, gets completely smeared out, resulting in a constant in-plane averaged surface-charge density as assumed in GCS theory. In particular, this shows that the image charges consistently represent the entire charge of the electrode, and no additional surface charge must be applied in this model.

D. First-order perturbation theory

It is generally difficult to make systematic improvements over classical GCS theory, and extensions are thus usually phenomenological in nature [54,55]. After showing that the MF level of our theoretical model corresponds to GCS theory, we are now in a position to improve the theory in a systematic way by going beyond the saddle-point approximation. We thereby focus on the capacitive response around the PZC, which allows for analytical calculations of perturbative corrections to the MF result. Accordingly, this section presents the development of a first-order extended GCS theory that incorporates coulombic correlation effects, specifically ion-ion and ion-image-charge correlations, with the latter representing interfacial ion-electron correlations. The first-order perturbative expressions are derived for the electrostatic potential, the ion densities, and the differential capacitance by keeping terms up to order ℓ^{-1} of the respective loop expansion in powers of ℓ . The obtained first-order results will be denoted by “1L”, short for “one loop”, due to the fact that the 1L level diagrammatically contains one self-energy loop [33].

1. Correlation function

The correlation function, $G(r, r')$, is the primary object of any perturbative analysis of the partition function and all its derived quantities. It was already explained that at the MF level, particles interact only via the average (mean) charge distributions. The correlation function effectively captures all interactions due to instantaneous “out-of-average” density fluctuations that are ignored at the MF level.

By inserting Eq. (40) into Eq. (42) one finds that, near the PZC, the correlation function G satisfies

$$(-\nabla_r \epsilon(r) \nabla_r + 2\beta q^2 n_{\text{ion}}^b \Theta(z - a)) G(r, r') = \delta(r - r'), \quad (57)$$

as shown in greater detail in Appendix A 5. Utilizing the in-plane translational invariance, $G(r, r') = G(r - r')$, the solution reads

$$G(r, r') = \frac{1}{4\pi\epsilon_B} \int_0^\infty dk J_0(k\rho) \frac{k}{\gamma(k)} \left(e^{-\gamma(k)|z'-z|} + e^{-\gamma(k)(z+z'-2a)} \left(1 - \frac{2k}{k + (\epsilon_B/\epsilon_I)\gamma(k) \tanh(ka)} \right) \right), \quad (58)$$

where J_0 is the zeroth Bessel function of the first kind, and $\gamma(k) = \sqrt{k^2 + \lambda_D^{-2}}$. Further details are given in Appendix A 6.

2. Interface correlation energy

The correlation function [Eq. (58)] evaluated at equal point (or coincident point), $r = r'$, is divergent. This divergence can be corrected by subtracting the (equally divergent) limiting expression for the equal-point correlation function in the bulk dielectric solvent (here water), which is given by

$$G_0(r, r) = \frac{1}{4\pi\epsilon_B} \int_0^\infty dk. \quad (59)$$

The renormalized (corrected) self energy

$$V(z) = \frac{q^2}{2} (G(r, r) - G_0(r, r)) \quad (60)$$

[in case of Eq. (58) only a function of z] quantifies the correlation energy of a single point charge at r compared to the self energy of a single ion in a bulk dielectric solvent [19,34,56]. An ion energetically favors moving from the bulk to position z if $V(z) < 0$, and, vice versa, requires

energy if $V(z) > 0$. Inserting Eq. (58) into Eq. (60), $V(z)$ splits into two finite parts,

$$V(z) = V_{\text{DH}} + V_{\text{int}}(z), \quad (61)$$

where V_{DH} is the known Debye-Hückel self energy of a charged particle in a bulk electrolyte solution [34,56],

$$V_{\text{DH}} = -\frac{q^2}{8\pi\epsilon_B\lambda_D}. \quad (62)$$

The additional component,

$$V_{\text{int}}(z) = \frac{q^2}{8\pi\epsilon_B} \int_0^\infty dk \frac{k}{\gamma(k)} e^{-2\gamma(k)(z-a)} \left(1 - \frac{2k}{k + (\epsilon_B/\epsilon_I)\gamma(k) \tanh(ka)} \right), \quad (63)$$

will be referred to as the *interface correlation energy* in the following, that arises due to correlations between ions in the solution and the electrode surface, i.e., it describes electron-ion correlations. The integral determining the interface correlation function in Eq. (63) is not amenable to an analytical solution. However, in the limit of infinite dilution ($\lambda_D \rightarrow \infty$), an analytical solution is given by

$$V_{\text{int}}(z) = \frac{q^2}{8\pi\epsilon_B\lambda_D} \left(\frac{e^{-2(z-a)/\lambda_D}}{2(z-a)/\lambda_D} \left(1 - \frac{{}_2F_1(1, z/a - 1, z/a; \frac{(\epsilon_B/\epsilon_I)-1}{(\epsilon_B/\epsilon_I)+1})}{((\epsilon_B/\epsilon_I)+1)/2} \right) - \frac{e^{-2z/\lambda_D}}{2z/\lambda_D} \frac{{}_2F_1(1, z/a, 1+z/a; \frac{(\epsilon_B/\epsilon_I)-1}{(\epsilon_B/\epsilon_I)+1})}{((\epsilon_B/\epsilon_I)+1)/2} \right), \quad (64)$$

with ${}_2F_1$ being the hypergeometric function. This central analytical result quantifies how electron-ion correlations modify the self-energy through their dependence on the Debye length λ_D and the interfacial parameters ϵ_I and a .

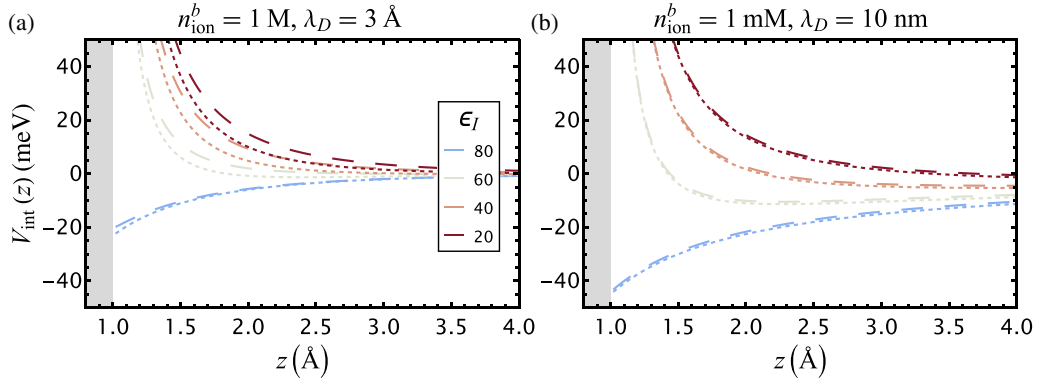


FIG. 2. The numerical solution (long-dashed) of the interface correlation function in Eq. (63) of an aqueous electrolyte solution with $\epsilon_B = 80$ and a charge-separation distance of $a = 1 \text{ \AA}$ for ionic concentrations 1M (a) and 1mM (b). For comparison, the analytical approximation Eq. (64) is shown as short-dashed curves. Shown are results for $\epsilon_I = 80$ (blue) down to $\epsilon_I = 10$ (red).

Figure 2 compares the full numerical solution for the interface correlation function [Eq. (63)] with its analytical approximation [Eq. (64)] for a charge-separation distance of $a = 1 \text{ \AA}$ at various values for ϵ_I and two different concentrations of an aqueous electrolyte solution characterized by $\epsilon_B = 80$. In concentrated solutions (a), i.e., for a short Debye length, the approximate analytical solution (short-dashed) of Eq. (64) agrees only at a qualitative level with the numerical solution (long-dashed), because the former was derived under the assumption of a large Debye length. Accordingly, in the regime of a large Debye length (b), i.e., in the dilute limit, the analytical and numerical solutions align very well independent of the values of other parameters. Further in-depth analysis of V_{int} is postponed to the results section (Sec. III).

3. Electrostatic potential

Expanding the exponential function in Eq. (38) in powers of ℓ and keeping only the terms up to (including) $\mathcal{O}(\ell^{-1})$ and setting $\ell = 1$ yields the electrostatic potential to 1L order,

$$\phi^{1L}(r) = \phi^{\text{MF}}(r) - i\beta \langle \delta\psi(r) S_I^{(3)} \rangle_G, \quad (65)$$

where $\langle \delta\psi(r) \rangle_G = 0$ since odd moments in $\delta\psi(r)$ vanish for Gaussian distributions. The first term on the rhs is the MF result [Eq. (49)] and the second term is the first-order correction, which depends on $S_I^{(3)}$ [defined in Eq. (36)]. As shown in Appendix A 7, inserting $S_I^{(3)}$ into Eq. (65) gives the electrostatic potential as an integral expression

$$\begin{aligned} \phi^{1L}(r) &= \phi^{\text{MF}}(r) + \Delta\phi^{1L}(r) \\ &= \phi^{\text{MF}}(r) + \frac{\epsilon_B}{\beta q \lambda_D^2} \int_{r' > a} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) G(r, r') \left(\frac{\beta q^2}{2} G(r', r') - \omega \right). \end{aligned} \quad (66)$$

An important fact here is that due to the factor $\sinh$ the correlation contribution $\Delta\phi^{1L}$ vanishes in the electrolyte bulk $z \rightarrow \infty$. This means that in the electrolyte bulk there is *no* correction of the electrostatic potential. This also means that the relation between electrode potential and the bulk electrostatic potential, Eq. (48), remains the same.

Clearly, the 1L correction directly depends on the correlation function $G(r, r')$ but also on the equal-point correlation function $G(r, r)$, which is infinite. The gauge constant $\omega = \beta \mu_g$ in Eq. (66) can be used to renormalize

the equal-point correlation function to a finite value. Physically, this gauge chemical potential allows tuning the ion concentrations to ensure identical electrolyte concentrations in mean-field and correlation-corrected models (under the same external reference chemical potentials or fugacities). Without adjustment of the gauge chemical potential, the respective (bulk) concentrations would differ due to the decreased activity coefficients under the effect of correlations [46]. Therefore, to choose an appropriate gauge chemical potential, it is necessary to consider the ion densities.

4. Ion densities

Truncating the expansion of the ion densities, Eq. (43), beyond $\mathcal{O}(\ell^{-1})$ yields,

$$\langle n_i(r) \rangle^{1L} = \lambda_i \Lambda_i^{-3} e^{-q_i \beta \phi^{1L}(r)} \exp \left(- \left(\frac{\beta q_i^2}{2} G(r, r) - \omega \right) \right), \quad (67)$$

which depends on the electrostatic potential in Eq. (66) and $G(r, r)$. As discussed before, in the electrolyte bulk, the 1L electrostatic potential correction vanishes ($\phi^{1L} = \phi^{MF}$). Also, far from the interface the influence of the electrode vanishes, $V_{\text{int}} = 0$ (see Fig. 2). Hence, according to Eq. (61), in the solution bulk the equal-point correlation function reduces to $(q_i^2/2)G(r, r) = V_{\text{DH}} + (q_i^2/2)G_0$. The ion density in the solution bulk is then

$$\langle n_i(\infty) \rangle^{1L} = e^{\beta \mu_i^{\text{eff}}} \Lambda_i^{-3}, \quad (68)$$

with an “effective” chemical potential,

$$\mu_i^{\text{eff}} = \mu_i - q_i \phi_0 - \beta^{-1} \log \gamma_i = \mu_+ - \beta^{-1} \log \gamma_i, \quad (69)$$

that is shifted compared to the MF result in Eq. (54) by the activity coefficient

$$\log \gamma_i = -\frac{\beta q_i^2}{8\pi \epsilon_B \lambda_D} + \frac{\beta q_i^2}{2} G_0(r, r) - \beta \mu_g. \quad (70)$$

The gauge chemical potential, μ_g , thus enables tuning the bulk ion density in the 1L theory to the same value as for the MF theory, which is required for a consistent comparison of the interfacial capacitance results between the MF and 1L level. Selecting

$$\omega = \beta \mu_g = -\frac{\beta q_i^2}{8\pi \epsilon_B \lambda_D} + \frac{\beta q_i^2}{2} G_0(r, r), \quad (71)$$

the reference activity coefficients in the electrolyte bulk become $\gamma_i = 1$ and the bulk ion densities at the MF and 1L levels of theory coincide [57],

$$\langle n_i(\infty) \rangle^{MF} = \langle n_i(\infty) \rangle^{1L}. \quad (72)$$

With the chosen gauge chemical potential [Eq. (71)], the ion densities become

$$\langle n_i(r) \rangle^{1L} = n_{\text{ion}}^b e^{-\beta q_i (\Delta \phi^{MF}(r) + \Delta \phi^{1L}(r))} e^{-\beta V_{\text{int}}(r)}. \quad (73)$$

Clearly, interfacial Coulomb correlations affect the ionic densities through both changes in electrostatic potential and the additional interface correlation energy. Note that the latter can also be interpreted as a spatially dependent activity coefficient

$$\log \gamma_i(z) = \beta V_{\text{int}}(z). \quad (74)$$

5. Capacitance

Calculating the electrode surface-charge density σ_M , from Eq. (19) yields

$$\begin{aligned} \sigma_M^{1L} &= -\epsilon_B \frac{\partial \phi^{1L}(r)}{\partial z} \Big|_{z=a} \\ &= -\epsilon_B \left(\frac{\partial \Delta \phi^{MF}(r)}{\partial z} \Big|_{z=a} + \frac{\partial \Delta \phi^{1L}(r)}{\partial z} \Big|_{z=a} \right), \end{aligned} \quad (75)$$

with a contribution to the charge density from the MF solution $\Delta \phi^{MF}$ and one from the 1L correction $\Delta \phi^{1L}$. As mentioned before, this article is entirely focused on the conditions around the PZC. Therefore, the cosh and sinh terms of the MF [Eq. (49)] and 1L [Eq. (66)] contributions are linearized to

$$\Delta \phi^{MF}(z) \approx \mathcal{E} \frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} e^{-(z-a)/\lambda_D}, \quad (76)$$

$$\begin{aligned} \Delta \phi^{1L}(z) &\approx \frac{1}{2} \frac{\beta \mathcal{E}}{\lambda_D} \frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \int_{z'=a}^z e^{-(z'-a)/\lambda_D} \\ &\quad \left(e^{-|z-z'|/\lambda_D} - e^{-(z+z')/\lambda_D} \right) V_{\text{int}}(z'), \end{aligned} \quad (77)$$

yielding

$$-\epsilon_B \frac{\partial \Delta \phi^{MF}(r)}{\partial z} \Big|_{z=a} \approx \frac{\epsilon_B}{(\epsilon_B/\epsilon_I)a + \lambda_D} \mathcal{E}, \quad (78)$$

$$\begin{aligned} -\epsilon_B \frac{\partial \Delta \phi^{1L}(r)}{\partial z} \Big|_{z=a} &\approx \frac{-\epsilon_B}{(\epsilon_B/\epsilon_I)a + \lambda_D} \mathcal{E} \\ &\quad \frac{\beta}{\lambda_D} \int_{z'=a}^z e^{-2z'/\lambda_D} V_{\text{int}}(z'). \end{aligned} \quad (79)$$

Thus, around the PZC, the metallic surface charge of Eq. (75) is given by

$$\sigma_M^{1L} = \frac{\epsilon_B}{(\epsilon_B/\epsilon_I)a + \lambda_D} \mathcal{E} \left(1 - \frac{\beta}{\lambda_D} \int_{z'=a}^z e^{-2z'/\lambda_D} V_{\text{int}}(z') \right). \quad (80)$$

Inserting Eq. (80) into the definition of the differential capacitance, Eq. (20), the result for the capacitance at 1L level can be expressed in terms of the MF GCS capacitance scaled by an additional 1L factor,

$$C_{1L} = R_{1L} \times C_{\text{GCS}}. \quad (81)$$

This shows that interface correlations modify the capacitance mathematically akin to a geometrical electrode surface roughness, as often invoked to explain discrepancies between experimental capacitance data and GCS predictions at the PZC [58–60]. Here, this factor has an entirely different physical origin in interfacial electron-ion

correlations, and we therefore denote it as the *interface correlation factor*,

$$R_{1L} = 1 - \frac{\beta}{\lambda_D} \int_a^\infty dz e^{-2z/\lambda_D} V_{\text{int}}(z). \quad (82)$$

The interface correlation factor arises primarily from an integral over the interface correlation energy, Eq. (64), that captures electron-ion correlations. Electrolyte concentration enters Eq. (82) directly via the prefactor and indirectly through the Debye length in V_{int} . The interfacial parameters a and ϵ_I affect the integral's lower boundary and V_{int} .

E. Clover approximation

In the previous section, the influence of electron-ion correlation effects on electrical double-layer properties such as interfacial capacitance at PZC have been calculated based on first-order (1L) perturbation theory. In the first part of this section, the second-order (two-loop) perturbation theory (2L) of the interfacial capacitance at PZC is calculated and compared in its magnitude to the 1L result. It is demonstrated that the 1L expansion becomes inaccurate for $a < 1 \text{ \AA}$, where the 2L order becomes significant in magnitude compared to the 1L order. The 2L expansion of the capacitance consists of several different contributions of which one is clearly more important than the others. In fact, when represented as a Feynman diagram, cf. Appendix A 8, the 1L and the dominant 2L contributions share a common structure, resembling a clover leaf with one and two leaves, respectively. In the second part of this section all possible Feynman diagrams of clover structure are added up, which leads to a capacitance formula of infinite order in perturbation theory, which we refer to as the *clover approximation*.

1. Second-order perturbation theory

To evaluate the accuracy of the first-order perturbation theory presented in Sec. II D, in this section the interface

correlation factor [cf. Eq. (82)] is derived to second order and compared with the first-order result. Expanding the electrostatic potential in Eq. (38) to second order similarly to Eq. (65) yields

$$\begin{aligned} \phi^{2L}(r) = \phi^{1L}(r) - i\beta\ell^{-2} & \left(\left\langle \delta\psi(r) S_I^{(5)} \right\rangle_G \right. \\ & \left. - \beta \left\langle \delta\psi S_I^{(3)} S_I^{(4)} \right\rangle_G - \frac{\beta^2}{3!} \left\langle \delta\psi(r) \left(S_I^{(3)} \right)^3 \right\rangle_G \right), \end{aligned} \quad (83)$$

where the first term on the rhs is the 1L result [Eq. (66)] and the remaining three Gaussian averages are the 2L correction to the electrostatic potential. In Appendix A 9, details on the calculation of the Gaussian averages are presented, yielding a lengthy expression for the electrostatic potential to second order shown in Eq. (A63).

In higher-order perturbation theory, many terms share common structures. A more compact way to keep track of all possible terms is to use diagrammatic methods to efficiently represent the perturbative expansion. For our theory, diagrammatic rules are presented in Appendix A 8. Figure 3(a) diagrammatically depicts the second-order expansion of the electrostatic potential, including all five contributing diagrams from Eq. (A64). Clover-1 represents the first-order contribution of ϕ^{1L} , while Clover-2 and the remaining three diagrams account for the second-order contributions.

Using the solution for the electrostatic potential [Eq. (A63)] and the definition of the capacitance [Eq. (20)], it is shown in Appendix A 9 that to second order, the capacitance can be written as

$$C_{2L} = R_{2L} \times C_{\text{GCS}}, \quad (84)$$

where

$$R_{2L} = 1 + \Delta R_{1\text{-clover}} + \Delta R_{2\text{-clover}} + \Delta R_{2\text{-rest}} \quad (85)$$

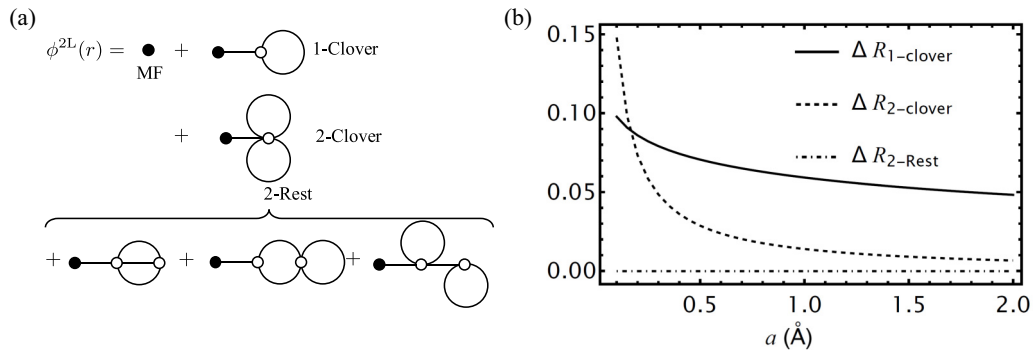


FIG. 3. (a) Diagrams contributing to the second-order perturbation theory of ϕ^{2L} . (b) Contributions to the interface correlation factor R_{2L} [Eq. (85)], evaluated at the PZC, as a function of the charge-separation distance a , for a fixed residual permittivity of $\epsilon_I = 20$ and ionic bulk concentration of $n_{\text{ion}}^b = 100 \text{ mM}$.

is the second-order interface correlation factor consisting of three contributions $\Delta R_{1\text{-clover}}$, $\Delta R_{2\text{-clover}}$, and $\Delta R_{2\text{-rest}}$ that are directly linked to the diagrammatic contributions shown in Fig. 3(a). Their mathematical form is given in Eq. (A71). In Fig. 3(b), the three contributions to the interface correlation factor from Eq. (85), evaluated at the PZC, are shown as functions of the charge-separation distance for a residual permittivity of $\epsilon_I = 20$ and a bulk ion concentration of $n_{\text{ion}}^b = 100$ mM, for which the analytical approximate expression for the interface correlation energy, Eq. (64), is accurate. The 1-clover contribution, $\Delta R_{1\text{-clover}}$, is larger than all second-order contributions for $a > 0.2$ Å. Among the second-order contributions, the 2-clover diagram corresponding to $\Delta R_{2\text{-clover}}$ is significantly more important than all the remaining ones combined, $\Delta R_{2\text{-rest}}$. Physically, this may be explained by the fact that in the dilute limit considered here, interactions involving multiple ions become increasingly unlikely due to large interionic distances. In the diagrammatic representation (see Appendix A 8), such interactions are indicated by straight lines. In Fig. 3(a), the 2-clover graph has only one pairwise interaction, while the graphs contributing to 2-rest have four, three, and two, from left to right. By lowering a , image-charge correlation effects become stronger, which can be seen by the increase in $\Delta R_{1\text{-clover}}$ and $\Delta R_{2\text{-clover}}$. Below $a \approx 1$ Å, the first-order expansion becomes inaccurate as the $\Delta R_{2\text{-clover}}$ contribution becomes a significant magnitude relative to $\Delta R_{1\text{-clover}}$.

Of the four second-order diagrams in Fig. 3(a), the 2-clover diagram clearly dominates. We therefore assume that the same holds at higher expansion orders and that

systematic improvements in accuracy can be achieved by accounting for clover-type diagrams of any order.

2. Infinite-order clover expansion

As demonstrated in the preceding section, diagrams depicting the clover structure, characterized by a single black internal line with one external leg on one side and self-energy loops on the other, have been identified as being of paramount significance. In this section we derive a more accurate formula for the interface correlation factor accounting for all possible clover diagrams. This allows us to significantly improve the applicability of the theory and compare our model results with experimental data in Sec. III.

Diagrams of clover structures have in common that they only contain one renormalized vertex of odd order (i.e., $S_I^{(3)}$ or $S_I^{(5)}$), as seen in the first-order and second-order clover diagrams in Fig. 3(a). The expansion of the electrostatic potential [Eq. (30)] in clover diagrams is shown in Fig. 4. Mathematically, the clover expansion of the electrostatic potential is given by

$$\phi^{\text{clover}}(r) = \phi^{\text{MF}}(r) - i \sum_{n=1}^{\infty} \beta \ell^{-n} \left\langle \delta \psi(r) S_I^{(2n+1)} \right\rangle_G. \quad (86)$$

All averages of $\delta\psi$ with $S_I^{(2n+1)}$ are readily computed since they follow a repetitive pattern, as shown in Appendix A 10. Upon inserting Eq. (A76) into Eq. (86) we find

$$\phi^{\text{clover}}(r) = \phi^{\text{MF}}(r) - \frac{\epsilon_B}{\beta q \lambda_D^2} \int_{r' > a} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) G(r, r') \left(e^{-\beta V_{\text{int}}(z')} - 1 \right). \quad (87)$$

Following Eqs. (19) and (20), the capacitance in clover approximation is then given by

$$C_{\text{clover}} = R_{\text{clover}} \times C_{\text{GCS}}, \quad (88)$$

$$\phi^{\text{clover}}(r) = \text{MF} + \text{1-clover} + \text{2-clover} + \text{3-clover} + \dots + \text{n-clover}$$

FIG. 4. Diagrammatic representation of the electrostatic potential in clover approximation, cf. Eq. (86).

with the interface correlation factor in clover approximation,

$$R_{\text{clover}} = 1 + \frac{1}{\lambda_D} \int_a^\infty dz e^{-2z/\lambda_D} (\exp(-\beta V_{\text{int}}(z)) - 1). \quad (89)$$

Equations (88) and (89) represent one of the key results of this work, demonstrating that the effect of electron-ion correlations (image charges) can be cast into a concise factor rescaling the mean-field (GCS) result. According to Eq. (89), this factor is determined by the interface correlation energy Eq. (63), which, in turn, describes the strength of the interfacial electron-ion correlations. On the other

hand, as emphasized earlier, other interfacial correlation effects, e.g., due to the microscopic structure of the solvent, are omitted in the present theory. It will be highly interesting for future works to explore whether such solvent effects can be included in a similarly defined correlation factor.

It should be noted that an alternative approach for treating image-charge effects has been presented by Wang and Wang [16]. Their work was based on Wang's nonperturbative field-theoretic framework for electrolytes in general dielectrically inhomogeneous media [14], which is also applicable to the case of metallic boundary conditions as considered in our theory. However, this nonperturbative method requires numerical solution of a set of coupled differential equations for the potential and Green's function. In contrast, our perturbative approach yielded a concrete analytical form for the capacitance in Eq. (88), capturing the influence of correlations in the form of the interface correlation factor, Eq. (89). As a conceptual difference, other works treating the image-charge effect via general dielectric boundary conditions introduced the electrode surface charge *ad hoc* into the model: surface and image charges appear as separate superimposed effects. In contrast, our approach emphasizes their identical nature: the ensemble of image charges represents the (instantaneous) distribution of the overall surface charge, which at the mean-field level gets averaged to a homogeneous surface-charge distribution.

It is interesting to draw a comparison of the present clover formalism to diagrammatic methods in quantum theory, where the mean-field level corresponds to the (self-consistent) Hartree approximation of the many-body Schrödinger equation. With a grain of salt, a formal analogy between the clover approximation and the random-phase approximation (RPA) can be seen, both representing an infinite resummation of a specific class of perturbative diagrams. It must be noted, however, that the detailed structure and physical meaning of the RPA

diagrams is different from the clover diagrams considered here.

III. RESULTS

In the following, the image-charge theory developed in the previous section is used to examine how electron-ion correlation effects affect the local properties of the EDL. It is thereby found to provide a novel and consistent explanation for the previously established discrepancies between GCS theory and experimental differential capacitance data.

A. Electron-ion correlations as attractive interaction

It is well established that image charges cause an attractive interaction between ions of an electrolyte solution and metallic surfaces [15,18,19,25,61]. However, the image-charge interaction is often considered an additional surface polarization effect that acts on top of the electrostatic interaction caused by the net (excess) surface charge of the metal electrode [15,19,24]. In the present theory, besides the image charges, no additional excess surface charge was applied. In fact, it was found that the image charges comprise the net surface-charge electrostatics, precisely reproducing GCS theory at the mean-field level (cf. Sec. II C). Image-charge interactions that go beyond MF electrostatics are described by the interface correlation energy $V_{\text{int}}(z)$ [Eq. (64)], which corresponds to the change in energy of an ion at a distance z from the metal surface caused by image-charge *correlations*, i.e., interfacial electron-ion correlations. The interface correlation energy is shown in Fig. 5(a) as a function of distance from the electrode surface. For $\epsilon_I = \epsilon_B$ (blue), $V_{\text{int}}(z)$ is strictly negative, indicating that ions gain energy by approaching the electrode due to attraction to their image charges. When ϵ_I is decreased, $V_{\text{int}}(z)$ turns to positive values near the electrolyte solution edge as ions must expend energy to approach a lower-permittivity region, which effectively corresponds to a

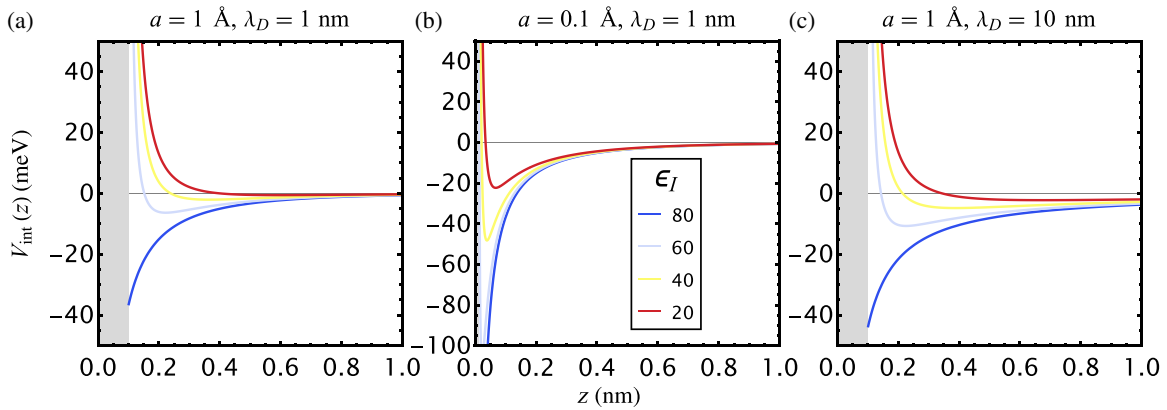


FIG. 5. Interface correlation energy V_{int} for an aqueous solution ($\epsilon_B = 80$) as a function of distance to the electrode surface for (a) $a = 1 \text{ \AA}$, $\lambda_D = 1 \text{ nm}$, (b) $a = 0.1 \text{ \AA}$, $\lambda_D = 1 \text{ nm}$, and (c) $a = 1 \text{ \AA}$, $\lambda_D = 10 \text{ nm}$ and several values of ϵ_I . The region closer than the charge-separation distance to the electrode surface is shown in light gray. It defines the minimum distance between the ionic charge and electronic counter charge.

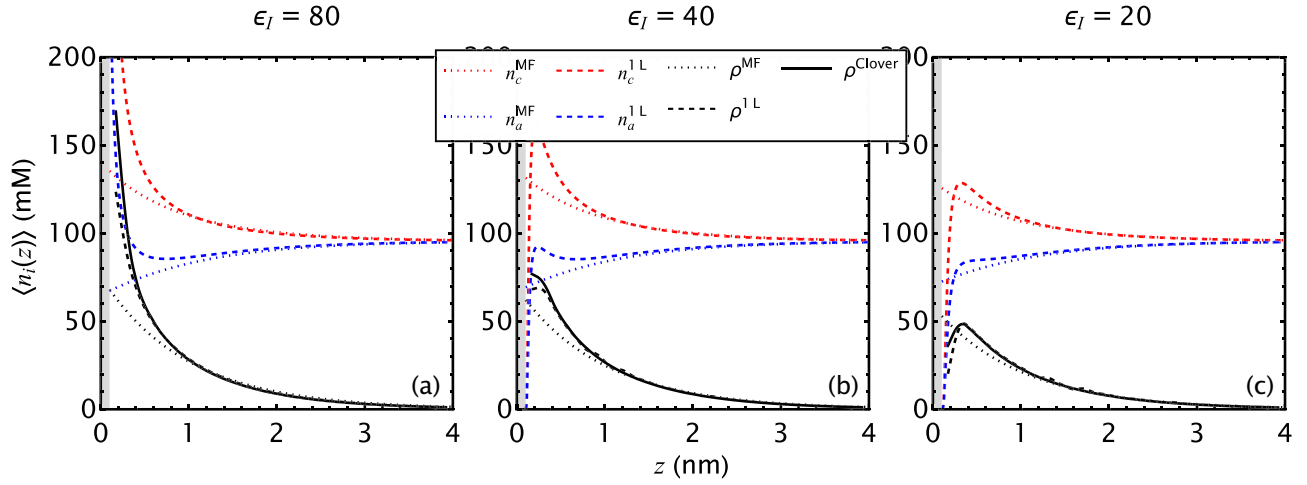


FIG. 6. Ionic and total charge densities in MF, 1L, and clover approximation for a 100-mM electrolyte solution with an applied electrode potential of $\mathcal{E} = -10$ mV. From left (a) to right (c), the residual permittivity ϵ_I is varied from a value of 80 down to 20, at a constant charge-separation distance of $a = 0.1$ nm.

(partial) desolvation of the ion. This demonstrates that V_{int} simultaneously accounts for the competing effects of electron-ion correlations and desolvation.

By decreasing the charge-separation distance a [Fig. 5(b)], the influence of electron-ion correlations becomes significantly enhanced as evident by the negative shift of V_{int} . Similarly, by decreasing the bulk electrolyte concentration from 100 mM [Fig. 5(a)] to 1 mM [Fig. 5(c)], the interfacial correlation energy becomes more negative, indicating a stronger attraction in more dilute solutions, which is due to the fact that the interaction between electronic and ionic charges is less screened.

In Fig. 6, we compare ion densities in the clover approximation with those from the MF and 1L models, using three different values for the residual permittivity, ϵ_I , while maintaining a fixed electrode potential of -10 mV versus $\mathcal{E}_{\text{pzc}}$, for $a = 1$ Å. For the clover approximation, the charge density,

$$\rho(r) = q(n_c(r) - n_a(r)), \quad (90)$$

was calculated from the second derivative of the electrostatic potential [Eq. (17)]. In the electrolyte bulk, both anion and cation densities are equal in all models, a consequence of electroneutrality. For the negative electrode potential, anion densities are lower than cation densities near the interface in the MF model, with 1L densities matching the MF solution at distances > 1 nm from the metal surface, corresponding to about one Debye length at 100 mM concentration. This is because the interfacial correlation energy (Fig. 5) becomes negligible at more than about one Debye length from the metal surface.

Strong deviations from the MF results are observed within a distance of one Debye length of the metal surface. For $\epsilon_I = \epsilon_B$ [Fig. 6(a)], the image-charge interaction

strongly increases both ion densities near the surface, leading to a divergence of the densities as a approaches zero. As the value of ϵ_I is decreased [Fig. 6(b)], the competition between the attractive image charge and the repulsive desolvation effects results in a distinct maximum in the charge density near the metal. Very close to $z = a$, the repulsive bound charge of the dielectric discontinuity at the solution edge causes the densities to decrease. Further decreasing ϵ_I increases the strength of this repulsive interaction and reduces the ion densities near $z = a$ compared to the MF solution, as shown in Fig. 6(c).

B. Capacitance at the PZC: Parsons-Zobel analysis

In a Parsons-Zobel (PZ) plot, the inverse of the measured, or simulated, capacitance is plotted against the inverse of the GC model capacitance (C_{GC}), the latter being effectively varied by changing the (bulk) electrolyte concentration, i.e., Debye length. The MF-GCS capacitance formula [Eq. (56)] predicts a linear relationship between C^{-1} and C_{GC}^{-1} with a slope of one. Figure 7 shows PZ plots of the capacitance predicted by the present theory for six different combinations of the residual dielectric permittivity ϵ_I and charge-separation distance a for an aqueous solution ($\epsilon_B = 80$). All curves in the same row correspond to the same charge-separation distance, while all PZ plots in the same column correspond to the same residual dielectric permittivity. The MF curve (black) corresponds to GCS theory. The shaded region indicates the range of higher concentrations where the approximate analytical solution of the interface correlation energy V_{int} , Eq. (64), employed in the 1L and clover models, becomes inaccurate, see Fig. 2(a).

It is apparent in Fig. 7 that the 1L and clover models, which include electron-ion correlation effects, exhibit PZ

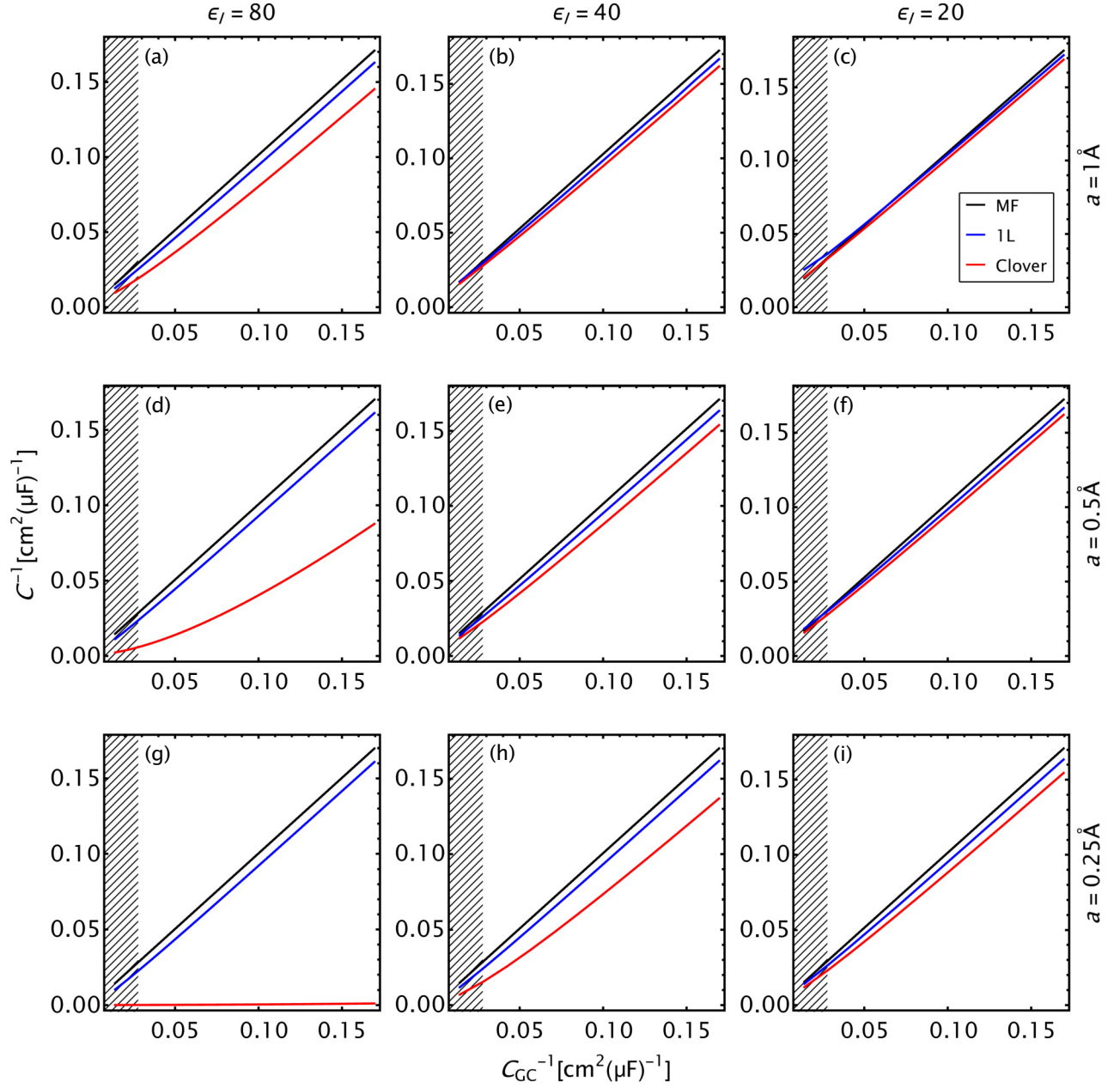


FIG. 7. Parsons-Zobel plots of the differential capacitance in MF (GCS), 1L, and clover approximation for various combinations of the residual dielectric permittivity ϵ_I and charge-separation distance a , while keeping $\epsilon_B = 80$ fixed. The shaded area indicates the range of higher concentrations where the approximate analytical solution of the interface correlation energy V_{int} , Eq. (64), employed in the 1L and clover models, becomes inaccurate.

slopes of less than one across all investigated parameter combinations, corresponding to larger values of the interfacial capacitance than predicted by GCS theory. Thereby, the capacitance in clover approximation is larger than at the 1L level for the same set of parameters. Notably, significant deviations are observed between the predictions from the clover-level theory in comparison to (mean-field) GCS theory even for low electrolyte concentrations (right-hand

part of the PZ plot), where GCS theory is typically assumed to be accurate. This indicates that electron-ion correlations can play a role in experimentally established discrepancies to GCS predictions around the potential of zero charge in the dilute limit.

The PZ slope of the capacitance curve is effectively tuned by the charge-separation distance. When a is very small, electron-ion correlation effects are significantly

affecting the interface correlation energy, cf. Fig. 5(b). In panel (g) of Fig. 7, the slope of the PZ plot of the clover approximation is nearly zero, a behavior typically attributed to pseudocapacitive charging due to ion adsorption that increases the capacitance beyond the GCS prediction [5,62]. Conversely, for larger a [Figs. 7(a)–7(c)], capacitance curves, which include electron-ion correlation effects, converge to GCS predictions. This shows that less-than-unity slopes in PZ plots, as routinely encountered in experimental data, could be a measure for the strength of interfacial correlations between ions and electrons.

Interestingly, PZ plots with similar ϵ_I/a ratios, such as those shown in panels (a), (e), and (i), or (b) and (f) of Fig. 7, display similar shapes. This suggests that a and ϵ_I are not independent parameters for the interfacial capacitance characteristics, similar to the Helmholtz capacitance in GCS theory. However, while in the latter, C_H only determines the y offset of the PZ plots, the parameters ϵ_I/a in the image-charge theory affect both the y intercept and the slope of the curves.

C. Quantitative agreement with experimental data

In the following, the theory of interfacial electron-ion correlations presented in this article is shown to provide a consistent explanation for the puzzling discrepancies between experimental capacitance data and GCS theory over a wide spectrum of electrode materials and electrolyte systems.

Using Eq. (88) for the differential capacitance at the PZC, we can directly test whether the theory is able to reproduce previously published experimental data in PZ plots. The fitting to the experimental capacitance data was performed manually with the residual permittivity (ϵ_I) and charge-separation distance (a) as the only adjustable parameters determining the PZ slope. An additional (concentration-independent) series capacitance C_{ext} is introduced to allow for vertical adjustments of the PZ

plots,

$$C^{-1} = C_{\text{ext}}^{-1} + R_{\text{clover}}^{-1} C_{\text{GCS}}^{-1}. \quad (91)$$

Unlike in GCS theory [Eq. (56)], where the compact layer capacitance C_H sets the y intercept and can be tuned independent from the slope, our image-charge theory [Eq. (88)] has no concentration independent part, because R_{clover}^{-1} affects both the compact layer and the diffuse layer contributions in C_{GCS} . However, since our primary interest lies in the explanation of anomalous PZ slopes, the *ad hoc* introduction of C_{ext} has no bearings on the further analysis.

The fitted parameter values for various experimental data sets are summarized in Table I, with corresponding comparisons between theory and experiment shown in Figs. 8 and 9. Bulk dielectric permittivities in the theoretical models were fixed based on literature values for the respective electrolyte solvents. As noted in Sec. III A, the charge-separation distance (a) and its dielectric permittivity (ϵ_I) are not independent parameters. Various combinations can yield almost identical capacitance curves. Therefore, ϵ_I was fixed to 25% of the bulk dielectric permittivity of the respective solvent, a somewhat arbitrary but not unreasonable choice reflecting the decreased effective permittivity at the direct interface in the absence of solvent dipolar orientation. For example, for the aqueous solutions, a value of $\epsilon_I = 20$ was chosen, corresponding to 25% of the bulk water permittivity. Accordingly, the model effectively had only two fit parameters: a and C_{ext} that were manually adjusted to match the theoretical PZ plots to the experimental data. Alternative combinations of values for ϵ_I and a yielding similar results are listed in Table II of the Appendix. Generally, smaller values of ϵ_I also require smaller values of a .

Four different electrode materials are compared: mercury, silver, gold, and platinum, in combination with aqueous electrolytes that are expected to exhibit negligible specific chemisorption, see Refs. [3,59,63–65,67]. Figure 8

TABLE I. Values of model parameters used to reproduce experimental capacitance data in Figs. 8 and 9. Literature references for the experimental data are indicated. The PZ slope refers to a linear fit of the experimental PZ plot. Fitted parameters for the capacitance model in Eq. (91) include the charge-separation distance a , interfacial permittivity ϵ_I , and external capacitance C_{ext} . The value of the bulk permittivity ϵ_B corresponds to the known permittivity of the respective solvent.

System	PZ slope	a (Å)	C_{ext}^{-1} (cm ² /μF)	ϵ_B	ϵ_I
Aqueous electrolytes					
Mercury-NaF [63]	0.97	1.8	0.021	80	20
Ag(111)-KPF ₆ [64]	0.85	0.3	0.013	80	20
Au(111)-KPF ₆ [65]	0.79	0.1	0.03	80	20
Pt(111)-HClO ₄ [3]	0.04	0.035	0.007	80	20
Organic electrolytes					
Au(111)-KPF ₆ DMSO [66]	0.57	0.2	0.04	46.7	12
Au(111)-KPF ₆ ACN [66]	0.28	0.25	0.02	37.4	10
Au(111)-KPF ₆ DG [66]	0.22	1.4	−0.08	7.23	2

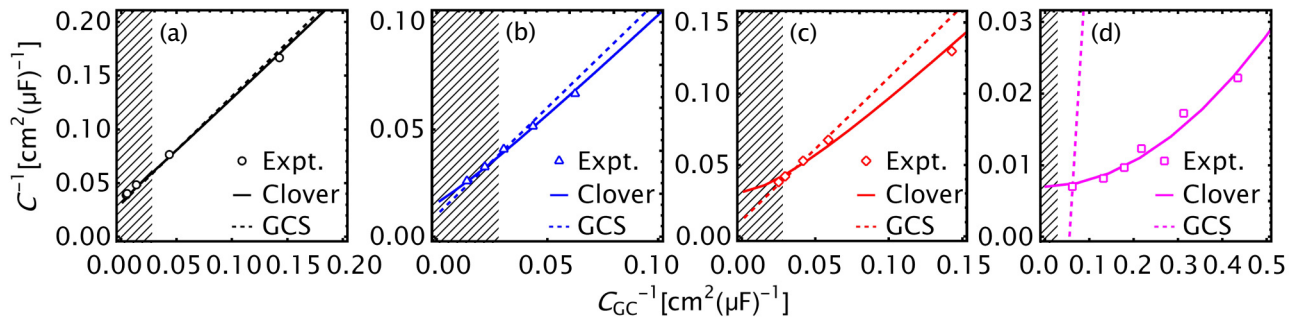


FIG. 8. Experimental PZ plots (symbols) for (a) mercury–NaF [63], (b) Ag(111)–KPF₆ [64], (c) Au(111)–KPF₆ [65], and (d) Pt(111)–HClO₄ [3] interfaces, along with model results from GCS theory (dashed lines) and clover theory (solid lines), Eq. (91), with respective model parameters given in Table I.

presents the corresponding PZ plots, demonstrating excellent quantitative agreement between the theoretical model and experimental data across all electrode materials. The model reproduces the decreased PZ slopes entirely through variations in the distance of closest approach of the ionic charge density to the image plane of the metal surface. For example, to achieve quantitative agreement with experimental data for a mercury electrode, a distance of 1.8 Å is obtained, corresponding to weak image-charge interactions and resulting in nearly perfect GCS behavior. In contrast, for the Pt(111) electrode, this distance is dramatically decreased to only 0.035 Å, where strong attractive interactions between ions and their image charges lead to significantly enhanced capacitance and a suppressed PZ slope. Of course, such a small value of a at a subatomic scale does not appear reasonable from the perspective of classical GCS theory, where a would be interpreted as the distance of closest approach of an ion to the metal surface atoms. The present theory, however, does not impose such a picture. Instead, a corresponds to the minimum distance between ions and their electronic counter (image) charges of the metal surface. Values smaller than typical interatomic distances are thus possible, as suggested by previous models accounting for ion–image-charge pairing

with an effective charge-separation distance well below the ion radius [17], as well as recent simulation results of Pt(111) interfaces where a significant fraction of the excess electron density was found to reside in the first interfacial water layer [68]. In Sec. IV, the meaning and interpretation of such small values of a are discussed in greater detail, with profound consequences for our perspective on interfacial charging processes.

Interestingly, the values of the charge-separation distance a appear to correlate with the wettability of the electrode materials. Specifically, more hydrophobic materials tend to exhibit larger charge-separation distances, while more hydrophilic ones show smaller ones. More hydrophilic surfaces are expected to allow ions and (electronic) image charges to approach more closely, because the effective separation between the metal’s image plane and the solvent dielectric boundary is reduced. In contrast, for more hydrophobic surfaces this gap becomes larger, which increases the energetic cost for (partially) desolvating ions near the interface. As a result, ions tend to remain farther from the electrode surface and, thus, from the respective image charges. A quantitative measure of wettability, i.e., hydrophilicity, is provided by the work of adhesion (W_{ad}), which reflects the strength

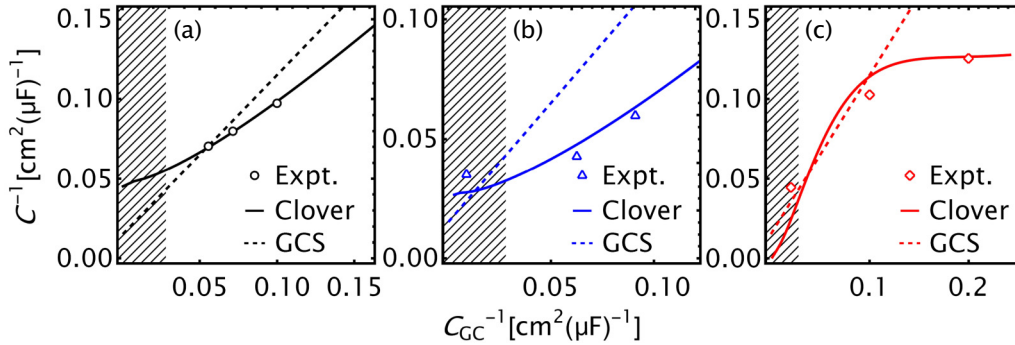


FIG. 9. Experimental PZ plots [66] (symbols) for Au(111) electrodes in contact with different KPF₆ electrolyte solutions with (a) DMSO, (b) ACN, and (c) DG as solvents, along with model results from GCS theory (dashed lines) and clover theory (solid lines), Eq. (91), with respective model parameters given in Table I.

of interaction between the electrode surface and water. In Ref. [69], computed values of W_{ad} for single-crystal surfaces show the trend $Ag < Au < Pt$, with platinum being the most hydrophilic. Mercury, although not included in this ranking, is well established as highly hydrophobic [70], and accordingly requires the largest value of the charge-separation distance in our model. This trend suggests a clear relationship: as hydrophilicity increases (from mercury to platinum), the charge-separation distance decreases, accompanied by stronger electron-ion correlations at the metal-water interface.

The present theory not only explains capacitance data for aqueous electrolytes, but equally holds for nonaqueous solvents with much smaller dielectric constants. We collected published experimental capacitance data for Au(111) electrodes in KPF₆ electrolyte solutions involving three different organic solvents, dimethyl sulfoxide (DMSO), acetonitrile (ACN), and diethylene glycol dimethyl ether (DG), with ϵ_B values ranging from 46.7 down to 7.23 (in addition to the case of the water solvent discussed before) to examine the role of the dielectric solvent in tuning the strength of interfacial electron-ion correlations. Similarly to the models for aqueous electrolytes, the value of ϵ_I was fixed to 25% of the bulk dielectric permittivity for each solvent, while the charge-separation distance a was manually adjusted to best match the experimental data, cf. Table I. Figure 9 presents the PZ plots of the Au(111)-KPF₆ capacitance data for the DMSO, ACN, and DG solvents. The quantitative agreement between the theoretical model and experimental data is very good, underscoring the robustness of the approach. The model explains the trend that as the bulk dielectric constant decreases, the slope of the PZ plot also decreases. This occurs because lower dielectric constants result in weaker screening of electrostatic interactions compared to water, which increases the interaction between ions and their electronic image charges. It is interesting that the model values of the Au(111)-KPF₆ charge-separation distance are very similar for water, DMSO, and ACN solvents. Therefore, the different PZ slopes of the respective capacitance curves can be directly related to the differences in dielectric permittivity of the solvents. Remarkably, while nearly linear PZ plots with a slightly positive curvature are predicted (and observed) for water [Fig. 8(c)] and DMSO [Fig. 9(a)] solvents with relatively large permittivities, the theory predicts a nonlinear PZ plot with a negative curvature for the case of DG solvent with a very low dielectric permittivity, in good agreement with the available experimental data [Fig. 9(c)]. These findings highlight the need for dedicated experiments, in particular, accurate capacitance measurements in dilute, nonaqueous electrolytes. Nonlinear PZ plots with a negative curvature in low- ϵ solvents are suggested as an experimentally accessible “smoking gun” of interfacial electron-ion correlations.

IV. DISCUSSION

Traditional GCS theory predicts a unity slope in Parsons-Zobel (PZ) capacitance plots. Experimental capacitance data usually presents smaller-than-one PZ slopes, meaning that the measured differential capacitance is higher than GCS predictions even in the limits of dilute electrolyte concentrations and weak surface charges (i.e., around the PZC) where MF-GCS theory is considered to be accurate. Such deviations have often been attributed to surface roughness, i.e., the difference between the geometric surface area (the area used for the normalization of the surface-charge density) and the (generally unknown) real surface area of the electrode [58–60]. However, similar discrepancies were observed for single-crystal electrode surfaces, where relevant surface roughness can be excluded [5,58]. As summarized in Table I, the extent of the deviations strongly depends on the electrode material, with a close-to-unity PZ slope for the case of mercury [63] to the extreme case of Pt(111) with a slope close to zero, corresponding to a strongly enhanced double-layer capacitance [3]. Coinciding with the centenary of GCS theory, the latter recent findings have triggered a vivid debate on the current understanding of the EDL properties in the GCS limit [8]. Several different explanations for the very low PZ slopes of Pt(111) have been proposed, involving the residual adsorption of OH[−] [7] or electrolyte (an)ions [5] on the electrode surface, or an additional weak surface-ion attractive potential [6], the origin of which however remained ambiguous. Image-charge interactions were discussed as one possible origin [6], since the experimental observations indicated that this attractive potential was acting on both anion and cation species, while being insensitive to their detailed chemical nature (e.g., Na⁺ or Li⁺). Image charges have been shown to contribute significantly to the anomalously large capacitance observed at the metal-ionic liquid interface [43,71]. At the same time, however, it was questioned whether image-charge effects would be sufficiently strong to explain the results for dilute electrolyte solutions. Two central questions were emphasized in a recent article [8]: First, why is the attractive interaction similar for all investigated electrolytes? Second, why is this interaction apparently stronger on Pt(111) than on other single-crystal metal surfaces or mercury?

The present theory offers a compelling answer to these questions, indeed demonstrating that image-charge (electron-ion) correlations provide a very likely explanation for the puzzling recent results on Pt(111). Moreover, it was shown that the latter represent a limiting case in the context of the general long-standing question in electrochemistry for the origin of nonunity PZ slopes. Quantified by the *interface correlation factor*, Eq. (89), electron-ion correlations were found to play an important role in shaping the electric double layer at the PZC by effectively

attracting ions toward the electrode surface. This mechanism enhances the differential capacitance in a way that is mathematically akin to the impact of surface roughness, but entirely different in physical nature.

Because the electron-ion correlations considered here are electrostatic in nature, the proposed mechanism is agnostic to the chemical nature of the electrolyte ions, meaning that the effective interaction is unspecific to the ion species. The interaction strength is primarily controlled by the charge-separation distance a between the ionic and electronic (image) charges, as well as the (bulk) dielectric constant of the electrolyte solvent. In aqueous electrolytes, the trend in PZ slopes across different metals was found to correlate with the hydrophilicity of the metal surfaces, reflected by the respective variations in the value of the charge-separation distance parameter within this theory, cf. Table I. The more hydrophobic metals, such as mercury, correspond to a larger effective separation of the electronic and ionic charge distributions, and vice versa for the more hydrophilic cases. Besides the results for aqueous systems, we consider it a remarkable success of our theory to also explain trends in PZ slopes for various nonaqueous electrolytes based on the dielectric permittivity of the respective solvents, cf. Fig. 9. These results strongly support the theory of electron-ion correlations as explanation for the experimental trends in PZ slopes across a variety of electrode-electrolyte systems.

The case of the aqueous Pt(111) system deserves further discussion. To fit the respective experimental data, a nearly zero value of the charge-separation distance parameter (a) was required. This cannot be purely explained by Pt(111) being rather hydrophilic, allowing for a closer approach of electrolyte ions to the metal surface. In fact, recent DFT simulations showed that the electronic charge distribution

of the Pt(111) surface penetrates to a significant depth into the interfacial water region [68]. While this certainly contributes to pushing the effective image plane closer to the electrolyte charge distribution, the effect would likely not be sufficient to explain the essentially zero value of a in the present theory. Instead, in the following we argue that the limit of $a \rightarrow 0$ corresponds to the transition from traditional EDL charging to (unspecific) ion adsorption. The theory thereby overcomes the conceptual distinction between double-layer and pseudocapacitive charging phenomena [72].

Figure 10(a) shows the traditional distinction between double-layer charging and ionic discharge during adsorption (pseudocapacitive charging), which correspond to different mechanisms of interfacial charge storage and transfer as described within the ideal polarizable and ideal nonpolarizable electrode models, respectively [73]. Double-layer charging, shown in the top part of Fig. 10(a), arises from the electrostatic accumulation of charge at the electrode-electrolyte interface. This process is commonly referred to as nonfaradaic, meaning that no electron transfer or electrochemical reaction occurs. The respective charging process is fundamentally described by GCS-based theories. On the other hand, pseudocapacitive charging due to ion adsorption, shown in the bottom part of Fig. 10(a), involves faradaic charge transfer across the electrode-electrolyte interface due to partial or complete discharge of the adsorbing ions. Such a charge-storage mechanism is characterized by a large apparent (pseudo)capacitance as compared to pure double-layer charging.

Within a mean-field description, such as GCS theory, double-layer and pseudocapacitive charging must be treated as two separate mechanisms. At the mean-field

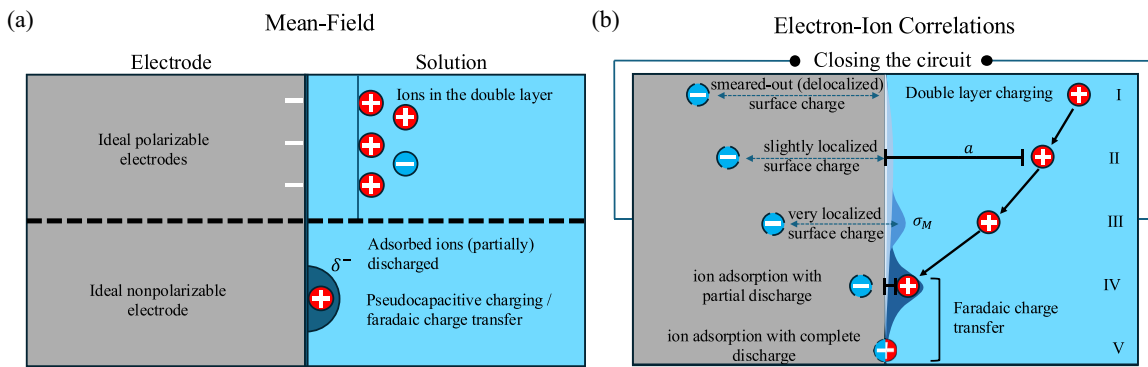


FIG. 10. (a) Comparison of the distinct models of an ideal polarizable electrode with double-layer charging (top) and an ideal nonpolarizable electrode with pseudocapacitive charging due to ion adsorption and discharge, i.e., faradaic charge transfer (bottom). (b) Unified model from double-layer charging to ion adsorption. A representative cation is shown as it approaches the metal surface. As the charge-separation distance a gets smaller from (I) to (V), the electronic image charge (dashed circles) gets closer to the surface and the corresponding physical surface charge gets more and more localized and contracted to the place of the approaching ion. In the limiting case (V) of $a \rightarrow 0$, the electronic (image) and ionic charge centers coincide and exactly cancel each other, corresponding to complete ionic discharge (integer charge transfer).

level, an ion in the electrolyte solution, regardless of its distance from the electrode surface, only interacts with the fully delocalized (in-plane averaged) electronic surface-charge density, which is a consequence of the neglect of coulombic correlations. As a consequence, the MF-GCS capacitance, Eq. (56), is bounded from above by the GC contribution (C_{GC}) that is independent of the charge-separation distance a . Letting $a \rightarrow 0$ only affects the Helmholtz contribution (C_H) that is acting in series to C_{GC} . Accordingly, pseudocapacitance must be incorporated into a MF model in a heuristic way either by adding an additional attractive potential for electrolyte ions to the electrode surface [6,8], or by explicitly introducing a species of adsorbed ions that form localized dipole moments at the electrode surface [5,7,72].

In our theory, pseudocapacitive charging and ion adsorption phenomena are naturally described at the beyond-MF level in the form of local electron-ion (image-charge) correlations. As such, the processes of double-layer charging and (unspecific) ion adsorption are conceptually unified, representing limiting cases of the same interfacial charging phenomenon. A continuous transition between these limits is provided by tuning the effective charge-separation distance a . In particular, the local electron-ion interactions captured by the interface correlation factor lead to a divergence of the overall interfacial capacitance [Eq. (88)] in the limit of $a \rightarrow 0$. This directly corresponds to the massive pseudocapacitive enhancement in the faradaic limit of complete ionic discharge. Fleischmann *et al.* [74] recently proposed a similar conceptual unification from double-layer charging in confined electrolyte pores to faradaic charge storage via ion intercalation in layered materials. Our findings show that interfacial electron-ion correlations are the conceptual link to extend this unified picture to (faradaic) charge transfer in ion adsorption at extended interfaces.

This conceptual unification is schematically visualized in Fig. 10(b), tracking a representative cation as it approaches the metal surface. In case (I), the charge-separation distance a is large. Consequently, the image charge is distant from the interface and the corresponding physical metallic surface charge is smeared out (very light blue distribution). In this limit, which is representative for the ideal polarizable electrode, the theory effectively becomes equivalent to a MF description, where the electronic charge density is constant over the surface and the EDL behaves as described by classical GCS theory. Moving to cases (II) and (III), the ionic charges and image charges approach each other at closer distances. The surface-charge density becomes more localized the closer the ions get to the metal (light blue and blue distributions). In this limit the local interaction and correlation with the image charge becomes important.

In case (IV), where a approaches the atomic scale, the electronic surface charge gets contracted to the position

of the approaching ion, forming a local surface dipole as in the EDL model by Skinner *et al.* [17]. The bound pair of ion and image electron can be viewed as a case of ion adsorption with partial discharge. This again highlights that the model parameter a must be understood as an effective separation distance between the electronic and ionic charges, and *not* as a minimum distance between ions and metal surface atoms as in GCS theory. Therefore, a can assume values of subatomic scale and, in the case of complete ionic discharge, turn to zero, corresponding to coinciding centers of charge of the local electronic and ionic charge densities. This limit of $a \rightarrow 0$ is shown as case (V) in Fig. 10(b) and represents ion adsorption with complete charge neutralization and integer charge transfer. The present theory thus provides a continuous transition from double-layer charging to ion adsorption and conceptually unifies both types of processes. Interfacial electron-ion correlations are thus shown to be the link for “closing the circuit” from EDL charging to ion adsorption. This unified interpretation highlights the continuity between these charging mechanisms rather than treating them as separate phenomena. The present theory is specifically developed to describe the effects of electron-ion correlations in the weak charging limit around the PZC and in dilute electrolyte solutions (GCS limit). Under such conditions, the effective surface coverages of adsorbed ions [cases (IV) and (V) in Fig. 10(b)] are small, and coverage effects due to finite ion sizes, as heuristically included in another recent model [19], can be neglected.

Of course, the limit of $a \rightarrow 0$ must be taken with a grain of salt in a classical theory like the one presented here that describes ions and image electrons as point charges. At (sub)atomic scales, the spatial distribution of the electronic image charge would require a quantum-mechanical treatment to capture its orbital structure. An accurate description of (ion-specific) chemisorption therefore goes beyond the scope of the present theory. Ion-adsorption processes described herein are independent of the chemical nature of the ion species, because they are solely driven by classical electrostatic interactions between ions and their electronic image charges. This unspecific character is in agreement with experimental results for Pt(111), where PZ slopes were found to be largely insensitive to the ion species in the electrolyte [6]. The present insights thus reconcile some of the previously proposed explanations for the drastically decreased PZ slopes on Pt(111) in terms of either a weak attractive ion-surface interaction or an effect of residual ion adsorption, both of which are identified as manifestations of interfacial electron-ion correlations.

V. CONCLUSION

In summary, a systematic extension of GCS theory for the EDL at metal-electrolyte interfaces was developed incorporating electron-ion correlations beyond the MF

level. Our theory treats the solvent with a primitive model as a (homogeneous) dielectric continuum in the electrolyte region. The theory is applicable in the weak charging limit and for dilute electrolyte solutions. By going beyond the mean-field approximation, our approach captures correlation effects, in particular ion-ion and ion-image-charge (ion-electron) correlations. At the mean-field level, i.e., within the classical Gouy-Chapman-Stern theory, the image charges are effectively averaged out in lateral (in-plane) directions, resulting in a uniform surface-charge distribution. As a consequence, the local nature of the interactions between individual ions and their image charges is lost. In contrast, our higher-order theory explicitly accounts for such local correlations and quantitatively describes the respective effects on the interfacial capacitance and EDL structure. This framework provides compelling explanations for long-standing discrepancies between experimental capacitance data and GCS predictions, thereby overcoming previous conceptual boundaries in the classification of interfacial charging phenomena. The key developments and findings include the following:

- (1) Correlations shape the EDL: In agreement with previous findings [15,16,41], the present theory highlights two competing correlation effects that govern the ion accumulation near the electrode surface at the PZC: attractive electron-ion (i.e., image-charge) and repulsive dielectric boundary interactions.
- (2) Image-charge effects explain anomalous slopes in Parsons-Zobel (PZ) plots: Decreased slopes in PZ plots result from ion-image-charge attraction, viz., electron-ion correlations. While, even for single-crystal electrodes, surface roughness was often postulated to explain discrepancies between experimental PZ slopes and GCS theory, the present findings show that this can be explained purely on the basis of electrostatic phenomena.
- (3) To explain the extremely low PZ slopes observed for Pt(111), a subatomic value of the effective charge-separation distance a is required within the present theory, representing the case of ion adsorption. In the limit of vanishing $a \rightarrow 0$, the electronic (image) charge completely neutralizes the ionic charge. Interfacial electron-ion correlations are thus connecting previous explanatory schemes of weak additional ion-surface interactions and ion adsorption.
- (4) The theory explains why hydrophobic metals such as mercury yield a near-unity PZ slope, corresponding to weak electron-ion correlations, while more hydrophilic metals exhibit decreased PZ slopes, representing stronger correlation effects. The PZ slope is thus identified as a fingerprint of interfacial electron-ion correlations.
- (5) Nonaqueous electrolytes with a lower solvent permittivity than water enhance coulombic interactions and correlation effects, resulting in nonlinear PZ plots. These findings suggest that additional measurements in nonaqueous electrolytes are required to gain further insights into electrostatic electron-ion correlations at electrochemical interfaces.
- (6) The theory conceptually unifies the mechanisms of double-layer charging and ion adsorption, commonly treated as different phenomena at the MF level. A continuous transition from double-layer charging to ion adsorption is provided by tuning the charge-separation distance a to zero, demonstrating that both processes can be regarded as the two sides of the same coin.

Future extensions of the theory are required for treating more concentrated solutions and analyzing the effect of electron-ion correlations on the charging characteristics across a wider potential range. Also, it will be highly interesting to account for dipolar correlations and solvent structure, as described in a recent model by Hedley *et al.* [9], in order to achieve a comprehensive treatment of interfacial electrostatic correlations and their effect on the charging characteristics and PZ plots.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available because they are owned by a third party and the terms of use prevent public distribution. The data are available from the authors upon reasonable request.

LIST OF SYMBOLS

C_{GCS} :	GCS capacitance
C_{GC} :	Gouy-Chapman capacitance
C_H :	Helmholtz capacitance
$\epsilon(r)$:	Dielectric permittivity
ϵ_I :	Inner layer permittivity
a :	Charge-separation distance
ϵ_B :	Bulk permittivity
U :	Coulombic potential energy

V :	Coulombic interaction	C^{MF} :	MF solution of the capacitance
ρ :	Charge density	J_0 :	Zeroth-order Bessel function of first kind
q_i :	Charge of ion type i	$V(z)$:	Renormalized self-energy
λ_i :	Ion fugacity of ion type i	V_{DH} :	Debye-Hückel self-energy
Z_{gc} :	Grand canonical partition function	V_{int} :	Interface correlation energy
ψ :	Hubbard-Stratonovic field	ϕ^{1L} :	Electrostatic potential in one-loop approximation
ψ_a :	Antisymmetric component of the HS field	$\langle n_i(r) \rangle^{\text{1L}}$:	Ion density in one-loop approximation
ψ_s :	Symmetric component of the HS field	γ_i :	Activity coefficient
S :	Action		
Λ_i :	Thermal wavelength of ion type i	σ_M^{1L} :	Surface-charge density in one-loop approximation
β :	Boltzmann constant	C_{1L} :	Differential capacitance in one-loop approximation
ϕ :	Electrostatic potential	R_{1L} :	Interface correlation factor in one-loop approximation
σ_M :	Surface-charge density	ϕ^{2L} :	Electrostatic potential in two-loop approximation
n_i :	Ion density	C_{2L} :	Differential capacitance in two-loop approximation
C_d :	Differential capacitance	R_{2L} :	Interface correlation factor in two-loop approximation
Ω :	Grand potential	ϕ^{clover} :	Electrostatic potential in clover approximation
$\mathcal{E}$:	Electrode potential	C_{clover} :	Differential capacitance in clover approximation
Q_M :	Total metallic charge	R_{clover} :	Interface correlation factor in clover approximation
$\mathcal{F}$:	Free energy		
μ_i :	Chemical potential of ion type i		
$\mu_{\pm}$:	Sum or difference between ion chemical potentials		
$\delta\psi$:	Fluctuations of the antisymmetric HS field		
Γ^n :	Bare vertex of order n		
μ_g :	Gauge chemical potential		
S_{int} :	Interacting part of the action		
S_I^n :	Renormalized vertex of order n		
G :	Correlation function		
ℓ :	Auxillary expansion parameter		
ϕ^{MF} :	MF solution of the electrostatic potential		
$\langle n_i(r) \rangle^{\text{MF}}$:	MF solution of the ion density		
λ_D :	Debye length		
n_i^b :	Ion bulk concentration		
σ_M^{MF} :	MF solution of the surface-charge density		

APPENDIX A: INTERMEDIATE STEPS OF THE DERIVATIONS IN THE THEORY SECTION

1. Derivation of the action in Eq. (14)

Inserting the standard Hubbard-Stratonovich (HS) transformation [37,38] into the grand canonical partition function, Eq. (5), yields

$$\mathcal{Z}_{\text{gc}}(\lambda_i) = \sum_{N_i=0}^{\infty} \lambda_i^{N_i} \prod_{i=a/c} \frac{1}{N_i! (\Lambda_i^3)^{N_i}} \prod_{j=1}^{N_i} \int d^3 r_{ij} \Theta(z_{ij} - a) \int D\psi \exp \left(-\beta \int_{r,r'} \psi(r) V^{-1}(r, r') \psi(r') - i\beta \int_r \psi(r) \rho(r) \right). \quad (\text{A1})$$

Substituting the charge density, Eq. (4), which accounts for both ions and their image charges, into Eq. (A1) and integrating over the delta functions gives

$$\begin{aligned} \mathcal{Z}_{\text{gc}}(\lambda_i) = & \sum_{N_i=0}^{\infty} \lambda_i^{N_i} \int D\psi \exp \left(-\beta \int_{r,r'} \psi(r) V^{-1}(r, r') \psi(r') \right) \\ & \times \prod_{i=a/c} \frac{1}{N_i! (\Lambda_i^3)^{N_i}} \prod_{j=1}^{N_i} \int d^3 r_{ij} \Theta(z_{ij} - a) \exp \left(-i\beta \sum_{i,j} q_i \left(\psi(r_{ij}) - \psi(r_{ij}^{\text{im}}) \right) \right). \end{aligned} \quad (\text{A2})$$

Since the integrand is independent of the particle index j , the product over all particles reduces to the N_i -fold of a single-particle contribution,

$$\mathcal{Z}_{\text{gc}}(\lambda_i) = \int D\psi \exp \left(-\beta \int_{r,r'} \psi(r) V^{-1}(r, r') \psi(r') \right) \prod_{i=a/c} \sum_{N_i=0}^{\infty} \frac{1}{N_i!} \left(\lambda_i \Lambda_i^{-3} \int_r \Theta(z-a) \exp(-i\beta q_i (\psi(r) - \psi(r^{\text{im}}))) \right)^{N_i}. \quad (\text{A3})$$

Applying the exponential series identity and using the definition of the inverse Coulomb operator,

$$V^{-1}(r, r') = -\nabla \left(\epsilon(r) \nabla \delta(r - r') \right), \quad (\text{A4})$$

along with partial integration, one arrives at Eq. (14).

2. Computing partial derivatives leading to Eqs. (26) and (27)

For calculating the partial derivatives of $\Omega(\mu_a, \mu_c)$ in Eq. (25) with respect to μ_+ and μ_- , the thermodynamic definition of the chemical potentials $\mu_i = \partial \mathcal{F} / \partial N_i$ is needed along with the inverse transformations $\mu_a = \mu_+ - \mu_-$ and $\mu_c = \mu_+ + \mu_-$, which follow immediately from Eqs. (23) and (24). Then the partial derivative of $\Omega(\mu_a, \mu_c)$ with respect to μ_- is given by

$$\begin{aligned} \frac{\partial \Omega(\mu_+, \mu_-)}{\partial \mu_-} &= \frac{\partial \mathcal{F}}{\partial N_a} \frac{\partial N_a}{\partial \mu_-} + \frac{\partial \mathcal{F}}{\partial N_c} \frac{\partial N_c}{\partial \mu_-} - \mu_+ \frac{\partial N_{\text{tot}}}{\partial \mu_-} - N_{\text{diff}} - \mu_- \frac{\partial N_{\text{diff}}}{\partial \mu_-} \\ &= \mu_a \frac{\partial N_a}{\partial \mu_-} + \mu_c \frac{\partial N_c}{\partial \mu_-} - \mu_+ \frac{\partial (N_c + N_a)}{\partial \mu_-} - N_{\text{diff}} - \mu_- \frac{\partial (N_c - N_a)}{\partial \mu_-} \\ &= \frac{\partial N_a}{\partial \mu_-} (\mu_a - (\mu_+ - \mu_-)) + \frac{\partial N_c}{\partial \mu_-} (\mu_c - (\mu_+ + \mu_-)) - N_{\text{diff}} \\ &= -N_{\text{diff}}, \end{aligned} \quad (\text{A5})$$

where in the second line the definitions of μ_i , N_{tot} , and N_{diff} were inserted. In the third line the inverse transformations were inserted into μ_+ and μ_- .

3. Dimensional analysis of Eq. (14)

It is well established in the functional integral literature (see, for instance, the pedagogical introduction in Ref. [75, Sec. 2.6, p. 31]) that general integrals of the form

$$I[\Xi] = \int_{-\infty}^{\infty} dx e^{-S[x]/\Xi}, \quad (\text{A6})$$

where $S[x]$ is some functional of variable x and $\Xi > 0$ is some parameter, are dominated by the maxima of the integrand, and consequently by the minima of $S(x)$, in the limit $\Xi \rightarrow 0$. Accordingly, the perturbative expansion with Ξ as the small parameter can be employed to evaluate such integrals perturbatively [50,75].

In our formulation Eq. (11), there is no apparent small parameter like Ξ . However, analogous to the scaling argument in Ref. [76], a small parameter can be found starting from the functional integral, Eq. (11) and a subsequent de-dimensionalization. In the main text, we refrain from such a construction to keep physical units. However, here it seems instructive to pursue this direction to derive the small parameter of our theory.

With action $S[\psi]$, given in Eq. (14). The HS field is rescaled as

$$\psi_a(r) = \frac{1}{\beta q} \tilde{\psi}_a(\tilde{r}), \quad r = \lambda_D \tilde{r},$$

where $\tilde{\psi}_a$ is a dimensionless fluctuation field. The spatial rescaling by the Debye length λ_D renders the integration measure dimensionless, $dr^3 = \lambda_D^3 d\tilde{r}^3$, and turns gradients into $\nabla_r = \lambda_D^{-1} \tilde{\nabla}$. Inserting these transformations into Eq. (14) leads to

$$\mathcal{Z}_{\text{gc}} = \int D\tilde{\psi}_a \exp \left(-\tilde{S}[\tilde{\psi}_a]/\Xi \right) \quad (\text{A7})$$

with the dimensionless action $\tilde{S}[\tilde{\psi}_a]$. Now the integral has the canonical form required by the perturbative expansion. All physical parameters now appear only in the global dimensionless prefactor

$$\Xi = \frac{\lambda_B}{\lambda_D}.$$

The Bjerrum length

$$\lambda_B = \frac{\beta q^2}{4\pi\epsilon_B}, \quad (\text{A8})$$

is defined as the distance at which two charges interact with energy β^{-1} , whereas the Debye length quantifies the

screening length of an electrolyte solution and is given for a univalent electrolyte by

$$\lambda_D = \sqrt{\frac{1}{8\pi\lambda_B n_{\text{ion}}^b}}, \quad (\text{A9})$$

where n_{ion}^b is the bulk concentration.

Following the same loop expansion employed within this paper, in Sec. II B, but now in terms of the nondimensional HS field $\tilde{\psi}_a$, the action is expanded around its saddle point $\tilde{\psi}_c$, which is conveniently expressed as

$$\tilde{\psi}_a(\tilde{r}) = \tilde{\psi}_c(\tilde{r}) + \Xi^{1/2} \delta\tilde{\psi}(\tilde{r}). \quad (\text{A10})$$

Writing Eq. (A10) represents a change of variables within the functional integral Eq. (A7) that does not change its result. However, choosing the change of variables with $\Xi^{1/2}$ in front of $\delta\tilde{\psi}$ is convenient as it renders the average with respect to $\tilde{G}$, shown in Eq. (A12), independent of Ξ . The benefit of this choice is highlighted below.

Performing a perturbative expansion, for example, for the dimensionless electrostatic potential $\tilde{\phi} = (\beta q)\phi$, yields

$$\begin{aligned} \tilde{\phi}(r) &= i\tilde{\phi}_c(\tilde{r}) + i\Xi^{1/2} \\ &\times \left\langle \delta\tilde{\psi}(\tilde{r}) \exp\left(-\Xi^{1/2} S_I^{(3)}[\delta\tilde{\psi}(\tilde{r})] + \mathcal{O}(\Xi^2)\right) \right\rangle_{\tilde{G}}, \end{aligned} \quad (\text{A11})$$

where the average with respect to $\tilde{G}$ is with respect to the Gaussian action

$$\langle \dots \rangle_{\tilde{G}} = \frac{1}{\mathcal{Z}_G} \int D\delta\tilde{\psi}(\dots) e^{-\frac{1}{2} \int_{\tilde{r},\tilde{r}'} \delta\tilde{\psi}(\tilde{r}) \tilde{G}^{-1}(\tilde{r},\tilde{r}') \delta\tilde{\psi}(\tilde{r}')}. \quad (\text{A12})$$

The key point to emphasize here is that, unlike Eq. (15), Eq. (A12) is completely independent of any physical parameters. Consequently, in functional averages such as Eq. (A11), the dependence on physical parameters, such as ion concentration, does not appear in the Gaussian probability distribution $\tilde{G}$ or in the renormalized vertices $S_I^{(n)}$. Instead, it enters solely through the prefactors Ξ . This is a direct consequence of Eq. (A10).

Expanding Eq. (A11) in Ξ yields expressions that are always ordered in powers of Ξ . Keeping only clover-type diagrams yields the clover approximation, presented in Sec. II E,

$$\tilde{\phi}^{\text{clover}}(\tilde{r}) = \tilde{\phi}^{\text{MF}}(\tilde{r}) - i \sum_{n=1}^{\infty} \Xi^n \left\langle \delta\tilde{\psi}(\tilde{r}) S_I^{(2n+1)} \right\rangle_{\tilde{G}}. \quad (\text{A13})$$

This shows that $\tilde{\phi}^{\text{clover}}$ is systematically expanded in powers of Ξ , and therefore, effectively in powers of λ_D^{-1} .

Hence, we identify Ξ^{-1} , or equivalently, the inverse Debye length, as the coupling parameter of our theory. Note that if we had chosen not to write our dimensionless fluctuation field according to Eq. (A10), some of the Ξ dependence would have been hidden in the Gaussian average $\left\langle \delta\tilde{\psi}(\tilde{r}) S_I^{(2n+1)} \right\rangle_{\tilde{G}}$, and the expansion would not be apparent in powers of Ξ , yet. In the end, when performing all averages, the result, of course, is again the same and independent of the choice in Eq. (A10).

In summary, within the loop expansion developed in Sec. II B, the accuracy improves as Ξ becomes small. Put differently, Ξ serves as the small parameter of the perturbative expansion. This corresponds to the regime $\lambda_D \gg \lambda_B$, i.e., weak electrostatic coupling characterized by low valency and low ionic strength.

4. Computing the MF electrostatic potential in Eq. (49)

Utilizing the ansatz $\phi^{\text{MF}}(r) = \phi_0 + \Delta\phi^{\text{MF}}(r)$, in the electrolyte region, $z > a$, the differential equation, Eq. (37), simplifies to

$$-\epsilon_B \nabla^2 \Delta\phi^{\text{MF}}(r) + 2qn_{\text{ion}}^b \sinh(\beta q_i \Delta\phi^{\text{MF}}(r)) = 0, \quad (\text{A14})$$

which is the well-known Poisson-Boltzmann equation that is solved by Ref. [53]

$$\begin{aligned} \phi^{\text{MF}}(r) &= \phi_0 + \frac{4}{\beta q} \operatorname{arctanh} \left(\tanh \left(\frac{\beta q (\phi^{\text{MF}}(a) - \phi_0)}{4} \right) \right. \\ &\quad \left. \times e^{-\lambda_D^{-1}(z-a)} \right), \end{aligned} \quad (\text{A15})$$

with the Debye length

$$\lambda_D = \sqrt{\frac{\epsilon_B}{2\beta q^2 n_{\text{ion}}^b}}. \quad (\text{A16})$$

Within the charge-separation distance ($0 < z < a$), Eq. (37) is solved by the ansatz $\phi^{\text{MF}}(r) = Az + B$, where $B = 0$ due to the asymmetry of ϕ^{MF} (due to the asymmetry boundary condition of ψ_a at $z = 0$), and A is fixed by the boundary conditions at $z = a$,

$$\epsilon_B \frac{\partial \phi^{\text{MF}}}{\partial z} \Big|_{z=a^+} - \epsilon_I \frac{\partial \phi^{\text{MF}}}{\partial z} \Big|_{z=a^-} = 0, \quad (\text{A17})$$

which leads to

$$A = \frac{\epsilon_B}{\epsilon_I} \frac{\partial \phi^{\text{MF}}}{\partial z} \Big|_{z=a^+}. \quad (\text{A18})$$

The continuity requirement at $z = a$ leads to a self-consistent equation for the value of ϕ^{MF} at $z = a$,

$$\begin{aligned} \phi^{\text{MF}}(a) &= \frac{\epsilon_B}{\epsilon_I} \frac{\partial \phi^{\text{MF}}}{\partial z} \Big|_{z=a} \\ &= \frac{2\epsilon_B}{\epsilon_I} \frac{a}{q\beta\lambda_D} \sinh\left(\frac{q\beta}{2} (\phi_0 - \phi^{\text{MF}}(a))\right), \quad (\text{A19}) \end{aligned}$$

which can not be solved analytically. For weakly charged surfaces, ϕ^{MF} varies only slightly between the bulk and

the interface. As a result, the argument of the sinh function ($\phi^{\text{MF}}(a) - \phi_0$), remains small. In this limit the sinh function can be linearized and Eq. (A19) is solved by $\phi^{\text{MF}}(a) = (\epsilon_B a / (\epsilon_B a + \epsilon_I \lambda_D)) \phi_0$. Substituting this result into Eq. (A15) yields the electrostatic potential on a MF level near PZC, shown in Eq. (49).

5. Deriving the correlation function in Eq. (57)

The second-order variational derivative is given by

$$\begin{aligned} \frac{\delta S}{\delta \psi(r) \delta \psi(r')} &= \frac{\delta}{\delta \psi(r)} \left(-\nabla \epsilon(r') \nabla \psi_a(r') + i \sum_{i=a/c} q_i \lambda_i \Lambda_i^{-3} \Theta(z' - a) e^{-i\beta q_i \psi_a(r')} \right) \\ &= -\nabla \epsilon(r') \nabla \delta(r, r') + \beta \sum_{i=a/c} q_i^2 \lambda_i \Lambda_i^{-3} \Theta(z' - a) e^{-i\beta q_i \psi_a(r')} \delta(r, r'). \quad (\text{A20}) \end{aligned}$$

The inverse correlation function [Eq. (40)] is obtained by replacing ψ_a in Eq. (A20) with the saddle-point field ψ_c , which is related to the electrostatic potential on a MF level via $\phi^{\text{MF}} = i\psi_c$ as shown in Eq. (49). Substituting Eq. (49) into Eq. (A20) then yields

$$G^{-1}(r, r') = -\nabla \epsilon(r') \nabla \delta(r, r') + 2\beta z^2 e_0^2 n_{\text{ion}}^b \cosh\left(4\text{arctanh}\left(\tanh\left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4}\right) e^{-\lambda_D^{-1}|z'-a|}\right)\right) \Theta(z' - a) \delta(r, r'). \quad (\text{A21})$$

Using the definition, Eq. (41), the correlation function satisfies the differential equation

$$-\nabla \epsilon(r') \nabla G(r, r') + 2\beta z^2 e_0^2 n_{\text{ion}}^{\text{bulk}} \cosh\left(4\text{arctanh}\left(\tanh\left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4}\right) e^{-\lambda_D^{-1}|z'-a|}\right)\right) G(r, r') = \delta(r - r'). \quad (\text{A22})$$

This work focuses on the region close to the PZC, which is characterized by $\mathcal{E} \ll 1$. For $\mathcal{E} \ll 1$ the nonlinearity in the equation above can be linearized, leading to Eq. (57).

6. Derivation of Eq. (58) with in-plane Fourier transformation of the correlation function

We follow the same procedure as Lau [34] or Netz [56] who provided the basis for the following calculations. Through the translational symmetry in xy direction, Fourier transforming the differential equation for the correlation function [Eq. (57)] yields

$$\begin{aligned} G(r, r') &= \frac{1}{\sqrt{2\pi}^2} \int d^2 k g(k, z, z') e^{ik_x(x-x')} e^{ik_y(y-y')} \\ &= \frac{1}{2\pi} \int d^2 k g(k, z, z') e^{ik \cdot \rho}, \quad (\text{A23}) \end{aligned}$$

which can be simplified by utilizing polar coordinates,

$$G(r, r') = \int_0^\infty dk k g(k, z, z') J_0(k \rho), \quad (\text{A24})$$

where J_0 is the zeroth Bessel function of first kind. Similarly, the Fourier transform of the delta function is

$$\delta(r - r') = \frac{1}{2\pi} \int dk \delta(z - z') k J_0(k \rho). \quad (\text{A25})$$

Lastly, rewriting the gradients in Eq. (57) in polar coordinates, yields an equation for g ,

$$(-\partial_z^2 + k^2 + \lambda_D^{-2}) g(k, z, z') = l_B \delta(z - z') \quad \text{for } |z| > a, \quad (\text{A26})$$

$$(-\partial_z^2 + k^2) g(k, z, z') = l_I \delta(z - z') \quad \text{for } |z| < a, \quad (\text{A27})$$

where

$$l_B = \frac{1}{2\pi \epsilon_B}, \quad l_I = \frac{1}{2\pi \epsilon_I}. \quad (\text{A28})$$

For a fixed $z' > a$, there are three regions to be distinguished,

$$(-\partial_z^2 + k^2 + \lambda_D^{-2}) h_{\pm}(k, z) = 0 \quad \text{for } z > a, \quad (\text{A29})$$

$$(-\partial_z^2 + k^2) g_{\pm}(k, z) = 0 \quad \text{for } -a < z < a, \quad (\text{A30})$$

$$g_{\pm}(k, z) = \exp(\pm kz). \quad (\text{A33})$$

$$(-\partial_z^2 + k^2 + \lambda_D^{-2}) h_{\pm}(k, z) = 0 \quad \text{for } z < -a, \quad (\text{A31})$$

with solutions

$$h_{\pm}(k, z) = \exp\left(\pm\sqrt{k^2 + \lambda_D^{-2}}z\right) \equiv \exp(\pm\gamma(k)z), \quad (\text{A32})$$

The boundary conditions are continuity in g across the three regions and discontinuity in the partial derivative of g with respect to z due to the delta functions at $z = z'$ and $z = -z'$, cf. Ref. [39]. This leads to a linear system of ten equations for ten unknown amplitude functions of z . For the purposes of this work, only the region $z > a$ is of interest, where the function g takes the form:

$$g(k, z, z') = \frac{l_B}{2\gamma(k)} \left(e^{-\gamma(k)|z'-z|} + e^{-\gamma(k)(z+z'-2a)} \left(1 - \frac{2k}{k + (\epsilon_B/\epsilon_I)\gamma(k) \tanh(ka)} \right) \right) \quad \forall z, z' > a. \quad (\text{A34})$$

Inserting Eq. (A34) into Eq. (A24) yields Eq. (58).

7. Computing the 1L electrostatic potential ϕ^{1L}

In this section the derivation of the first-order correction to the electrostatic potential is discussed in detail.

a. Computation of $S_I^{(3)}$

For the sake of clarity, the first nonvanishing part of the expanded action [Eq. (36)] is repeated here,

$$S_I^{(3)}[\psi_c] = \int_{r,r'} \frac{\delta S_{\text{int}}[\psi, \{\lambda_i^0 \omega\}]}{\delta \psi(r)} \Big|_{\psi=\psi_c} \delta \psi(r) + \frac{1}{3!} \int_{r,r',r''} \Gamma^{(3)}(\{\lambda_i^0\}, r, r', r'') \delta \psi(r) \delta \psi(r') \delta \psi(r''). \quad (\text{A35})$$

Clearly, computing Eq. (A35) requires computing the first and third functional derivative of the action Eq. (14). The first variational derivative of the action is given by

$$\frac{\delta S_{\text{int}}[\psi, \{\lambda_i^0 \omega\}]}{\delta \psi(r)} \Big|_{\psi=\psi_c} = i \sum_{i=a/c} q_i \lambda_i \omega \Lambda_i^{-3} \Theta(z-a) e^{-i\beta q_i \psi_c(r)}, \quad (\text{A36})$$

and insertion of the saddle point $\psi_c = i^{-1} \phi^{\text{MF}}$ [Eq. (49)] simplifies the expression to

$$\frac{\delta S_{\text{int}}[\psi, \{\lambda_i^0 \omega\}]}{\delta \psi(r)} \Big|_{\psi=\psi_c} = -\frac{i\epsilon_B \omega}{\beta q \lambda_D^2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \Theta(z-a). \quad (\text{A37})$$

In a similar fashion, the third variational derivative yields

$$\frac{\delta^3 S}{\delta \psi(r) \delta \psi(r') \delta \psi(r'')} = -i\beta^2 \sum_{i=a/c} q_i^3 \lambda_i \Lambda_i^{-3} \Theta(z'-a) e^{-i\beta q_i \psi_a(r)} \delta(r', r'') \delta(r, r'), \quad (\text{A38})$$

and evaluating at the saddle point gives

$$\sum_{i=a/c} q_i^3 \lambda_i \Lambda_i^{-3} e^{-i\beta q_i \psi_c(r)} = 2q_i^3 n_{\text{ion}}^b \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right), \quad (\text{A39})$$

which yields the bare vertex of order 3,

$$\Gamma^{(3)}(\{\lambda_i^0\}, r, r', r'') = i\beta q \epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \Theta(z' - a) \delta(r', r'') \delta(r, r'). \quad (\text{A40})$$

Inserting Eq. (A40) into the second part on the rhs of Eq. (A35) and integrating over r'' and r''' leads to

$$\int_{r, r', r''} \Gamma^{(3)}(\{\lambda_i^0\}, r, r', r'') \delta\psi(r) \delta\psi(r') \delta\psi(r'') = i\beta q \epsilon_0 \lambda_D^{-2} \int_{r>a} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\beta q \mathcal{E}}{4} \right) e^{-|z|/\lambda_D} \right) \right) \delta\psi(r)^3. \quad (\text{A41})$$

In summary, inserting Eq. (A41) and Eq. (A37) into Eq. (A35) one arrives at the expression for the renormalized vertex of order 3,

$$S_I^{(3)}[\psi_c] = - \int_{r>a} i\epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \left(\frac{\omega}{\beta q} \delta\psi(r) - \frac{1}{3!} \beta q \delta\psi(r)^3 \right). \quad (\text{A42})$$

b. Computation of the Gaussian averages

Inserting Eq. (A42) into Eq. (65) shows that obtaining ϕ^{1L} requires computing the average

$$\begin{aligned} \langle \delta\psi(r) S_I^{(3)} \rangle_G &= - \int_{r'>a} i\epsilon_0 \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) \\ &\quad \left(\frac{\omega}{\beta q} \langle \delta\psi(r) \delta\psi(r') \rangle_G - \frac{1}{3!} \beta q \langle \delta\psi(r) \delta\psi(r')^3 \rangle_G \right). \end{aligned} \quad (\text{A43})$$

The average $\langle \delta\psi(r) \delta\psi(r') \rangle_G$ is defined by Eq. (41). Since the averages are with respect to a Gaussian (quadratic) action, higher-order moments than two can be computed using Wicks theorem [77],

$$\langle \delta\psi(r) \delta\psi(r')^3 \rangle_G = 3 \beta^{-1} G(r, r') 1 \beta^{-1} G(r', r'). \quad (\text{A44})$$

The “3” on the rhs is due to the fact that there are three possible combinations to pair $\delta\psi(r)$ with $\delta\psi(r')$. Once $\delta\psi(r)$ is paired to $\delta\psi(r')$, there is only “1” possibility to pair two $\delta\psi(r')$. Inserting Eq. (A44) into Eq. (A43) yields

$$\begin{aligned} \langle \delta\psi(r) S_I^{(3)} \rangle_G &= \int_{r'>a} \frac{1}{\beta^2 q} \left(i\epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) \right) \\ &\quad \times G(r, r') \left(\frac{\beta q^2}{2} G(r', r') - \omega \right), \end{aligned} \quad (\text{A45})$$

which when inserted into Eq. (65) leads to Eq. (66).

8. Diagrammatic representation of Gaussian averages

At higher orders in perturbation theory, additional terms appear in the expansion of any observable quantity of interest, e.g., the electrostatic potential. To systematically identify the relevant corrections, it is helpful to represent them diagrammatically, following conventions from quantum field theory [77]. This section outlines the diagrammatic approach adopted in this work and introduces the basic rules for simplifying such expansions. It is generally distinguished between two types of diagrams: those

involving simple polynomials [e.g., $\delta\psi(r_i)^m$] and those built from renormalized vertices (e.g., $S_I^{(3)}$). Renormalized in this context means that the bare vertices yield unphysical infinite corrections, for instance, to the electrostatic potential. Through the choice of a gauge chemical potential in Eq. (34), the vertex is renormalized to a finite result.

a. Diagrammatic rules

First, the individual components of the diagrams are introduced. A polynomial $\delta\psi(r_i)^m$ is represented by dot

(•) (with label r_i) connected to m lines called external legs. The correlation function $G(r_i, r_j)$ acts as a propagator between the dots at (r_i) and (r_j) , depicted as a line connecting (r_i) and (r_j) .

Second, the Gaussian average of diagrams is defined. Wick's theorem states that a Gaussian expectation value is given by the sum of all possible pairings [77]

$$\begin{aligned} & \langle \delta\psi(r_1) \delta\psi(r_2) \cdots \delta\psi(r_{2n}) \rangle_G \\ &= \sum_{\text{pairings of } r_1, \dots, r_{2n}} \langle \delta\psi(r_{k_1}) \delta\psi(r_{k_2}) \rangle_G \\ & \quad \cdots \langle \delta\psi(r_{k_{2n-1}}) \delta\psi(r_{k_{2n}}) \rangle_G. \end{aligned} \quad (\text{A46})$$

A pairing is nothing but a propagator, i.e., $\langle \delta\psi(r_n) \delta\psi(r_m) \rangle_G = \beta^{-1} G(r_n, r_m)$ [cf. Eq. (41)], and is therefore symbolized by a line connecting the dot at r_n with a dot at r_m . Figure 11 diagrammatically represents the Gaussian average in Eq. (A44). The dot r has one leg for $\delta\psi(r)$, while the dot at r' has three for $\delta\psi(r')^3$. The only possible pairing configuration is shown on the right-hand side, where $\delta\psi(r)$ pairs with one leg at r' (three options), and the remaining two legs at r' pair uniquely. This graphical representation corresponds to the mathematical expression on the rhs of Eq. (A44).

Using the diagrammatic rules, one can readily compute, for instance, the Gaussian average involving a bare vertex

$$\begin{aligned} & \langle \delta\psi(r) \Gamma^{(3)}[\{\lambda_i\}] \rangle_G \\ &= \int_{r' > a} i\epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) \left(\frac{1}{3!} \beta q \langle \delta\psi(r) \delta\psi(r')^3 \rangle_G \right) \\ &= \int_{r' > a} \frac{1}{\beta^2 q} \left(i\epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) G(r, r') \left(\frac{\beta q^2}{2} G(r', r') \right). \end{aligned} \quad (\text{A47})$$

b. Diagrams of a renormalized vertex

The diagrammatics as presented above help calculating Gaussian averages involving polynomials $\delta\psi(r)^m$ explicitly. However, as shown in the calculation of $\langle \delta\psi(r) S_I^{(3)} \rangle_G$ in Eq. (A43) a computation of a renormalized vertex requires several Gaussian averages such as $\langle \delta\psi(r) \delta\psi(r') \rangle$ and $\langle \delta\psi(r) \delta\psi(r')^3 \rangle$, which makes computation of higher-order renormalized vertices cumbersome. However, it was shown in Eq. (A47) that the result of computing a bare [Eq. (A47)] or renormalized vertex Eq. (A45), in the end, just differs by a shift of the equal-point correlation function by ω . In other words, mathematically a Gaussian average involving a renormalized vertex can be treated as a Gaussian average of a bare vertex but with replacing all equal-point correlation functions by

$$\frac{\beta q^2}{2} G(r', r') \rightarrow \frac{\beta q^2}{2} G(r', r') - \omega. \quad (\text{A48})$$

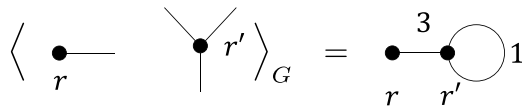


FIG. 11. Graphical representation of the Gaussian average $\langle \delta\psi(r) \delta\psi^3(r') \rangle_G = 3\beta^{-1} G(r, r') 1\beta^{-1} G(r', r')$.

With this knowledge, we choose a diagrammatic representation of a renormalized vertex. We diagrammatically represent $S_I^{(n)}$ by an empty dot with n external legs, see for instance $S_I^{(n)}$ in Fig. (12). To translate back to an integral expression, the result of the Wick contraction in terms of Green's functions is multiplied by the vertex function and then integration is performed over the internal spatial coordinates. The final vertex determines the spatial variable of the overall expression. For instance, for Fig. 12, the integral expression is shown in Eq. (A45).

9. Details of second-order perturbation theory

To evaluate the accuracy of the 1L approximation, it is useful to examine the next order in the perturbation series. This serves two purposes. First, it shows when the perturbation theory begins to break down (typically

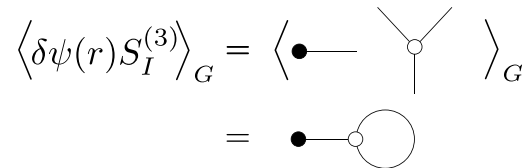


FIG. 12. Graphical representation of the Gaussian average in Eq. (65) and the result Eq. (A43).

when second-order contributions become larger than the first-order term). Second, if the second-order term consists of several parts, we can identify which contribution is dominant.

a. Computing ϕ^{2L}

To compute the electrostatic potential to second order in perturbation theory, one must expand the exponential in Eq. (38) up to second order,

$$\begin{aligned}\phi^{2L}(r) &= i\psi_c(r) + i\ell^{-1/2}\langle\delta\psi(r)\rangle \\ &\approx i\psi_c(r) + i\ell^{-1/2}\left\langle\delta\psi(r)e^{-\beta\ell^{-1/2}S_I^{(3)}-\beta\ell^{-1}S_I^{(4)}-\beta\ell^{-3/2}S_I^{(5)}-\beta\ell^{-2}S_I^{(6)}}\right\rangle_G \\ &= \phi^{1L}(r) + i\ell^{-3/2}\left(-\beta\left\langle\delta\psi(r)S_I^{(4)}\right\rangle_G + \frac{\beta^2}{2}\left\langle\delta\psi S_I^{(3)}S_I^{(3)}\right\rangle_G\right) \\ &\quad + \ell^{-2}\left(-\beta\left\langle\delta\psi(r)S_I^{(5)}\right\rangle_G + \beta^2\left\langle\delta\psi S_I^{(3)}S_I^{(4)}\right\rangle_G + \frac{\beta^3}{3!}\left\langle\delta\psi(r)\left(S_I^{(3)}\right)^3\right\rangle_G\right) + \mathcal{O}(\ell^{-5/2}),\end{aligned}\quad (\text{A49})$$

with

$$S_I^{(3)} = \Gamma^{(3)}[\{\lambda_i^0\}] + \int_r \frac{\delta S_{\text{int}}[\psi, \lambda_i^0 \omega]}{\delta \psi(r)} \Big|_{\psi=\psi_c} \delta \psi(r), \quad (\text{A50})$$

$$S_I^{(4)} = \Gamma^{(4)}[\{\lambda_i^0\}] + \frac{1}{2} \int_{r,r'} \delta \psi(r) \frac{\delta^2 S_{\text{int}}[\psi, \{\lambda_i^0 \omega\}]}{\delta \psi(r) \delta \psi(r')} \Big|_{\psi=\psi_c} \delta \psi(r'), \quad (\text{A51})$$

$$S_I^{(5)} = \Gamma^{(5)}[\{\lambda_i^0\}] + \Gamma^{(3)}[\{\lambda_i^0 \omega\}] + \int_r \delta \psi(r) \frac{\delta S_{\text{int}}[\psi, \lambda_i^0 \omega^2/2]}{\delta \psi(r)} \Big|_{\psi=\psi_c}. \quad (\text{A52})$$

All Gaussian averages with an odd number of $\delta\psi$ fields vanish, e.g., $\left\langle\delta\psi(r)S_I^{(4)}\right\rangle_G = 0$, which yields Eq. (83).

b. Computing the capacitance C^{2L}

To compute the capacitance, one needs an explicit expression for the electrostatic potential [Eq. (A50)] first. Starting from Eq. (A38), subsequent functional differentiations with respect to $\delta\psi$ yield higher-order vertex functions, cf. Eqs. (32) and (33). For the second-order expansion of the electrostatic potential one needs $\Gamma^{(3)}$, $\Gamma^{(4)}$ and $\Gamma^{(5)}$, which are given by

$$\Gamma^{(3)}[\{\lambda_i^0\}] = \int_{r>a} (+1)(\beta q) \left(i\epsilon_B \lambda_D^{-2} \sinh \left(4 \text{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \right) \delta \psi(r)^3, \quad (\text{A53})$$

$$\Gamma^{(4)}[\{\lambda_i^0\}] = \int_{r>a} (-i)(\beta q)^2 \left(i\epsilon_B \lambda_D^{-2} \cosh \left(4 \text{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \right) \delta \psi(r)^4, \quad (\text{A54})$$

$$\Gamma^{(5)}[\{\lambda_i^0\}] = \int_{r>a} (-1)(\beta q)^3 \left(i\epsilon_B \lambda_D^{-2} \sinh \left(4 \text{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \right) \delta \psi(r)^5. \quad (\text{A55})$$

Inserting the bare vertices [Eqs. (A53), (A54) and (A55)] into the expressions for the renormalized vertices [Eqs. (A50), (A51) and (A52)] yields

$$S_I^{(3)} = +\beta q \int_{r>a} i\epsilon_B \lambda_D^{-2} \sinh \left(4 \text{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \left(\frac{1}{3!} \delta \psi(r)^3 - \frac{\omega}{\beta^2 q^2} \delta \psi(r) \right), \quad (\text{A56})$$

$$S_I^{(4)} = +\beta^2 q^2 \int_{r>a} \epsilon_B \lambda_D^{-2} \cosh \left(4 \text{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \left(\frac{1}{4!} \delta \psi(r)^4 - \frac{1}{2} \frac{\omega}{\beta^2 q^2} \delta \psi(r)^2 \right), \quad (\text{A57})$$

$$S_I^{(5)} = (-1)\beta^3 q^3 \int_{r>a} \left(i\epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z-a|} \right) \right) \right) \\ \times \left(\frac{1}{5!} \delta\psi(r)^5 - \frac{\omega}{3!} \frac{1}{\beta^2 q^2} \delta\psi(r)^3 + \frac{1}{\beta^4 q^4} \frac{\omega^2}{2} \delta\psi(r) \right). \quad (\text{A58})$$

Inserting the explicit expressions for the renormalized vertices above into the expression for the 2L electrostatic potential [Eq. (A49)] and applying Wick's theorem (Appendix A 8), for instance

$$\langle \delta\psi(r) \delta\psi(r_1)^3 \rangle_G = 3\beta^{-1} G(r, r_1) \beta^{-1} G(r_1, r_1), \quad (\text{A59})$$

$$\langle \delta\psi(r) \delta\psi(r_1)^5 \rangle_G = 5 \cdot 3\beta^{-1} G(r, r_1) \beta^{-2} G(r_1, r_1)^2, \quad (\text{A60})$$

yields two different terms that contribute to ϕ^{2L} apart from the 1L contribution [already computed in Eq. (A45)]:

$$\langle \delta\psi(r) S_I^{(5)} \rangle_G = \int_{r'>a} (-1) \frac{1}{\beta^2 q} \left(i\epsilon_B \lambda_D^{-2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) \right) \\ \times G(r, r') \frac{1}{2} \left(\frac{\beta q^2}{2} G(r', r') - \omega \right)^2, \quad (\text{A61})$$

$$\langle \delta\psi(r) S_I^{(3)} S_I^{(4)} \rangle_G = (-i)\beta^3 q^3 \epsilon_B^2 \lambda_D^{-4} \int_{r'>a} \int_{r''>a} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) \\ \times \cosh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z''-a|} \right) \right) \left(\frac{1}{6} \beta^{-4} G(r, r'') G(r'', r')^3 \right. \\ \left. + G(r, r') G(r', r'')^2 \frac{1}{2\beta^5 q^2} \left(\frac{\beta q^2}{2} G(r'', r'') - \omega \right) \right. \\ \left. + \frac{1}{\beta^6 q^4} G(r, r'') G(r', r'') \left(\frac{\beta q_i^2}{2} G(r', r') - \omega \right) \left(\frac{\beta q_i^2}{2} G(r'', r'') - \omega \right) \right). \quad (\text{A62})$$

At this point vacuum diagrams have been discarded as they do not contribute to Gaussian averages. The term with $\langle \delta\psi(r) (S_I^{(3)})^3 \rangle_G$ from Eq. (A49) is omitted because it does not contribute to the differential capacitance. This is due to the fact that $(S_I^{(3)})^3$ is proportional to $\sinh^3(\dots \mathcal{E})$, which vanishes when taking the derivative with respect to the electrode potential $\mathcal{E}$ at $\mathcal{E} = 0$, as required for computing the capacitance. Inserting Eqs. (A61) and Eq. (A62) into Eq. (A49) and using the gauge chemical potential in Eq. (71) yields the electrostatic potential in 2L approximation. Further linearizing the cosh and sinh functions yields the electrostatic potential in 2L approximation around PZC,

$$\phi^{2L}(r) = \phi^{\text{MF}}(r) + \Delta\phi^{1\text{-clover}}(r) + \Delta\phi^{2\text{-clover}}(r) + \Delta\phi^{2\text{-rest}}(r), \quad (\text{A63})$$

with

$$\phi^{\text{MF}}(r) = i\psi_c(r), \quad (\text{A64})$$

$$\Delta\phi^{1\text{-clover}}(r) = \frac{\epsilon_B}{\lambda_D^2} \frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \mathcal{E} \int_{r'>a} e^{-\lambda_D^{-1}|z'-a|} G(r, r') (\beta V_{\text{int}}(r')), \quad (\text{A65})$$

$$\Delta\phi^{2\text{-clover}}(r) = -\frac{\epsilon_B}{\lambda_D^2} \frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \mathcal{E} \int_{r'>a} e^{-\lambda_D^{-1}|z'-a|} G(r, r') \frac{1}{2} (\beta V_{\text{int}}(r'))^2, \quad (\text{A66})$$

$$\Delta\phi^{2\text{-rest}}(r) = \frac{\epsilon_B^2}{\lambda_D^4} \frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \mathcal{E} \int_{r'>a} \int_{r''>a} e^{-\lambda_D^{-1}|z'-a|} \left(\frac{1}{6} \beta^2 q^4 G(r, r'') G(r', r'')^3 \right. \\ \left. + \frac{\beta q^2}{2} G(r, r') G(r', r'')^2 (\beta V_{\text{int}}(r'')) + G(r, r'') G(r'', r') (\beta V_{\text{int}}(r')) (\beta V_{\text{int}}(r'')) \right). \quad (\text{A67})$$

Applying the same reasoning as in the 1L calculation, the metallic surface charge is evaluated using Eq. (19), together with

$$\left. \frac{\partial}{\partial z} \left(e^{-|z-z'|/\lambda_D} - e^{-(z+z')/\lambda_D} \right) \right|_{z=0} = 2 \frac{e^{-z'/\lambda_D}}{\lambda_D}, \quad (\text{A68})$$

and subsequently the differential capacitance using Eq. (20) yields

$$C_{2L} = R_{2L} \times C_{\text{GCS}}. \quad (\text{A69})$$

The interface correlation factor on a 2L level,

$$R_{2L} = 1 + \Delta R_{1\text{-clover}} + \Delta R_{2\text{-clover}} + \Delta R_{2\text{-rest}}, \quad (\text{A70})$$

consist of three different contributions $\Delta R_{1\text{-clover}}$, $\Delta R_{2\text{-clover}}$ and $\Delta R_{2\text{-rest}}$, which are given by

$$R_{1\text{-clover}} = -\frac{\beta}{\lambda_D} \int_a^\infty dz e^{-2z/\lambda_D} V_{\text{int}}(z), \quad (\text{A71})$$

$$R_{2\text{-clover}} = \frac{1}{2} \frac{\beta^2}{\lambda_D^2} \int_a^\infty dz e^{-2z/\lambda_D} V_{\text{int}}(z)^2, \quad (\text{A72})$$

$$\begin{aligned} R_{2\text{-rest}} = & -\frac{1}{2} \frac{\beta^2}{\lambda_D^2} \int_a^\infty dz' \int_a^\infty dz'' \left(\frac{2}{3} \frac{q^4 \pi \epsilon_B}{\lambda_D} e^{-(z'+z'')/\lambda_D} \int_0^\infty d\rho' \rho' G(\rho', z', z'')^3 + 2 \frac{q^2 \pi \epsilon_B}{\lambda_D} e^{-2z'/\lambda_D} \right. \\ & \times \left. \int_0^\infty d\rho'' \rho'' G(\rho'', z', z'')^2 V_{\text{int}}(z'') + e^{(-z'+z'')/\lambda_D} \left(e^{-|z'-z''|/\lambda_D} - e^{-(z'+z'')/\lambda_D} \right) V_{\text{int}}(z') V_{\text{int}}(z'') \right). \end{aligned} \quad (\text{A73})$$

10. Computing the electrostatic potential in Clover approximation given in Eq. (87)

It is possible to compute all averages in Eq. (86) as they follow a repetitive pattern. The first term to compute ($n = 3$) is given by the 1L results that has been computed in Eq. (A45),

$$\left\langle \delta\psi(r) S_I^{(3)} \right\rangle_G = \int_{r'>a} (+1) \frac{i\epsilon_B}{\beta^2 q \lambda_D^2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) G(r, r') (\beta V_{\text{int}}(z')). \quad (\text{A74})$$

Similarly, from the 2L computations [Eq. (A61)] it is known that

$$\left\langle \delta\psi(r) S_I^{(5)} \right\rangle_G = \int_{r'>a} (-1) \frac{i\epsilon_B}{\beta^2 q \lambda_D^2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) G(r, r') \frac{1}{2} (\beta V_{\text{int}}(z'))^2. \quad (\text{A75})$$

From this one deduces that n th order of the clover expansion is given by

$$\left\langle \delta\psi(r) S_I^{(2n+1)} \right\rangle_G = - \int_{r'>a} \frac{i\epsilon_B}{\beta^2 q \lambda_D^2} \sinh \left(4 \operatorname{arctanh} \left(\tanh \left(\frac{\lambda_D}{(\epsilon_B/\epsilon_I)a + \lambda_D} \frac{\beta q \mathcal{E}}{4} \right) e^{-\lambda_D^{-1}|z'-a|} \right) \right) G(r, r') \frac{(-1)^n}{n!} (\beta V_{\text{int}}(z'))^n. \quad (\text{A76})$$

Upon inserting Eqs. (A76) into Eq. (86) and using

$$\sum_{n=1}^{\infty} \frac{(-x)^n}{n!} = e^{-x} - 1 \quad (\text{A77})$$

one arrives at Eq. (87).

TABLE II. Various combinations of parameter values that achieve qualitatively similar model curves as those shown in Figs. 8 and 9.

	a for $\epsilon_I = 20$	a for $\epsilon_I = 40$	a for $\epsilon_I = 60$	a for $\epsilon_I = 80$
Aqueous electrolytes/hydrophobic-to-hydrophilic interfaces from top to bottom				
Mercury-NaF [63]	1.8 Å	4 Å	6 Å	8 Å
Ag(111)-KPF ₆ [64]	0.3 Å	0.6 Å	1 Å	1.7 Å
Au(111)-KPF ₆ [65]	0.1 Å	0.21 Å	0.36 Å	0.7 Å
Pt(111)-HClO ₄ [3]	0.035 Å	0.07 Å	0.13 Å	0.27 Å
	a for $\epsilon_I = 0.25\epsilon_B$	a for $\epsilon_I = \epsilon_B$	ϵ_B	
Organic electrolytes				
Au(111)-KPF ₆ DMSO [66]	0.2 Å	1.3 Å	46.7	
Au(111)-KPF ₆ ACN [66]	0.25 Å	1.5 Å	37.4	
Au(111)-KPF ₆ DG [66]	1.4 Å	6 Å	7.23	

APPENDIX B: ALTERNATIVE MODEL PARAMETERS FOR THE COMPARISON TO EXPERIMENTAL DATA

The model parameters ϵ_I and a are not independent when determined by comparison to experimental data. Several combinations of the respective parameter values exists that give similar results for the capacitance curves. In addition to the parameter values shown in Table I, which were used for the plots in Figs. 8 and 9, the parameter values shown in Table II yield qualitatively similar results. The parameters presented in Table I correspond to the first column in Table II. When the value of ϵ_I is increased, the required value for a also increases. For instance, for the mercury electrode, the choice of $\epsilon_I = 20$ requires a value of $a = 1.8$ Å, while $\epsilon_I = 80$ leads to $a = 8$ Å. This can be explained by the fact that the desolvation effect is stronger at lower ϵ_I , which requires a lower value for a to enhance the attractive effect of electron-ion correlations. Interestingly, an approximately linear relationship between the values of ϵ_I and a is observed, which means that the ratio of ϵ_I/a is the key parameter in controlling the model fitting to the experimental data.

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