

A Gaussian field approach to the planar electric double layer structures in electrolyte solutions

Cite as: J. Chem. Phys. 158, 174104 (2023); doi: 10.1063/5.0138568

Submitted: 13 December 2022 • Accepted: 17 April 2023 •

Published Online: 1 May 2023



View Online



Export Citation



CrossMark

Tiejun Xiao¹  and Xueyu Song^{2,a)} 

AFFILIATIONS

¹ Guizhou Provincial Key Laboratory of Computational Nano-Material Science, Guizhou Synergetic Innovation Center of Scientific Big Data for Advanced Manufacturing Technology, Guizhou Education University, Guiyang 550018, People's Republic of China

² Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011, USA

^{a)} Author to whom correspondence should be addressed: xsong@iastate.edu

ABSTRACT

In this work, the planar, electric, double-layer structures of non-polarizable electrodes in electrolyte solutions are studied with Gaussian field theory. A response function with two Yukawa functions is used to capture the electrostatic response of the electrolyte solution, from which the modified response function in the planar symmetry is derived analytically. The modified response function is further used to evaluate the induced charge density and the electrostatic potential near an electrode. The Gaussian field theory, combined with a two-Yukawa response function, can reproduce the oscillatory decay behavior of the electric potentials in concentrated electrolyte solutions. When the exact sum rules for the bulk electrolyte solutions and the electric double layers are used as constraints to determine the parameters of the response function, the Gaussian field theory could at least partly capture the nonlinear response effect of the surface charge density. Comparison with results for a planar electrode with fixed surface charge densities from molecular simulations demonstrates the validity of Gaussian field theory.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0138568>

I. INTRODUCTION

Electric double layer (EDL) is crucial to understand the screening effect of free ions to the charged surfaces, which has wide applications in understanding the instability of colloidal suspension,^{1–3} the capacitance of electrodes with various geometry,^{4–7} the ionic transport in nano channels,^{8–10} the charging behavior of super capacitors,^{11–13} and even the electrochemical reactions near solid–liquid interfaces.^{14–16}

The mean field theories provide very useful insight into the EDL structures in electrolyte solutions. The most widely used mean field theory for the EDLs is the Gouy–Chapman (GC) theory, where the ionic radial distribution function is treated with the Poisson–Boltzmann (PB) approach.^{2,17} When the surface charge density is low, one can further use the linearized Poisson–Boltzmann (LPB) theory or equivalently the Debye–Hückel (DH) theory to treat the EDLs.^{18–20} Both the GC theory and the DH theory use the inverse Debye length k_D to capture the electrostatic response of free ions. As a consequence, these two theories imply that the electric potential, as well as induced charge density near an electrode, is a simple exponential decay function in space, and, hence, cannot predict the

oscillatory decay charge density profile around an electrode in concentrated electrolyte solutions. To capture the correlations beyond the mean field theory in concentrated electrolyte solutions, such as the nonlocal response of polar solvent, the nonlocal response of salt species, and the interplay between polar species and the salt species, a nonlocal dielectric function can be used in the study of EDLs.^{21–24} Or equivalently, multiple screening lengths are introduced to understand the EDLs in systems with strong electrostatic coupling, as suggested in the dressed ion theory,^{25–27} the modified PB theory^{28–30} and the molecular DH theory,^{31–33} such that the electric potential near an electrode consists of several exponential decay functions. The nonlinear effect for electrodes with high polarization is also of special interest,^{34–36} which are relevant for the understanding of super-capacitors and electrochemical kinetics.

In this study, a Gaussian field theory is used to understand the planar EDL of electrodes in electrolyte solutions. In particular, the Gaussian field theory was first developed by Chandler and co-workers for fluids with short-range interactions³⁷ and was later extended to solvation dynamics in polar fluids.^{38,39} As the Gaussian field theory uses the perspective of solvent and solute to deal with the solvent's linear response to the solute, the nonlinear response

effect due to the surface charge density of an electrode needs to be incorporated in the overall response. To this end, exact sum rules for electrolyte solutions and EDLs, such as the charge neutrality condition, the Stillinger–Lovett (SL) second moment condition and the contact theorems, are used as constraints to determine some parameters in a two-Yukawa (TY) response function. When the two-Yukawa response function obtained from the sum rule constraints is used for concentrated electrolyte solutions, the oscillatory decay behavior of the electric potential near the electrode can be reproduced from the Gaussian field theory quantitatively when comparisons with Monte Carlo (MC) simulations are made. Furthermore, the differential capacitance as a function of surface charge also agrees with simulation results qualitatively. It should be noted that the current approach represents a general strategy to go beyond the mean field theory systematically by incorporating multiple screening lengths of the electrolyte solution, and the non-linear response is captured by the exact sum rules.

This paper is organized as following. In Sec. II, the planar electric double layer is presented with the Gaussian field theory, combined with a two-Yukawa response function, where the sum rules are used to determine the parameters of the two-Yukawa response function. In Sec. III, applications to an electrode in an electrolyte solution, where simulation results are known, are presented to demonstrate the utility of our current approach. A brief summary of our findings is given in Sec. IV.

II. A GAUSSIAN FIELD APPROACH TO THE PLANAR ELECTRIC DOUBLE LAYER IN RESTRICTED, PRIMITIVE-MODEL ELECTROLYTE SOLUTIONS

A. Model of a planar, non-polarizable electrode in a RPM electrolyte solution

A schematic plot of a planar, non-polarizable electrode in a restrictive primitive model (RPM) electrolyte solution is shown in Fig. 1, where the solution is constrained in the right half plane $z > 0$, and the electrode with a surface charge density σ is located at $z = -b$. The RPM electrolyte solution is used to simplify the presentation, but the developed theory can be used for any ionic fluid with a known dielectric function, and extension to models of polarizable electrodes is also straightforward.

Both the ions and the electrode are located in a dielectric background with a dielectric constant ϵ_s . An ion of the RPM electrolyte is characterized by a charged hard sphere. The cations and anions

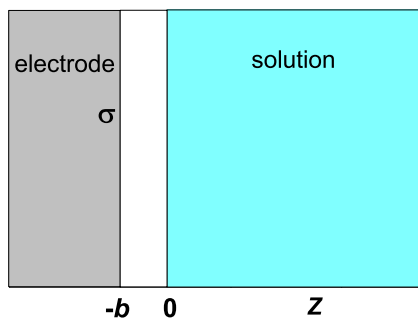


FIG. 1. A schematic plot of a non-polarizable electrode in an electrolyte solution.

have the same diameter d but opposite charge numbers. q_i denotes the charge of cation and anion species ($i = 1, 2$), n_s the total particle number density, and $\beta = 1/(k_B T)$ the reduced inverse temperature.

The inverse Debye length reads $k_D = \sqrt{\frac{4\pi\beta q_s^2 n_s}{\epsilon_s}}$, with $q_s = |q_{1,2}|$. Due to the hard sphere interaction, there is a space near the electrode that the ions cannot penetrate. As one can see, $b = d/2$ is the length scale of this excluded space.

The external field produced by the surface charge density σ at $z = -b$ is

$$\psi(\mathbf{r}) = \psi(z) = -\frac{4\pi}{\epsilon_s} \sigma (z + b). \quad (1)$$

When the surface charge density is nonzero, the free ions will form an induced charge density around the electrode. Considering the excluded volume effect of the electrode, the induced charge density can be determined from the linear response theory.^{39,40}

$$\rho^{ind}(\mathbf{r}) = \int \chi^{(m)}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}', \quad (2)$$

where $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ is the modified response function of the bulk solution in the presence of the electrode. In general, $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ is determined by the bulk response function $\chi(|\mathbf{r} - \mathbf{r}'|)$ and the boundary condition around the solute. When the hard sphere interactions between the electrode and the ions are turned off, the modified response function $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ reduces to the bulk response function $\chi(|\mathbf{r} - \mathbf{r}'|)$. More details about the modified response function and the Gaussian field theory are discussed in Appendix A.

Due to the planar symmetry of the system, it would be convenient to introduce the Bessel–Fourier component $F(z, z'; Q)$ for a function $F(\mathbf{r}, \mathbf{r}')$ ⁴¹

$$\begin{aligned} F(\mathbf{r}, \mathbf{r}') &= \frac{1}{2\pi} \int_0^\infty dQ Q J_0(Q\rho) F(z, z'; Q), \\ F(z, z'; Q) &= 2\pi \int_0^\infty d\rho \rho J_0(Q\rho) F(\mathbf{r}, \mathbf{r}'), \end{aligned} \quad (3)$$

where $\rho = \sqrt{|\mathbf{r} - \mathbf{r}'|^2 - (z - z')^2}$, $\mathbf{r} = (x, y, z)$ is the coordinate, Q is the Fourier component conjugated to (x, y) , and $J_0(\rho)$ is the zeroth Bessel function.

Using Eq. (3), the Bessel–Fourier component of $\psi(\mathbf{r})$ reads

$$\psi(z; Q) = -\frac{8\pi^2 \sigma (z + b) \delta(Q)}{\epsilon_s Q}, \quad (4)$$

with $\delta(Q)$ the Dirac delta function.

In the planar symmetry, the induced charge density depends only on variable z such that $\rho^{ind}(\mathbf{r}) = \rho^{ind}(z)$. Using the Bessel–Fourier component $\chi^{(m)}(z, z'; Q)$ of $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$, the induced charge density in planar symmetry can be rewritten as

$$\begin{aligned} \rho^{ind}(z) &= \frac{1}{2\pi} \int_0^\infty dQ Q \int_0^\infty dz' \chi^{(m)}(z, z'; Q) \psi(z'; Q), \\ &= -\frac{4\pi\sigma}{\epsilon_s} \int_0^\infty dQ \delta(Q) \int_0^\infty dz' \chi^{(m)}(z, z'; Q) (z' + b), \\ &= -\frac{4\pi\sigma}{\epsilon_s} f(z; 0), \end{aligned} \quad (5)$$

where

$$f(z; Q) \equiv \int_0^\infty dz' \chi^{(m)}(z, z'; Q)(z' + b).$$

The electric potential $\phi(z)$ in the solution region is related to $\rho^{ind}(z)$ via the Poisson equation

$$\frac{d^2\phi(z)}{dz^2} = -\frac{4\pi}{\epsilon_s} \rho^{ind}(z), \quad z > 0. \quad (6)$$

Note that there is no induced charge in the region $-b < z < 0$, and the Poisson equation reduces to

$$\frac{d^2\phi(z)}{dz^2} = 0, \quad -b < z < 0. \quad (7)$$

As long as the induced charge density $\rho^{ind}(z)$ is known, Eqs. (6) and (7) can be used to determine the electric potential $\phi(z)$.

Denote $\chi(k) = \int \chi(r) e^{-ik \cdot r} d\mathbf{r}$ as the three-dimensional Fourier transform of $\chi(r)$. The DH theory uses only one length scale $1/k_D$ treated at the mean field level and leads to a response function $\chi(k)_{DH} = -\frac{\epsilon_s}{4\pi} \frac{k^2 k_D^2}{k^2 + k_D^2} = -\frac{k_D^2 \epsilon_s}{4\pi} \left(1 - \frac{k_D^2}{k^2 + k_D^2}\right)$. Based on this response function, the Gaussian field theory leads to $\phi(z > 0)_{DH} = \frac{4\pi}{\epsilon_s} \frac{\sigma}{k_D} e^{-k_D z}$, which is exactly the same as that obtained from the LPB theory—³² hence the equivalency between this formulation and the conventional mean field approach (LPB or linearized Gouy–Chapman) for this model. The DH theory always predicts an exponentially decaying electric potential and is not able to capture the correlated response of concentrated electrolytes. Without breaking the presentation of our main result, details of these results are summarized in [Appendixes B and C](#).

B. Planar EDL from a two-Yukawa response function

Motivated by our work on the molecular Debye–Hückel theory,³¹ which used multiple Debye screening lengths to capture the correlated response, a two-Yukawa (TY) response function for concentrated electrolyte solutions

$$\chi(k)_{TY} = -\frac{\kappa^2 \epsilon_s}{4\pi} \left(1 - \frac{C_1 k_1^2}{k^2 + k_1^2} - \frac{C_2 k_2^2}{k^2 + k_2^2}\right) \quad (8)$$

is used as a starting point to study the EDL problem in the presence of correlated responses of an electrolyte solution. In r -space, the response function containing two Yukawa functions reads

$$\begin{aligned} \chi(\mathbf{r} - \mathbf{r}')_{TY} &= -\frac{\kappa^2 \epsilon_s}{4\pi} \left[\delta^{(3)}(\mathbf{r} - \mathbf{r}') - \frac{C_1 k_1^2}{4\pi} \frac{e^{-k_1 |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} - \frac{C_2 k_2^2}{4\pi} \frac{e^{-k_2 |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \right]. \quad (9) \end{aligned}$$

As one can see, there are two length scale parameters, $1/k_1$ and $1/k_2$, in this response function, which are obtained from the roots of the dielectric function of the electrolyte solution;³¹ hence, our formulation is not restricted to a particular type of electrolyte model. The Bessel–Fourier component of $\chi(\mathbf{r} - \mathbf{r}')$ is⁴¹

$$\begin{aligned} \chi(z - z'; Q)_{TY} &= -\frac{\kappa^2 \epsilon_s}{4\pi} \left[\delta(z - z') - \frac{C_1 k_1^2}{2\Gamma_1} e^{-\Gamma_1 |z - z'|} - \frac{C_2 k_2^2}{2\Gamma_2} e^{-\Gamma_2 |z - z'|} \right], \quad (10) \end{aligned}$$

with $\Gamma_1 = \sqrt{Q^2 + k_1^2}$ and $\Gamma_2 = \sqrt{Q^2 + k_2^2}$.

The solution of $\chi_{in}^{-1}(z, z'; Q)_{TY}$ and the modified response function $\chi^{(m)}(z, z'; Q)_{TY}$ can be evaluated analytically, as shown in [Appendix D](#). The final result for the modified response function reads

$$\begin{aligned} \chi^{(m)}(z, z'; Q)_{TY} &= -\frac{\kappa^2 \epsilon_s}{4\pi} \left[\delta(z - z') - \frac{C_1 k_1^2}{2\Gamma_1} e^{-\Gamma_1 |z - z'|} \right. \\ &\quad \left. - \frac{C_2 k_2^2}{2\Gamma_2} e^{-\Gamma_2 |z - z'|} - \sum_{i,j=1,2} \alpha_{ij} e^{-\Gamma_i z - \Gamma_j z'} \right], \quad (11) \end{aligned}$$

with the coefficient α_{ij} defined in [Appendix D](#).

The analytical form of $\chi^{(m)}(z, z'; Q)$ is now used to determine the function $f(z; 0)$ defined in Eq. (5) and the induced charge density $\rho^{ind}(z)$. It should be emphasized that only the $Q = 0$ component of the response function is used here, as the surface charge is uniform; otherwise, other Q -components will be needed (hence, the screening lengths will be modified) for inhomogeneous surface charges.

After some calculations (details in [Appendix D](#)), it is found that $f(z; 0)$ is independent of the parameter b , the excluded region between the solution and the electrode (see [Fig. 1](#)):

$$f(z; 0) = \frac{\epsilon_s \kappa^2}{4\pi} (\delta_1 e^{-k_1 z} + \delta_2 e^{-k_2 z}), \quad (12)$$

with $\delta_i = \frac{C_i}{2k_i} + \sum_{j=1,2} \frac{\alpha_{ij}^0}{k_j^2}$ ($i = 1, 2$) and $\alpha_{ij}^0 = \lim_{Q \rightarrow 0} \alpha_{ij}$.

Denoting $D_1 \equiv \frac{\delta_1 \kappa^2}{k_1} = \frac{(k_1 - k_3) k_2}{(k_1 - k_2) k_3}$ and $D_2 \equiv \frac{\delta_2 \kappa^2}{k_2} = \frac{(k_2 - k_3) k_1}{(k_2 - k_1) k_3}$, Eqs. (5) and (12) lead to the induced charge density

$$\rho^{ind}(z) = -\frac{4\pi\sigma}{\epsilon_s} f(z; 0) = -\sigma (D_1 k_1 e^{-k_1 z} + D_2 k_2 e^{-k_2 z}). \quad (13)$$

The cumulated induced charge density reads

$$\sigma^{ind} = \int_0^\infty \rho^{ind}(z) dz = -\sigma (D_1 + D_2). \quad (14)$$

One can check that $D_1 + D_2 = 1$, so that the local charge neutrality condition $\sigma^{ind} = -\sigma$ is fulfilled.

With the analytical form of $\rho^{ind}(z)$ in Eq. (13), the electric potential $\phi(z)$ can be determined from Eqs. (6) and (7). Note that the electric potential satisfies $\phi(z \rightarrow \infty) = 0$ and $\frac{d\phi(z \rightarrow \infty)}{dz} = 0$. After integrating Eq. (6) twice, it is found that

$$\phi(z) = \frac{4\pi\sigma}{\epsilon_s} \left(\frac{D_1}{k_1} e^{-k_1 z} + \frac{D_2}{k_2} e^{-k_2 z} \right), \quad z \geq 0. \quad (15)$$

The electric potential $\phi(z)$ in the range $-b < z < 0$ is a linear function of z :

$$\phi(z) = V_0 - \frac{4\pi\sigma}{\epsilon_s} (z + b), \quad -b < z < 0, \quad (16)$$

with $V_0 = \frac{4\pi\sigma}{\epsilon_s} (b + \frac{D_1}{k_1} + \frac{D_2}{k_2})$ the electric potential on the electrode surface.

Here are some observations on the parameters $k_{1,2}$ in the TY response function. The parameters $k_{1,2}$ are related to the first two

effective inverse Debye lengths of the bulk system and can be easily evaluated from the bulk longitudinal dielectric function $\epsilon_l(k)$.³¹ In general, k_1 and k_2 depend on the reduced Debye parameter $K_D = k_D d$. When the electrostatic coupling is weak, or, equivalently, K_D is small, both k_1 and k_2 are real numbers, and then the electric potential is a simple decay function. When K_D is larger than a critical value K_c , k_1 and k_2 become a pair of conjugate complex numbers, such that $k_{1,2} = k_R \pm ik_I$.^{42,43} In this case, D_1 and D_2 also become a pair of complex conjugates, and then Eq. (15) can be rewritten as $\phi(z) = \frac{4\pi\sigma}{\epsilon_s} \gamma e^{-k_R z} \cos[k_I z + \psi_0]$, with the two parameters γ and ψ_0 determined by $k_{1,2}$ and $D_{1,2}$. Then, it is easy to see that the electric potential becomes an oscillatory decaying function with decay rate $1/k_R$ and oscillation period $1/k_I$. In general, the values of k_R and k_I depend on k_D in an implicit way, which, in turn, depends on the approximation used and needs to be solved numerically. According to our previous study on concentrated RPM electrolytes,⁴³ k_I is an increase function of k_D , so that the period of the oscillation decreases as the coupling strength increases.

C. A two-Yukawa response function built from exact sum rules

Until now, the parameters in the TY response function have not been specified. In general, one may treat the response function $\chi(k)$ as a pure solvent property, and then all five parameters $\{k_{1,2}, \kappa, C_{1,2}\}$ used in Eq. (8) are independent of the surface charge density σ of the electrode; hence, the formulation will be a linear response approach. However, an effective charge density, or charge renormalization, is necessary to capture the nonlinear response effect of electrolyte solutions.²⁵

To build a response model, taking into account the nonlinear response effect, while introducing the effective charge density in a self-consistent manner, the parameters $k_{1,2}$ are kept as properties of the bulk solution, but the other parameters $\{\kappa, C_{1,2}\}$ depend on the electrode-ion interactions and, hence, are σ -dependent. To this end, the exact sum rules for electrolyte solutions and EDLs are used to determine these parameters in the TY response function, as long as $k_{1,2}$ for the bulk solution are known.

There are exact sum rules for the bulk solution and the EDLs, such as the charge neutrality condition, the homogeneous Stillinger-Lovett (SL) second moment condition for bulk solution,⁴⁴ and the contact theorems for EDLs.⁴⁵⁻⁴⁸ These sum rules are used as constraints for the parameters used in the TY model, which serve as a charge renormalization mechanism, to capture the nonlinear response. The charge neutrality condition leads to the first constraint

$$C_1 + C_2 = 1. \quad (17)$$

As one shall see, the homogeneous SL condition leads to the second constraint in Eq. (18), while the inhomogeneous SL condition or the nonlocal contact theorem for $g_d(z)$ eventually leads to the third constraint in Eq. (27). To this end, the sum rules play a vital role in building our self-consistent theory.

The application of the SL condition is a bit more subtle. Strictly speaking, the original SL condition applies only to a homogeneous bulk electrolyte solution. The inhomogeneity of the electrolytes solutions in the presence of the electrode originates from the short-ranged, wall-ion interaction and the long-ranged, wall-ion electrostatic interaction. A generalized form of the SL condition for

inhomogeneous electrolytes has been derived by Carnie and Chan,⁴⁹ which is the nonlocal contact theorem.⁵⁰ When the charge density of the electrode is low, it is expected that the presence of the electrode has only a minor effect on the electrostatic response of the confined solution; therefore, the homogeneous SL condition is still a reasonable constraint for the electrolyte in the presence of a charged electrode. A similar idea has been used in the study of polar fluids confined between two plain dipolar layers, where the dielectric function of the confined solvent is approximated by that of the bulk solvent.⁵¹ The SL condition $\lim_{k \rightarrow 0} \frac{-4\pi\chi(k)}{\epsilon_s k^2} = 1$ ^{31,44} leads to the second constraint

$$\kappa^2 = \frac{k_1^2 k_2^2}{C_2 k_1^2 + C_1 k_2^2}. \quad (18)$$

As one shall see in Sec. III, numerical results imply that the parameters $\{\kappa, C_{1,2}\}$ only have a weak dependence on the surface charge density σ ; therefore, one may conclude that the homogeneous SL condition is a reasonable constraint for the electrode-solution system.

Note that there are contact theorems on the EDL in electrolyte solutions.⁴⁵⁻⁴⁸ Denote $g_s(z) = [g_1(z) + g_2(z)]/2$ and $g_d(z) = [g_1(z) - g_2(z)]/2$, with $g_i(z)$ the singlet distribution function of the cation ($i=1$) and anion species ($i=2$) around the electrode. The function $g_d(z)$ is evaluated as

$$g_d(z) = \frac{\rho^{ind}(z)}{q_s \rho_s} = -\frac{b_e}{k_D} (D_1 k_1 e^{-k_1 z} + D_2 k_2 e^{-k_2 z}), \quad (19)$$

where $b_e = \frac{4\pi\beta q_s \sigma}{\epsilon_s k_D}$ is a dimensionless surface charge density, and the relation $\frac{\sigma}{q_s \rho_s} = \frac{b_e}{k_D}$ is used. Equation (19) leads to a contact value

$$g_d(0) = -\frac{b_e}{k_D} (D_1 k_1 + D_2 k_2). \quad (20)$$

The nonlocal contact theorem for $g_d(z)$ is an exact sum rule for the EDL, which can be used to incorporate the nonlinear response effect and to derive the third constraint. The exact nonlocal contact theorem for $g_d(z)$ ⁴⁷ reads

$$g_d(0) = \beta q_s \int_0^\infty g_s(z) \frac{d\phi(z)}{dz} dz. \quad (21)$$

In order to apply the nonlocal contact theorem, $g_s(z)$ needs to be specified. Denote $t(z) \equiv \beta q_s \frac{d\phi(z)}{dz}$. It is found that

$$\begin{aligned} t(z) &= -\frac{4\pi\beta q_s \sigma}{\epsilon_s} (D_1 e^{-k_1 z} + D_2 e^{-k_2 z}), \\ &= -b_e k_D (D_1 e^{-k_1 z} + D_2 e^{-k_2 z}), \quad z \geq 0. \end{aligned} \quad (22)$$

The charge neutrality condition $D_1 + D_2 = 1$ leads to $t(0) = -b_e k_D$. Inspired by the exact local contact theorem $g_s(0) = a + b_e^2/2$ ^{45,46} and the PB expression of the $g_s(z)$,⁴⁷ $g_s(z)$ is approximated as a quadratic function of $\phi(z)$:

$$g_s(z) \simeq g_0(z) + \frac{b_e^2}{2} \left(\frac{D_1}{k_1} e^{-k_1 z} + \frac{D_2}{k_2} e^{-k_2 z} \right)^2 \bigg/ \left(\frac{D_1}{k_1} + \frac{D_2}{k_2} \right)^2, \quad z > 0, \quad (23)$$

where $g_0(z)$ is the Percus–Yevick (PY) singlet hard sphere distribution function, which can be evaluated analytically using the zone expansion method.⁵² It is known that $g_0(0) = a$, with $a = \beta P/n_s$ the osmotic coefficient for a hard sphere fluid with particle number density n_s .⁴⁰ According to Eq. (23), it is easy to check that $g_s(0) = a + b_e^2/2$; hence, the local contact theorem for $g_s(z)$ is fulfilled. Using the contact value $a = g_0(0)$ and its derivative $a_1 = \frac{dg_0(z=0)}{dz}$ as input, we further approximate $g_0(z)$ by

$$g_0(z) \simeq 1 + Me^{-\Lambda z}, \quad z > 0, \quad (24)$$

with $M = a - 1$ and $\Lambda = -a_1/a$.

When Eqs. (19) and (22)–(24) are inserted into Eq. (21), one can find another expression for the contact value of $g_d(z)$. After some straightforward calculations, Eq. (21) reduces to

$$g_d(0) = \int_0^\infty g_s(z)t(z)dz = -b_e k_D f_0(D_1, D_2), \quad (25)$$

with

$$\begin{aligned} f_0(D_1, D_2) &= \frac{D_1}{k_1} + \frac{D_2}{k_2} + M \left(\frac{D_1}{k_1 + \Lambda} + \frac{D_2}{k_2 + \Lambda} \right) + f_1(D_1, D_2), \\ f_1(D_1, D_2) &= \frac{b_e^2}{2} \left[\frac{D_1^3}{3k_1^3} + \frac{D_2^3}{2k_2 + k_1} \left(\frac{2}{k_1 k_2} + \frac{1}{k_1^2} \right) \right. \\ &\quad \left. + \frac{D_1 D_2^2}{k_1 + 2k_2} \left(\frac{2}{k_1 k_2} + \frac{1}{k_2^2} \right) + \frac{D_2^3}{3k_2^3} \right] / \left(\frac{D_1}{k_1} + \frac{D_2}{k_2} \right)^2. \end{aligned} \quad (26)$$

Comparing Eqs. (20) and (25), one can find that the self-consistency requirement leads to the third constraint

$$D_1 k_1 + D_2 k_2 = k_D^2 f_0(D_1, D_2). \quad (27)$$

Note that $D_1 + D_2 = 1$, $D_1 = (k_1 - k_3)k_2 / [(k_2 - k_3)k_3]$ and $\kappa = k_1 k_2 / k_3$. When $k_{1,2}$ of the bulk solution is known, Eqs. (17), (18), and (27) form a set of closed equations for the three unknowns $\{\kappa, C_{1,2}\}$ in the TY response function. To this end, a combination of Gaussian field theory with a TY response function and the sum rules, such as the charge neutrality condition, the SL second moment condition, and the nonlocal contact theorem, provides a complete solution to the EDL problem.

In practice, Eqs. (17), (18), and (27) can be solved numerically. There are several solutions from these equations, and only the solution with $\kappa > 0$ is physically reasonable. According to the above procedure, it is easy to see that the parameters $C_{1,2}$ and κ used in the Gaussian field theory depend on the surface charge density σ , and then the nonlinear response effect of the surface charge density can be captured.

One may note that there are other ways to construct the response function with two length scales $1/k_1$ and $1/k_2$. In our previous study, an extended DH theory with a fourth order gradient term was used for concentrated electrolyte solutions, where the electric potential $\phi(r)$ in the solution fulfills $\nabla^2 \phi(\mathbf{r}) = \kappa^2 \phi(\mathbf{r}) + L_Q^2 \nabla^4 \phi(\mathbf{r})$.³³ This theory is equivalent to using a different longitudinal dielectric response function $\epsilon_l(k) = \epsilon_s(1 + \kappa^2/k^2 + L_Q^2 k^2)$ and a response function $\chi(k) = -\frac{\kappa^2 \epsilon_s}{4\pi} [1 - \epsilon_s/\epsilon_l(k)] = -\frac{\epsilon_s}{4\pi} \left[k^2 - \frac{1}{L_Q^2} \left(1 - \frac{\kappa^2 + \kappa^4}{k^2 + \kappa^2 + L_Q^2 k^4} \right) \right] = -\frac{\epsilon_s}{4\pi} \left[k^2 - \frac{1}{L_Q^2} \left(1 - \frac{C_5}{k^2 + k_1^2} - \frac{C_6}{k^2 + k_2^2} \right) \right]$,

with $k_{1,2} = \frac{\sqrt{(1 \mp \sqrt{1 - 4\kappa^2 L_Q^2})/2}}{L_Q}$, $C_5 + C_6 = \frac{1}{L_Q^2}$, and $C_5 k_2^2 + C_6 k_1^2 = \frac{\kappa^2}{L_Q^2}$. In r -space, the response function reads $\chi(\mathbf{r} - \mathbf{r}') = -\frac{\epsilon_s}{4\pi} \left[-\nabla^2 \delta^{(3)}(\mathbf{r}) - \frac{1}{L_Q^2} \left(\delta^{(3)}(\mathbf{r}) - \frac{C_5}{4\pi} \frac{e^{-k_5|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} - \frac{C_6}{4\pi} \frac{e^{-k_6|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \right) \right]$. This new response function can also be used in the Gaussian field theory to treat the EDLs. However, due to the existence of a fourth order gradient term $\nabla^4 \phi(\mathbf{r})$, an extra term $\nabla^2 \delta^{(3)}(\mathbf{r})$ appears in the response function $\chi(r)$ and renders the application of the Gaussian field model to be fairly complicated. Extension of the Gaussian field theory to an electrolyte with such a response function is underway, which is really the impetus for the current study, due to the uncertainty of the boundary conditions with two length scales in the response model.³³

To summarize, a TY response function is used for the bulk solution and leads to a complete solution for the EDL problems. Note that the effective Debye parameters $k_{1,2}$ become a pair of conjugate complex numbers, as long as the electrostatic coupling is strong enough Eq. (15) implies that the electric potential $\phi(z)$ becomes an oscillatory exponential decay function. With the charge neutrality condition, the SL second moment condition, and the nonlocal contact theorem for $g_d(z)$ as constraints, the parameters in the TY model can be uniquely determined as long as the first two effective Debye parameters $k_{1,2}$ of the bulk solution are known. As shown in Sec. III, the TY response function can be used to reproduce the oscillatory decaying electric potential and hence goes beyond the DH approach to describe correlated dielectric responses beyond the mean field approach.

III. APPLICATIONS TO THE EDL IN AN RPM IONIC FLUID

In this section, the Gaussian field theory is applied to the EDL in an ionic fluid studied by Lamperki and Kłos⁵³ using Monte Carlo (MC) simulations. The system is a 1:1 RPM electrolyte, where the ion diameter is $d = 4 \text{ \AA}$, the packing fraction is $\eta = 0.35$, the relative dielectric constant of the background is $\epsilon_r = 10$, and the temperature is $T = 1400 \text{ K}$. Denote the cation and anion species as species 1 and 2. The charge of the cation and anion species is $q_1 = -q_2 = q_s = e_0$, with e_0 the elementary charge. $\epsilon_s = 4\pi\epsilon_0\epsilon_r$ is the dielectric constant used in the Gaussian unit, and ϵ_0 is the permittivity in vacuum. The total particle number density is $n_s = 6\eta/(\pi d^3)$. The inverse Debye length is $k_D = \sqrt{4\pi\beta q_s^2 n_s/\epsilon_s} \simeq 1.25 \text{ \AA}^{-1}$. The length parameter b in the EDL model is $b = d/2 = 2 \text{ \AA}$. The surface charge density on the electrode is σ and leads to a dimensionless surface charge density $b_e = \frac{4\pi\beta q_s \sigma}{\epsilon_s k_D}$.

Note that the hyper-netted-chain (HNC) integral equation theory leads to a very accurate description of simple electrolytes over a very large range of parameter space;^{54–56} hence, HNC theory will be used to determine some parameters of the bulk solvent in the Gaussian field model. The HNC theory is used to evaluate the total correlation functions $h_{ij}(r)$ of the ionic species, from which the dielectric function $\epsilon_l(k)$ of the bulk system is determined. Due to the symmetry of the RPM electrolyte solution, $h_{11}(r) = h_{22}(r)$ and $h_{12}(r) = h_{21}(r)$. Denote $h_D(r) = [h_{11}(r) - h_{12}(r)]/2$ as the asymmetric part of the total correlation function $h_{ij}(r)$. The

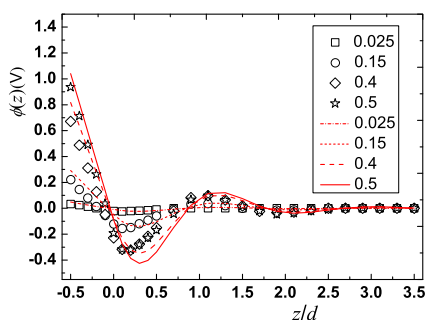
TABLE I. Parameters used in the TY response model. The MC results of V_0 are from Fig. 6 of Ref. 53.

σ (C/m ²)	κ (Å ⁻¹)	$C_{1,2}$	$D_{1,2}$	V_0 (V) (theory)	V_0 (V) (MC)
0.025	0.929	$0.5 \pm 1.303i$	$0.5 \mp 0.343i$	0.048	0.034
0.15	0.910	$0.5 \pm 1.336i$	$0.5 \mp 0.331i$	0.29	0.22
0.4	0.832	$0.5 \pm 1.488i$	$0.5 \mp 0.287i$	0.82	0.67
0.5	0.804	$0.5 \pm 1.555i$	$0.5 \mp 0.270i$	1.04	0.94

function $M(k) \equiv 1 - \epsilon_s/\epsilon_l(k) = \frac{k_D^2}{k^2} [1 + n_s h_D(k)]$ is fitted to a half-empirical function $f(k) = \frac{a_0 k^2}{k^4 + (a_1 k^2 - a_2) \cos(b_1 k) + a_3 k \sin(b_1 k) + a_2}$.³² The Debye parameters k_l can be evaluated numerically by solving $\epsilon_l(k = ik_l) = 0$, or, equivalently, $k^4 + (a_1 k^2 - a_2) \cos(b_1 k) + a_3 k \sin(b_1 k) + a_2 = 0$. The first two roots of $\epsilon_l(k)$ are a pair of conjugate numbers $k_{1,2} \simeq (0.334 \pm 0.869i) \text{ \AA}^{-1}$, which is used to construct the TY response function $\chi(k) = -\frac{\kappa^2 \epsilon_s}{4\pi} (1 - \frac{C_1 k_1^2}{k^2 + k_1^2} - \frac{C_2 k_2^2}{k^2 + k_2^2})$. For the packing fraction $\eta = 0.35$ and hard sphere diameter $d = 4 \text{ \AA}$, the PY theory⁵² leads to $a = g_0(0) \simeq 4.02$ and $a_1 = \frac{d g_0(z=0)}{dz} \simeq -3.25 \text{ \AA}^{-1}$, and then the parameters M and Λ introduced in Eq. (24) are $M = a - 1 = 3.02$ and $\Lambda = -a_1/M = 1.075 \text{ \AA}^{-1}$, respectively.

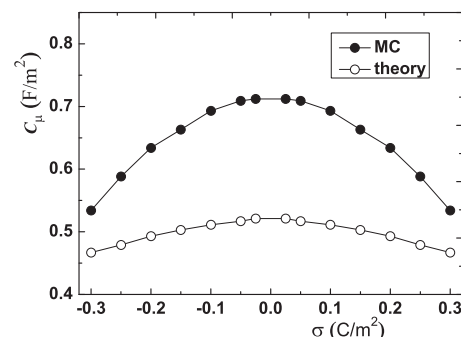
Following the discussion in Sec. II B, we solve Eqs. (17), (18), and (27) numerically and find the physically reasonable solution for $\{\kappa, C_{1,2}\}$ and the coefficients $D_{1,2}$. Using these parameters, the potential V_0 on the electrode surface is evaluated as $V_0 = \frac{4\pi\sigma}{\epsilon_s} (b + \frac{D_1}{k_1} + \frac{D_2}{k_2})$. For $\sigma = 0.025, 0.15, 0.4, 0.5 \text{ C/m}^2$, the numerical results for $\kappa, C_{1,2}, D_{1,2}, V_0$ are shown in Table I. As one can see, $\kappa, C_{1,2}$ and $D_{1,2}$ only have a weak dependence on the surface charge density σ , so that the SL condition in Eq. (18) is a reasonable constraint for the confined electrolyte solution. The predicted results for V_0 are in reasonably good agreement with the MC simulations, given that there are no adjustable parameters in the theory.

With $D_{1,2}$, the electric potential $\phi(z)$ is evaluated using Eqs. (15) and (16), and the results are shown in Fig. 2. As one can see, the Gaussian field theory leads to a reasonable description of the EDL under four different surface charge densities, where the electric

**FIG. 2.** Electric potential $\phi(z)$ near a metallic electrode in an ionic fluid, where the surface charge density on the electrode is $\sigma = 0.025, 0.15, 0.4, 0.5 \text{ C/m}^2$. The results from Monte Carlo simulations (Fig. 6 in Ref. 53) are denoted by symbols, while results from the Gaussian field theory are denoted by lines.

potentials in the electrolyte region are oscillatory decay functions. However, the depth of the first valley of $\phi(z)$ from Gaussian field theory is a bit larger than that from simulations for large charge density. According to our previous study on RPM electrolytes,³¹ four screening length scales may be necessary to capture the ionic correlation of the ionic fluids with strong coupling, so that the two-Yukawa response function may be inadequate for the electrostatic interaction of the ionic fluid studied. This could be one reason for the discrepancy between the theory and the MC results. Another reason may be due to the limitation of the Gaussian field theory, where the effective charge density is not considered explicitly, and the nonlinear response effect is only partly accounted for in Eq. (23).

The Gaussian field theory is also used to study the differential capacitance $C_\mu = \frac{d\sigma}{dV_0}$ of an electrode. The differential capacitance is an important thermodynamic property of a planar electrode immersed in an electrolyte solution. It is known that the differential capacitance has a nontrivial dependence on the surface potential V_0 , which could be a bell shape or a camel shape, depending on the properties of the electrolytes.^{57,58} These effects have been studied with nonlinear mean field theories and density functional theories.^{59,60} Note that the MC results for C_μ in Ref. 53 is shown as a function of σ rather than V_0 . In order to compare with the MC results, the numerical results for C_μ as a function of σ are shown in Fig. 3. As one can see, when the surface charge density is lower than 0.3 C/m^2 , the Gaussian field theory predicts $0.47 \text{ F/m}^2 < C_\mu < 0.52 \text{ F/m}^2$, which is in fair agreement with the MC results $0.53 \text{ F/m}^2 < C_\mu < 0.71 \text{ F/m}^2$. The Gaussian field theory predicts that C_μ is a bell shape function of the charge density σ , which is the same as the simulation results.

**FIG. 3.** Differential capacitance C_μ as a function of the surface charge density σ . The results from Monte Carlo simulations (Fig. 8 in Ref. 53) are denoted by filled circles, while results from the Gaussian field theory are denoted by hollow circles. The lines are guides to the eye.

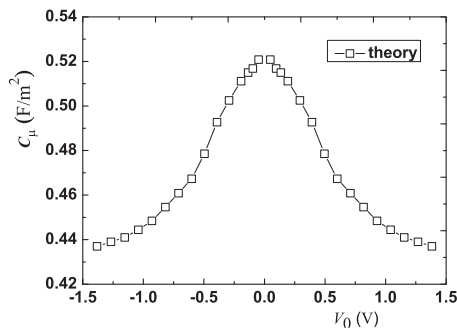


FIG. 4. The differential capacitance C_μ as a function of the surface potential V_0 . The results from theory are denoted by hollow squares. The lines are guides to the eyes.

The numerical results for C_μ as a function of V_0 are shown in Fig. 4, where the MC results are not available in Ref. 53. As one can see, C_μ from the Gaussian field theory is also a bell shape function of V_0 . As a comparison, the conventional GC theory predicts that C_μ is always an increasing function of V_0 and hence cannot describe the saturation effect in the large electric potential regime.⁵⁷ To this end, the Gaussian field model leads to a fairly good description of the differential capacitance, given that the electric potential V_0 is not really high.

IV. CONCLUDING REMARKS

In summary, the planar, electric, double-layer structure of a non-polarizable electrode in electrolyte solutions is studied using the Gaussian field theory combined with a two-Yukawa response function. The modified response function in the planar symmetry is derived analytically, which is further used to evaluate the induced charge density and the electrostatic potential near an electrode. The Gaussian field theory using a two-Yukawa response function can reproduce the oscillatory decay behavior of the electric potentials in concentrated electrolyte solutions. When the exact sum rules, such as charge neutrality condition, the Stillinger-Lovett second moment condition, and the contact theorem of the electric double layer, are used as constraints to determine the parameters of the response function, the Gaussian field theory could partially capture the non-linear response effect of the surface charge density. Applications to electrodes with fixed surface charge density demonstrates the validity of the Gaussian field theory, by comparing with Monte Carlo simulations.

ACKNOWLEDGMENTS

T. Xiao acknowledges the financial support from the National Natural Science Foundation of China (NSFC) (Grant No. 21863001), and a startup package from Guizhou Education University. X. Song is supported by the Division of Chemical and Biological Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC02-07CH11358 with Iowa State University.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Tiejun Xiao: Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Methodology (equal); Validation (equal); Visualization (equal); Writing – original draft (equal). **Xueyu Song:** Conceptualization (equal); Funding acquisition (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

APPENDIX A: MODIFIED RESPONSE FUNCTION FROM A GAUSSIAN FIELD APPROACH

The Gaussian field theory uses the concept of solvent and solute to deal with the linear response of the solution so that the excluded volume effect of a solute can be accounted for in a simple manner. Specifically, the solute will generate an excluded volume in which the solvent species cannot enter and, hence, modifies the local response function. Denote the exclude volume of the solute as the “in” region and the volume occupied by the solvent as the “out” region. The modified response function $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ in the Gaussian field model reads^{37,39}

$$\chi^{(m)}(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r} - \mathbf{r}') - \Delta\chi(\mathbf{r}, \mathbf{r}'), \quad (\text{A1})$$

with

$$\Delta\chi(\mathbf{r}, \mathbf{r}') = \int_{in} d\mathbf{r}'' \int_{in} d\mathbf{r}''' \chi(\mathbf{r} - \mathbf{r}'') \chi_{in}^{-1}(\mathbf{r}'', \mathbf{r}''') \chi(\mathbf{r}''' - \mathbf{r}'), \quad (\text{A2})$$

and the inverse function $\chi_{in}^{-1}(\mathbf{r}'', \mathbf{r}''')$ is defined as

$$\int_{in} \chi_{in}^{-1}(\mathbf{r}, \mathbf{r}'') \chi(\mathbf{r}'' - \mathbf{r}') d\mathbf{r}'' = \delta^{(3)}(\mathbf{r} - \mathbf{r}'), \mathbf{r}, \mathbf{r}' \in in, \quad (\text{A3})$$

with $\delta^{(3)}(\mathbf{r})$ the three-dimensional Dirac function. It is easy to check that $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ vanishes in the “in” region, such that $\chi^{(m)}(\mathbf{r}, \mathbf{r}') = 0$ for $\mathbf{r} \in in$ or $\mathbf{r}' \in in$. According to Eqs. (A1)–(A3), $\chi^{(m)}(\mathbf{r}, \mathbf{r}')$ is a response function in the “out” region, which needs to be evaluated, given the pure solvent response function $\chi(\mathbf{r} - \mathbf{r}')$ and the geometry of the solute.

It is interesting to note that the modified response function can also be evaluated in a different way. Consider a charged solute in an electrolyte solution. Define $t(k) \equiv 1/\chi(k)$ as a new response function in k -space. The linear response theory also implies that $\psi(\mathbf{r}) = \int t(\mathbf{r} - \mathbf{r}') \rho^{ind}(\mathbf{r}') d\mathbf{r}'$, with $\psi(\mathbf{r})$ the bare electric potential generated by the solute and $t(\mathbf{r})$ the inverse Fourier transform of $t(k)$. It is found that $\rho^{ind}(\mathbf{r}) = 0$ for $\mathbf{r} \in in$ due to the excluded volume effect. Then, the response equation reads $\psi(\mathbf{r}) = \int_{out} t(\mathbf{r} - \mathbf{r}') \rho^{ind}(\mathbf{r}') d\mathbf{r}'$ for $\mathbf{r} \in out$. Note that Eq. (2) reduces to $\rho^{ind}(\mathbf{r}) = \int_{out} \chi^{(m)}(\mathbf{r}, \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}'$ for $\mathbf{r} \in out$. It is found that

$\int_{out} t(\mathbf{r}-\mathbf{r}'')\chi^{(m)}(\mathbf{r}'',\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$ for $\mathbf{r},\mathbf{r}' \in out$. Define $t_{out}^{-1}(\mathbf{r},\mathbf{r}')$ as the functional inverse of $t(\mathbf{r}-\mathbf{r}')$ in the “out” region, such that $\int_{out} t(\mathbf{r}-\mathbf{r}'')t_{out}^{-1}(\mathbf{r}'',\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$ with $\mathbf{r},\mathbf{r}' \in out$. As one can see, the relation $\chi^{(m)}(\mathbf{r},\mathbf{r}') = t_{out}^{-1}(\mathbf{r},\mathbf{r}')$ is valid for a solute with general geometry and provides another route to compute the modified response function. In a previous study on the dielectric response in a polar solvent, similar results had been derived by Kornyshev⁵¹ and Georgievskii and co-workers.⁶¹ In [Appendixes C and D](#), it is verified that $\chi^{(m)}(\mathbf{r},\mathbf{r}')$ from these two routes are the same for the special case of a one/two-Yukawa response function.

For the EDL problem with planar symmetry, the “in” region is defined for the left plane $z < 0$ while the “out” region is defined for the right plane $z > 0$. Denote $\chi^{(m)}(z,z';Q)$, $\Delta\chi^{(m)}(z,z';Q)$ and $\chi_{in}^{-1}(z,z';Q)$ as the Bessel-Fourier component of $\chi^{(m)}(\mathbf{r},\mathbf{r}')$, $\Delta\chi^{(m)}(\mathbf{r},\mathbf{r}')$ and $\chi_{in}^{-1}(\mathbf{r},\mathbf{r}')$, respectively. Then it is found that

$$\chi^{(m)}(z,z';Q) = \chi(z-z';Q) - \Delta\chi(z,z';Q), \quad (\text{A4})$$

with

$$\Delta\chi(z,z';Q) = \int_{-\infty}^0 dz'' \int_{-\infty}^0 dz''' \chi(z-z'';Q) \times \chi_{in}^{-1}(z'',z''';Q)\chi(z'''-z';Q), \quad (\text{A5})$$

and the inverse function $\chi_{in}^{-1}(z,z';Q)$ is defined as

$$\int_{-\infty}^0 \chi_{in}^{-1}(z,z'';Q)\chi(z''-z';Q)dz'' = \delta(z-z'), \quad z < 0 \text{ and } z' < 0. \quad (\text{A6})$$

It is easy to check that

$$\chi^{(m)}(z,z';Q) \equiv 0, \quad z < 0 \text{ or } z' < 0. \quad (\text{A7})$$

Given the bulk response function $\chi(z,z';Q)$, the main mathematical problem in the Gaussian field theory is to determine $\chi^{(m)}(z,z';Q)$ in the “out” region $z,z' > 0$.

APPENDIX B: PLANAR EDL FROM THE DH RESPONSE FUNCTION

Before computing the modified response function, the response function of the bulk electrolyte solution needs to be specified. Considering an electrolyte solution at low concentrations, the DH theory leads to $\epsilon_l(k)_{DH} = \epsilon_s(1 + k_D^2/k^2)$,⁴⁰ and then

$$\chi(k)_{DH} = -\frac{k_D^2\epsilon_s}{4\pi} \left(1 - \frac{k_D^2}{k^2 + k_D^2} \right). \quad (\text{B1})$$

In r-space, the DH response function contains a single Yukawa function

$$\chi(\mathbf{r}-\mathbf{r}')_{DH} = -\frac{k_D^2\epsilon_s}{4\pi} \left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') - \frac{k_D^2}{4\pi} \frac{e^{-k_D|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \right]. \quad (\text{B2})$$

The Bessel-Fourier component of $\chi(\mathbf{r}-\mathbf{r}')$ is⁴¹

$$\chi(z-z';Q)_{DH} = -\frac{k_D^2\epsilon_s}{4\pi} \left[\delta(z-z') - \frac{k_D^2}{2\Gamma} e^{-\Gamma|z-z'|} \right], \quad (\text{B3})$$

with $\Gamma = \sqrt{Q^2 + k_D^2}$. The inverse function in the range $z,z' < 0$ reads⁴¹

$$\chi_{in}^{-1}(z,z';Q)_{DH} = -\frac{4\pi}{k_D^2\epsilon_s} \left[\delta(z-z') + \frac{k_D^2}{2g} e^{-g|z-z'|} - \frac{(g-\Gamma)^2}{2g} e^{g(z+z')} \right], \quad (\text{B4})$$

with $g = Q$. The modified response function $\chi^{(m)}(z,z';Q)_{DH}$ in the range $z,z' > 0$ reads

$$\chi^{(m)}(z,z';Q)_{DH} = -\frac{k_D^2\epsilon_s}{4\pi} \left[\delta(z-z') - \frac{k_D^2}{2\Gamma} e^{-\Gamma|z-z'|} - \frac{(\Gamma-g)^2}{2\Gamma} e^{-\Gamma(z+z')} \right]. \quad (\text{B5})$$

$\chi^{(m)}(z,z';Q)$ is used to determine the function $f(z;Q) \equiv \int_0^\infty dz' \chi^{(m)}(z,z';Q)(z'+b)$ and $f(z;0)$. After some straightforward calculations, it is found that

$$f(z;0) = \frac{k_D\epsilon_s}{4\pi} e^{-k_D z}. \quad (\text{B6})$$

According to Eq. (5), the induced charge density reads

$$\rho^{ind}(z) = -\frac{4\pi\sigma}{\epsilon_s} f(z;0) = -k_D\sigma e^{-k_D z}. \quad (\text{B7})$$

Detailed derivations of the modified response function and the function $f(z;0)$ are summarized in [Appendix C](#).

With the analytical form of $\rho^{ind}(z)$ in Eq. (B7), the electric potential $\phi(z)$ can be determined from Eqs. (6) and (7). Note that the electric potential satisfies $\phi(z \rightarrow \infty) = 0$ and $\frac{d\phi(z \rightarrow \infty)}{dz} = 0$. After integrating Eq. (6) twice, it is found that

$$\phi(z)_{DH} = \frac{4\pi}{\epsilon_s} \frac{\sigma}{k_D} e^{-k_D z}, \quad z \geq 0. \quad (\text{B8})$$

The electric potential $\phi(z)$ in the range $-b < z < 0$ is a linear function of z :

$$\phi(z)_{DH} = V_0 - \frac{4\pi\sigma}{\epsilon_s} (z+b), \quad -b < z < 0, \quad (\text{B9})$$

with $V_0 = \frac{4\pi\sigma}{\epsilon_s} (b + \frac{1}{k_D})$ the electric potential on the electrode. Note that the Debye parameter k_D is a positive number; Eq. (B8) implies that the electric potential $\phi(z)$ is always a simple exponential decay function. These results from the Gaussian field theory are exactly the same as those from the LPB theory;³² so, one can conclude that the Gaussian field theory does lead to a different perspective to the EDL problem. This work can also be regarded as an extension of the Gaussian field theory of polar fluids by Song and Chandler³⁹ to dilute electrolyte solutions, given that the dielectric response function for polar fluids is replaced by that of electrolyte solutions, but even for this case, it is highly nontrivial, due to the functional inverse of the response function in a confined region.

Note that there are contact theorems on the EDL in the electrolyte solutions⁴⁵⁻⁴⁸ which are exact sum rules; it would be of interest to see whether the contact theorems are fulfilled by the DH theory. Denote $g_s(z) = [g_1(z) + g_2(z)]/2$ and $g_d(z) = [g_1(z) - g_2(z)]/2$, with $g_i(z)$ the singlet distribution function of

the cation ($i = 1$) and anion species $i = 2$ around the electrode. As the Gaussian field theory in this study only treats the electrostatic interaction, we just test the DH theory for the contact value of $g_d(z)$. The exact nonlocal contact theorem for $g_d(z)$ ⁴⁷ reads

$$g_d(z=0) = \beta q_s \int_0^\infty g_s(z) \frac{d\phi(z)}{dz} dz. \quad (\text{B10})$$

Note that the induced charge density $\rho^{ind}(z)$ is related to $g_d(z)$ via $\rho^{ind}(z) = q_s \rho_s g_d(z)$;⁴⁸ $g_d(z)$ is evaluated as

$$g_d(z) = \frac{\rho^{ind}(z)}{q_s \rho_s} = -\frac{\sigma k_D}{q_s \rho_s} e^{-k_D z} = -b_e e^{-k_D z}, \quad (\text{B11})$$

with $b_e = \frac{4\pi\beta q_s \sigma}{\epsilon_s k_D}$, a dimensionless surface charge density. Equation (B11) directly leads to a contact value of $g_d(z)$ as

$$g_d(z=0) = -b_e. \quad (\text{B12})$$

In order to apply the nonlocal contact theorem for $g_d(z)$, an analytical expression for $g_s(z)$ is required. Define $t(z) \equiv \beta q_s \frac{d\phi(z)}{dz}$. The Gaussian field theory with a DH response function leads to $t(z) = -b_e k_D e^{-k_D z}$ for $z \geq 0$ and $t(z=0) = -b_e k_D$. In the limit of low particle number density $n_s \rightarrow 0$, the osmotic coefficient $a = \beta P/n_s = 1$. One may construct $g_s(z)$ as $g_s(z) = 1 + b_e^2 e^{-2k_D z}/2$, inspired by the linearized Gouy–Chapman result, so that the exact contact theorem $g_s(z=0) = a + b_e^2/2$ ^{45,46} is fulfilled. Then, Eqs. (B8) and (B10) lead to another expression for the contact value of $g_d(z)$

$$g_d(z=0) = \int_0^\infty [1 + b_e^2 e^{-2k_D z}/2] t(z) dz = -b_e (1 + b_e^2/6). \quad (\text{B13})$$

Comparing Eqs. (B12) and (B13), one can check that the contact theorems for $g_d(z)$ can only be satisfied in the low surface charge density limit $b_e \rightarrow 0$.

APPENDIX C: MODIFIED RESPONSE FUNCTION $\chi^{(m)}(z, z'; Q)$ FOR AN ELECTROLYTE SOLUTION WITH A DH RESPONSE FUNCTION

Consider a planar electrode immersed in an electrolyte solution. Due to the planar symmetry, any function $F(\mathbf{r}, \mathbf{r}')$ can be expanded with its Bessel–Fourier component $F(z, z'; Q)$ via Eq. (3). The function $\Delta\chi(z, z'; Q)$ defined in the Gaussian field theory reads

$$\Delta\chi(z, z'; Q) = \int_{-\infty}^0 dz'' \int_{-\infty}^0 dz''' \chi(z-z''); Q \chi_{in}^{-1}(z'', z'''); Q \times \chi(z''-z'); Q, \quad z > 0 \text{ and } z' > 0. \quad (\text{C1})$$

The functional inverse $\chi_{in}^{-1}(z, z'; Q)$ is defined via

$$\int_{-\infty}^0 \chi_{in}^{-1}(z, z''; Q) \chi(z''-z'); Q dz'' = \delta(z-z'), \quad z < 0 \text{ and } z' < 0. \quad (\text{C2})$$

For the DH response function $\chi(\mathbf{r}-\mathbf{r}') = -\frac{k_D^2 \epsilon_s}{4\pi} \left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') - \frac{k_D^2}{4\pi} \frac{e^{-k_D |\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \right]$, its Bessel–Fourier component reads

$$\chi(z-z'); Q = -\frac{k_D^2 \epsilon_s}{4\pi} \left[\delta(z-z') - \frac{k_D^2}{2\Gamma} e^{-\Gamma|z-z'|} \right], \quad (\text{C3})$$

with $\Gamma = \sqrt{k_D^2 + Q^2}$. The functional inverse of $\chi(z-z'; Q)$ in the region $z, z' < 0$ reads⁴¹

$$\chi_{in}^{-1}(z, z'; Q) = -\frac{4\pi}{k_D^2 \epsilon_s} \left[\delta(z-z') + \frac{k_D^2}{2g} e^{-g|z-z'|} - \frac{(g-\Gamma)^2}{2g} e^{g(z+z')} \right], \quad z < 0 \text{ and } z' < 0, \quad (\text{C4})$$

with $g = Q$. When $z, z' > 0$ and $z'', z''' < 0$, it is found that $\delta(z-z'') = 0$, $\delta(z'-z''') = 0$, $z-z'' > 0$, and $z'-z''' > 0$. So Eq. (C1) with $z > 0$ and $z' > 0$ can be rewritten as

$$\Delta\chi(z, z'; Q) = -\frac{k_D^2 \epsilon_s}{4\pi} \frac{k_D^4}{4\Gamma^2} \int_{-\infty}^0 dz'' \int_{-\infty}^0 dz''' e^{-\Gamma(z-z'')-\Gamma(z'-z''')} \times \left[\delta(z''-z''') + \frac{k_D^2}{2g} e^{-g|z''-z'''|} - \frac{(g-\Gamma)^2}{2g} e^{g(z''+z''')} \right]. \quad (\text{C5})$$

Equation (C5) can be evaluated as

$$\Delta\chi(z, z'; Q) = -\frac{k_D^2 \epsilon_s}{4\pi} \frac{(\Gamma-g)^2}{2\Gamma} e^{-\Gamma(z+z')}. \quad (\text{C6})$$

So, finally, we have

$$\chi^{(m)}(z, z'; Q) = \chi(z, z'; Q) + \Delta\chi(z, z'; Q) = -\frac{k_D^2 \epsilon_s}{4\pi} \left[\delta(z-z') - \frac{k_D^2}{2\Gamma} e^{-\Gamma|z-z'|} - \frac{(\Gamma-g)^2}{2\Gamma} e^{-\Gamma(z+z')} \right]. \quad (\text{C7})$$

As discussed in Appendix A, a different way to derive the modified response function is to evaluate the functional inverse $t_{out}^{-1}(z, z'; Q)$ of the new response function $t(z, z'; Q)$. For the DH response function $\chi(k) = \frac{k_D^2 \epsilon_s}{4\pi} \left(1 - \frac{k_D^2}{k^2 + k_D^2} \right)$, the new response function $t(k) \equiv 1/\chi(k) = -\frac{4\pi}{k_D^2 \epsilon_s} \left(1 + \frac{k_D^2}{k^2} \right)$. In the \mathbf{r} -space, the new response function reads $t(\mathbf{r}-\mathbf{r}') = -\frac{4\pi}{k_D^2 \epsilon_s} \left[\delta^{(3)}(\mathbf{r}-\mathbf{r}') + \frac{k_D^2}{4\pi} \frac{1}{|\mathbf{r}-\mathbf{r}'|} \right]$. The Bessel–Fourier component $t(z, z''; Q)$ of $t(\mathbf{r}-\mathbf{r}')$ is $t(z-z''); Q = -\frac{4\pi}{k_D^2 \epsilon_s} \left[\delta(z-z'') + \frac{k_D^2}{2g} e^{-g|z-z''|} \right]$ with $g = Q$. Denote $t_{out}^{-1}(z, z'; Q)$ as the functional inversion of $t(z, z''; Q)$, such that $\int_0^\infty t(z, z''; Q) t_{out}^{-1}(z'', z'); Q dz'' = \delta(z-z')$, with $z, z' > 0$. It is found that $t_{out}^{-1}(z, z'; Q) = -\frac{k_D^2 \epsilon_s}{4\pi} \left[\delta(z-z') - \frac{k_D^2}{2\Gamma} e^{-\Gamma|z-z'|} - \frac{(\Gamma-g)^2}{2\Gamma} e^{-\Gamma(z+z')} \right] = \chi^{(m)}(z, z'; Q)$.

The function $f(z; Q) \equiv \int_0^\infty dz' \chi^{(m)}(z, z'; Q) (z'+b)$ reduces to

$$f(z; Q) = -\frac{k_D^2 \epsilon_s}{4\pi} \left[\left(1 - \frac{k_D^2}{\Gamma^2} \right) (z+b) - \frac{k_D^2 (1-\Gamma b) + (\Gamma-g)^2 (1+\Gamma b)}{2\Gamma^3} e^{-\Gamma z} \right]. \quad (\text{C8})$$

Setting $Q = 0$, the $f(z; 0)$ function reduces to

$$f(z; 0) = -\frac{k_D^2 \varepsilon_s}{4\pi} \left(0 - \frac{1}{k_D} e^{-k_D z} \right) = \frac{k_D \varepsilon_s}{4\pi} e^{-k_D z}. \quad (\text{C9})$$

APPENDIX D: DETAILS FOR $\chi^{(m)}(z, z'; Q)$ WITH A TWO-YUKAWA RESPONSE FUNCTION

Here are some observations about the bulk response function of the RPM electrolyte solutions. As noted by Chandler, the Gaussian field theory of a solvent is equivalent to an integral equation theory with a suitable closure relation, so that $\chi(k)$ is related to the total correlation function $h_{ij}(r) = g_{ij}(r) - 1$ and direct correlation function $c_{ij}(r)$ between the solvent species i and j .³⁷ The exact response function $\chi(k)$ is related to the bulk longitudinal dielectric function $\varepsilon_l(k)$ via $\chi(k) = -\frac{k^2 \varepsilon_s}{4\pi} [1 - \frac{\varepsilon_s}{\varepsilon_l(k)}]$.⁴⁰ Denote $f_{ij}(k) = \int f_{ij}(r) e^{-ikr} d\mathbf{r}$ as the three-dimensional Fourier transform of a function $f_{ij}(r)$. Due to the symmetry of the system, it is found that $f_{11}(r) = f_{22}(r)$ and $f_{12}(r) = f_{21}(r)$ for $f_{ij}(r) = h_{ij}(r), c_{ij}(r)$. One can introduce $f_D(r) = [f_{11}(r) - f_{12}(r)]/2$ as the asymmetric part of the function f_{ij} . The Ornstein-Zernike equation leads to $[1 + n_s h_D(k)][1 - n_s c_D(k)] = 1$.⁶² The function $M(k) \equiv 1 - \varepsilon_s/\varepsilon_l(k)$ can be evaluated as $M(k) = \frac{k_D^2}{k^2} [1 + n_s h_D(k)]$,^{31,40} so that $\chi(k) = -\frac{k_D^2 \varepsilon_s}{4\pi} [1 + n_s h_D(k)] = -\frac{k_D^2 \varepsilon_s}{4\pi} \frac{1}{[1 - n_s c_D(k)]}$. The mean spherical approximation has been recognized as the closure relation in Ref. 37 for the Gaussian field model. However, other closure relations may also be used to build approximated response functions. The random phase approximation (RPA) closure assumes $c_D(r) = -\frac{\beta q_k^2}{\varepsilon_s r} = -\frac{k_D^2}{4\pi n_s r}$ ⁴⁰ and leads to a DH response function $\chi(k)_{DH} = -\frac{\varepsilon_s}{4\pi} \frac{k_D^2}{k^2 + k_D^2}$. A modified RPA closure with $c_D(r) = -\frac{\beta q_k^2}{\varepsilon_s r} - \frac{C_3 e^{-k_3 r}}{4\pi n_s r}$ leads to $\chi(k) = -\frac{k_D^2 \varepsilon_s}{4\pi} \frac{1}{[1 + k_D^2/k^2 + C_3/(k^2 + k_3^2)]}$, which can be rewritten as $\chi(k) = -\frac{k_D^2 \varepsilon_s}{4\pi} [1 - \frac{C_1 k_1^2}{k^2 + k_1^2} - \frac{C_2 k_2^2}{k^2 + k_2^2}]$ and is related to the two-Yukawa response function defined in Eq. (8). In the context of the generalized mean spherical approximation of RPM electrolyte solutions, the modified RPA has also been adopted to build an integral equation theory with thermodynamic consistency.^{63,64} Therefore, our approach developed in this work can also be used to develop a self-consistent theory of pure electrolyte solutions.

Consider an electrolyte solution with a two-Yukawa response function, with

$$\chi(k) = -\frac{\kappa^2 \varepsilon_s}{4\pi} \left[1 - \frac{C_1 k_1^2}{k^2 + k_1^2} - \frac{C_2 k_2^2}{k^2 + k_2^2} \right], \quad (\text{D1})$$

with $C_1 + C_2 = 1$ the charge neutrality condition and $\kappa^2 = k_1^2 k_2^2 / (C_2 k_1^2 + C_1 k_2^2)$ the Stillinger-Lovett second moment condition.⁴⁴ The new response function, defined as $t(k) \equiv 1/\chi(k)$, can be rewritten as

$$t(k) = -\frac{4\pi}{\kappa^2 \varepsilon_s} \left[1 + \frac{C_3}{k^2 + k_3^2} + \frac{C_4}{k^2 + k_4^2} \right], \quad (\text{D2})$$

with

$$k_3 = \sqrt{C_2 k_1^2 + C_1 k_2^2}, k_4 = 0,$$

$$C_3 = \frac{k_3^2 (C_1 k_1^2 + C_2 k_2^2) - (C_1 + C_2) k_1^2 k_2^2}{k_3^2 - k_4^2},$$

and

$$C_4 = \frac{k_4^2 (C_1 k_1^2 + C_2 k_2^2) - (C_1 + C_2) k_1^2 k_2^2}{k_4^2 - k_3^2} = \kappa^2.$$

The response function and the new response function in r -space reads

$$\begin{aligned} \chi(\mathbf{r} - \mathbf{r}') &= -\frac{\kappa^2 \varepsilon_s}{4\pi} \left[\delta^{(3)}(\mathbf{r} - \mathbf{r}') - \frac{C_1 k_1^2}{4\pi} \frac{e^{-k_1 |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} - \frac{C_2 k_2^2}{4\pi} \frac{e^{-k_2 |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} \right], \\ t(\mathbf{r} - \mathbf{r}') &= -\frac{4\pi}{\kappa^2 \varepsilon_s} \left[\delta^{(3)}(\mathbf{r} - \mathbf{r}') + \frac{C_3}{4\pi} \frac{e^{-k_3 |\mathbf{r} - \mathbf{r}'|}}{|\mathbf{r} - \mathbf{r}'|} + \frac{C_4}{4\pi} \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right]. \end{aligned} \quad (\text{D3})$$

The relation $t(k)\chi(k) \equiv 1$ leads to $\int d\mathbf{r}'' t(\mathbf{r} - \mathbf{r}'') \chi(\mathbf{r}'' - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. So, the new response function $t(\mathbf{r} - \mathbf{r}')$ is just the inverse function of $\chi(\mathbf{r} - \mathbf{r}')$ in the whole space $0 < r, r' < \infty$.

The Bessel-Fourier component of $\chi(\mathbf{r} - \mathbf{r}')$ and $t(\mathbf{r} - \mathbf{r}')$ reads

$$\begin{aligned} \chi(z - z'; Q) &= -\frac{\kappa^2 \varepsilon_s}{4\pi} \left[\delta(z - z') - \frac{C_1 k_1^2}{2\Gamma_1} e^{-\Gamma_1 |z - z'|} - \frac{C_2 k_2^2}{2\Gamma_2} e^{-\Gamma_2 |z - z'|} \right], \\ t(z - z'; Q) &= -\frac{4\pi}{\kappa^2 \varepsilon_s} \left[\delta(z - z') + \frac{C_3}{2\Gamma_3} e^{-\Gamma_3 |z - z'|} + \frac{C_4}{2\Gamma_4} e^{-\Gamma_4 |z - z'|} \right], \end{aligned} \quad (\text{D4})$$

where

$$\Gamma_i = \sqrt{k_i^2 + Q^2}, i = 1, 2, 3, 4.$$

The finite space functional inverse $\chi_{in}^{-1}(z, z'; Q)$ of $\chi(z - z'; Q)$ is defined via

$$\int_{-\infty}^0 \chi_{in}^{-1}(z, z''; Q) \chi(z'' - z'; Q) dz'' = \delta(z - z'), \quad z < 0 \text{ and } z' < 0. \quad (\text{D5})$$

Note that $t(z - z'; Q)$ is the functional inverse of $\chi(z - z'; Q)$ in the whole space; the following trial solution of $\chi_{in}^{-1}(z, z'; Q)$ can be constructed by adding terms proportional to $e^{\Gamma_j z + \Gamma_l z'}$ to $t(z - z'; Q)$:

$$\begin{aligned} \chi_{in}^{-1}(z, z'; Q) &= -\frac{4\pi}{\kappa^2 \varepsilon_s} \left[\delta(z - z') + \frac{C_3}{2\Gamma_3} e^{-\Gamma_3 |z - z'|} + \frac{C_4}{2\Gamma_4} e^{-\Gamma_4 |z - z'|} \right. \\ &\quad \left. + \sum_{j,l=3,4} \alpha_{jl} e^{\Gamma_j z + \Gamma_l z'} \right], \quad z < 0 \text{ and } z' < 0. \end{aligned} \quad (\text{D6})$$

One may note that the functional inverse of a two-Yukawa response function has been discussed by Kornyshev and co-workers,⁴¹ where a similar trial solution has been introduced. However, the expression in Ref. 33 is incorrect, but did inspire our trial solution, where the cross terms such as $e^{\Gamma_3 z + \Gamma_4 z'}$ and $e^{\Gamma_4 z + \Gamma_3 z'}$ are neglected. When the trial solution is inserted into Eq. (D5), one can find an equation for which the left hand side and right hand side can be rearranged as a linear combination of exponential terms. By matching the coefficients of exponential terms $e^{\Gamma_j z + \Gamma_l z'}$, the constraints for the parameters $\{\alpha_{jl}\}$ are derived. After some lengthy calculations, it is found that

$$\begin{aligned}\alpha_{33} &= \frac{C_3}{2\Gamma_3} \left(\frac{\Gamma_4 - \Gamma_1}{\Gamma_3 + \Gamma_1} - \frac{\Gamma_4 - \Gamma_2}{\Gamma_3 + \Gamma_2} \right) / \left(\frac{\Gamma_4 - \Gamma_1}{\Gamma_3 - \Gamma_1} - \frac{\Gamma_4 - \Gamma_2}{\Gamma_3 - \Gamma_2} \right), \\ \alpha_{34} &= \frac{C_3}{2\Gamma_3} \left(\frac{\Gamma_3 - \Gamma_1}{\Gamma_3 + \Gamma_1} - \frac{\Gamma_3 - \Gamma_2}{\Gamma_3 + \Gamma_2} \right) / \left(\frac{\Gamma_4 - \Gamma_1}{\Gamma_3 - \Gamma_1} - \frac{\Gamma_4 - \Gamma_2}{\Gamma_3 - \Gamma_2} \right), \\ \alpha_{43} &= \frac{C_4}{2\Gamma_4} \left(\frac{\Gamma_4 - \Gamma_1}{\Gamma_4 + \Gamma_1} - \frac{\Gamma_4 - \Gamma_2}{\Gamma_4 + \Gamma_2} \right) / \left(\frac{\Gamma_4 - \Gamma_1}{\Gamma_3 - \Gamma_1} - \frac{\Gamma_4 - \Gamma_2}{\Gamma_3 - \Gamma_2} \right), \\ \alpha_{44} &= \frac{C_4}{2\Gamma_3} \left(\frac{\Gamma_3 - \Gamma_1}{\Gamma_4 + \Gamma_1} - \frac{\Gamma_3 - \Gamma_2}{\Gamma_4 + \Gamma_2} \right) / \left(\frac{\Gamma_4 - \Gamma_1}{\Gamma_3 - \Gamma_1} - \frac{\Gamma_4 - \Gamma_2}{\Gamma_3 - \Gamma_2} \right).\end{aligned}\quad (D7)$$

One can check that $\alpha_{34} = \alpha_{43}$ so that the symmetry condition $\chi_{in}^{-1}(z, z'; Q) = \chi_{in}^{-1}(z', z; Q)$ is fulfilled.

The modified response function can also be derived analytically. When $z, z' > 0$ and $z'', z''' < 0$, it is found that $\delta(z - z'') = 0$, $\delta(z' - z''') = 0$, $z - z'' > 0$, and $z' - z''' > 0$. Using the analytical form of $\chi_{in}^{-1}(z, z'; Q)$, $\Delta\chi(z, z'; Q)$, defined in the out region, reads

$$\Delta\chi(z, z'; Q) = -\frac{\kappa^2 \epsilon_s}{4\pi} \sum_{ij} \frac{C_i k_i^2}{2\Gamma_i} \frac{C_j k_j^2}{2\Gamma_j} a_{ij} e^{-\Gamma_i z - \Gamma_j z'}, \quad (D8)$$

with $a_{ij} = \left\{ \frac{1}{\Gamma_i + \Gamma_j} + \sum_k \frac{C_k}{2\Gamma_k} \left[\frac{1}{(\Gamma_j - \Gamma_k)} \left(\frac{1}{\Gamma_i + \Gamma_k} \right) - \frac{1}{(\Gamma_i + \Gamma_j)} \right] + \sum_{kl} \frac{\alpha_{kl}}{(\Gamma_i + \Gamma_k)(\Gamma_j + \Gamma_l)} \right\}$. The modified response function reads

$$\begin{aligned}\chi_{in}^{(m)}(z, z'; Q) &= -\frac{4\pi}{\kappa^2 \epsilon_s} \left[\delta(z - z') - \sum_{i=1,2} \frac{C_i k_i^2}{2\Gamma_i} e^{-\Gamma_i |z - z'|} \right. \\ &\quad \left. - \sum_{i,j=1,2} \frac{C_i k_i^2}{2\Gamma_i} \frac{C_j k_j^2}{2\Gamma_j} a_{ij} e^{-\Gamma_i z - \Gamma_j z'} \right].\end{aligned}\quad (D9)$$

As noted in Appendix A, the modified response function can also be evaluated from the functional inverse of the new response function $t(z, z'; Q)$ in the right half plane. The functional inverse of $t(z - z'; Q)$ in the right half plane is defined as

$$\int_0^\infty t_{out}^{-1}(z, z''; Q) t(z'' - z'; Q) dz'' = \delta(z - z'), \quad z > 0 \text{ and } z' > 0. \quad (D10)$$

Note that both $t(z - z'; Q)$ and $\chi(z - z'; Q)$ are of two-Yukawa function form; the procedure to solve $\chi_{in}^{-1}(z, z'; Q)$ can be used to solve $t_{out}^{-1}(z, z'; Q)$. The final solution reads

$$\begin{aligned}t_{out}^{-1}(z, z'; Q) &= -\frac{4\pi}{\kappa^2 \epsilon_s} \left[\delta(z - z') - \sum_{i=1,2} \frac{C_i k_i^2}{2\Gamma_i} e^{-\Gamma_i |z - z'|} \right. \\ &\quad \left. - \sum_{i,j=1,2} \alpha_{ij} e^{-\Gamma_i z - \Gamma_j z'} \right],\end{aligned}\quad (D11)$$

with

$$\begin{aligned}\alpha_{11} &= \frac{C_1 k_1^2}{2\Gamma_1} \left(\frac{\Gamma_2 - \Gamma_4}{\Gamma_1 + \Gamma_4} - \frac{\Gamma_2 - \Gamma_3}{\Gamma_1 + \Gamma_3} \right) / \left(\frac{\Gamma_2 - \Gamma_4}{\Gamma_1 - \Gamma_4} - \frac{\Gamma_2 - \Gamma_3}{\Gamma_1 - \Gamma_3} \right), \\ \alpha_{12} &= \frac{C_1 k_1^2}{2\Gamma_1} \left(\frac{\Gamma_1 - \Gamma_4}{\Gamma_1 + \Gamma_4} - \frac{\Gamma_1 - \Gamma_3}{\Gamma_1 + \Gamma_3} \right) / \left(\frac{\Gamma_2 - \Gamma_4}{\Gamma_1 - \Gamma_4} - \frac{\Gamma_2 - \Gamma_3}{\Gamma_1 - \Gamma_3} \right), \\ \alpha_{21} &= \frac{C_2 k_2^2}{2\Gamma_2} \left(\frac{\Gamma_2 - \Gamma_4}{\Gamma_2 + \Gamma_4} - \frac{\Gamma_2 - \Gamma_3}{\Gamma_2 + \Gamma_3} \right) / \left(\frac{\Gamma_2 - \Gamma_4}{\Gamma_1 - \Gamma_4} - \frac{\Gamma_2 - \Gamma_3}{\Gamma_1 - \Gamma_3} \right), \\ \alpha_{22} &= \frac{C_2 k_2^2}{2\Gamma_1} \left(\frac{\Gamma_1 - \Gamma_4}{\Gamma_2 + \Gamma_4} - \frac{\Gamma_1 - \Gamma_3}{\Gamma_2 + \Gamma_3} \right) / \left(\frac{\Gamma_2 - \Gamma_4}{\Gamma_1 - \Gamma_4} - \frac{\Gamma_2 - \Gamma_3}{\Gamma_1 - \Gamma_3} \right).\end{aligned}\quad (D12)$$

One can check that $\frac{C_i k_i^2}{2\Gamma_i} \frac{C_j k_j^2}{2\Gamma_j} a_{ij} = \alpha_{ij}$ ($i, j = 1, 2$) are always fulfilled, so it is found that $\chi^{(m)}(z, z'; Q) = t_{out}^{-1}(z, z'; Q)$ given $z, z' > 0$. Note that the expressions of α_{ij} are a bit simpler than $\frac{C_i k_i^2}{2\Gamma_i} \frac{C_j k_j^2}{2\Gamma_j} a_{ij}$; hence, in Sec. II, we use the expression $t_{out}^{-1}(z, z'; Q)$ instead of $\chi^{(m)}(z, z'; Q)_{TY}$ with $z, z' > 0$.

Using the modified response function, now we can evaluate the induced charge density. The function $f(z; Q)$ introduced in Eq. (5) reads

$$\begin{aligned}f(z; Q) &= \frac{\epsilon_s \kappa^2}{4\pi} \left[\left(1 - \frac{C_1 k_1^2}{\Gamma_1^2} - \frac{C_2 k_2^2}{\Gamma_2^2} \right) (z + b) \right. \\ &\quad \left. - \sum_{i=1,2} e^{-\Gamma_i z} \left(\frac{C_i k_i^2 (1 - \Gamma_i b)}{2\Gamma_i^3} + \sum_{j=1,2} \frac{\alpha_{ij} (1 + \Gamma_j b)}{\Gamma_j^2} \right) \right].\end{aligned}\quad (D13)$$

Denote $\alpha_{ij}^0 = \lim_{Q \rightarrow 0} \alpha_{ij}$ and $\delta_i = \frac{C_i}{2k_i} + \sum_j \frac{\alpha_{ij}^0}{k_j^2}$. In the small Q limit, it is found that $\lim_{Q \rightarrow 0} \left(1 - \frac{C_1 k_1^2}{\Gamma_1^2} - \frac{C_2 k_2^2}{\Gamma_2^2} \right) = 0$, $\lim_{Q \rightarrow 0} \left(-\frac{C_i k_i^2 \Gamma_i}{2\Gamma_i^3} + \sum_{j=1,2} \frac{\alpha_{ij} \Gamma_j}{\Gamma_j^2} \right) = 0$ for $i = 1, 2$. Then $f(z; 0)$ is independent of the parameter b

$$f(z; 0) = \frac{\epsilon_s \kappa^2}{4\pi} (\delta_1 e^{-k_1 z} + \delta_2 e^{-k_2 z}). \quad (D14)$$

REFERENCES

- J.-P. Hansen and H. Löwen, *Annu. Rev. Phys. Chem.* **51**, 209 (2000).
- C. J. van Oss, *Interfacial Forces in Aqueous Media* (CRC Press, 2006).
- J. Mewis and N. J. Wagner, *Colloidal Suspension Rheology* (Cambridge University Press, 2012).
- H. Wang and L. Pilon, *J. Phys. Chem. C* **115**, 16711 (2011).
- H. Ji, X. Zhao, Z. Qiao, J. Jung, Y. Zhu, Y. Lu, L. L. Zhang, A. H. MacDonald, and R. S. Ruoff, *Nat. Commun.* **5**, 3317 (2014).
- S. Zhou, *J. Chem. Phys.* **151**, 064710 (2019).
- C. Pan, S. Yi, and Z. Hu, *Phys. Chem. Chem. Phys.* **21**, 14858 (2019).
- K.-D. Huang and R.-J. Yang, *Nanotechnology* **18**, 115701 (2007).
- F. Baldessari, *J. Colloid Interface Sci.* **325**, 526 (2008).
- Y. Green, *J. Chem. Phys.* **154**, 084705 (2021).
- C. Lian, M. Janssen, H. Liu, and R. van Roij, *Phys. Rev. Lett.* **124**, 076001 (2020).
- L. Scalfi, M. Salanne, and B. Rotenberg, *Annu. Rev. Phys. Chem.* **72**, 189 (2021).
- T. Aslyamov and M. Janssen, *Electrochim. Acta* **424**, 140555 (2022).
- J. K. Hwang and A. Warshel, *J. Am. Chem. Soc.* **109**, 715 (1987).
- A. Rosspeintner, B. Lang, and E. Vauthey, *Annu. Rev. Phys. Chem.* **64**, 247 (2013).
- J. M. Paz-Garcia, B. Johannesson, L. M. Ottosen, A. B. Ribeiro, and J. M. Rodriguez-Maroto, *Electrochim. Acta* **150**, 263 (2014).
- D. Andelman, *Handbook of Biological Physics* (Elsevier, 1995), Vol. 1, pp. 603–642.
- B. Duplantier, R. E. Goldstein, V. Romero-Rochn, and A. I. Pesci, *Phys. Rev. Lett.* **65**, 508 (1990).
- P. Attard, *Curr. Opin. Colloid Interface Sci.* **6**, 366 (2001).
- G. V. Bossa and S. May, *Membranes* **11**, 129 (2021).
- A. A. Kornyshev and M. A. Vorotyntsev, *Surf. Sci.* **101**, 23 (1980).
- A. A. Kornyshev, *Electrochim. Acta* **26**, 1 (1981).
- A. A. Kornyshev, E. Spohr, and M. A. Vorotyntsev, “Electrochemical interfaces: At the border line,” in *Encyclopedia of Electrochemistry* (Wiley Online Library, 2007).

- ²⁴A. Levy, M. Bazant, and A. Kornyshev, *Chem. Phys. Lett.* **738**, 136915 (2020).
- ²⁵R. Kjellander, *Phys. Chem. Chem. Phys.* **18**, 18985 (2016).
- ²⁶R. Kjellander, *J. Chem. Phys.* **148**, 193701 (2018).
- ²⁷R. Kjellander, *Phys. Chem. Chem. Phys.* **22**, 23952 (2020).
- ²⁸L. B. Bhuiyan, C. W. Outhwaite, and D. Henderson, *J. Chem. Phys.* **123**, 034704 (2005).
- ²⁹L. B. Bhuiyan and C. W. Outhwaite, *J. Colloid Interface Sci.* **331**, 543 (2009).
- ³⁰C. W. Outhwaite and L. B. Bhuiyan, *Condens. Matter Phys.* **22**, 23801 (2019).
- ³¹T. Xiao and X. Song, *J. Chem. Phys.* **135**, 104104 (2011).
- ³²T. Xiao and X. Song, *J. Chem. Phys.* **141**, 134104 (2014).
- ³³T. Xiao and X. Song, *J. Phys. Chem. A* **125**, 2173 (2021).
- ³⁴R. Burt, G. Birkett, and X. S. Zhao, *Phys. Chem. Chem. Phys.* **16**, 6519 (2014).
- ³⁵C.-Y. Li, M. Chen, S. Liu, X. Lu, J. Meng, J. Yan, H. D. Abruña, G. Feng, and T. Lian, *Nat. Commun.* **13**, 5330 (2022).
- ³⁶J. M. Griffin, A. C. Forse, W.-Y. Tsai, P.-L. Taberna, P. Simon, and C. P. Grey, *Nat. Mater.* **14**, 812 (2015).
- ³⁷D. Chandler, *Phys. Rev. E* **48**, 2898 (1993).
- ³⁸X. Song, D. Chandler, and R. A. Marcus, *J. Phys. Chem.* **100**, 11954 (1996).
- ³⁹X. Song and D. Chandler, *J. Chem. Phys.* **108**, 2594 (1998).
- ⁴⁰J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
- ⁴¹A. A. Kornyshev, A. I. Rubinshtein, and M. A. Vorotyntsev, *J. Phys. C: Solid State Phys.* **11**, 3307 (1978).
- ⁴²L. M. Varela, M. García, and V. Mosquera, *Phys. Rep.* **382**, 1 (2003).
- ⁴³T. Xiao, *Electrochim. Acta* **178**, 101 (2015).
- ⁴⁴F. H. Stillinger, Jr. and R. Lovett, *J. Chem. Phys.* **49**, 1991 (1968).
- ⁴⁵D. Henderson and L. Blum, *J. Chem. Phys.* **69**, 5441 (1978).
- ⁴⁶D. Henderson, L. Blum, and J. L. Lebowitz, *J. Electroanal. Chem.* **102**, 315 (1979).
- ⁴⁷M. Holovko, J. P. Badiali, and D. Di Caprio, *J. Chem. Phys.* **123**, 234705 (2005).
- ⁴⁸M. Holovko, J. P. Badiali, and D. Di Caprio, *J. Chem. Phys.* **127**, 014106 (2007).
- ⁴⁹S. L. Carnie and D. Y. C. Chan, *Chem. Phys. Lett.* **77**, 437 (1981).
- ⁵⁰L. Blum, *Adv. Chem. Phys.* **78**, 171–222 (1990).
- ⁵¹A. A. Kornyshev, *J. Electroanal. Chem.* **204**, 79 (1986).
- ⁵²D. Henderson and W. R. Smith, *J. Stat. Phys.* **19**, 191 (1978).
- ⁵³S. Lamperski and J. Klos, *J. Chem. Phys.* **129**, 164503 (2008).
- ⁵⁴B. Larsen, *J. Chem. Phys.* **68**, 4511 (1978).
- ⁵⁵E. Gutiérrez-Valladares, M. Lukšič, B. Millán-Malo, B. Hribar-Lee, and V. Vlachy, *Condens. Matter Phys.* **14**, 33003 (2011).
- ⁵⁶H. Jiang and H. Adidharma, *Mol. Simul.* **41**, 727 (2015).
- ⁵⁷A. A. Kornyshev, *J. Phys. Chem. B* **111**, 5545 (2007).
- ⁵⁸Z. A. H. Goodwin, G. Feng, and A. A. Kornyshev, *Electrochim. Acta* **225**, 190 (2017).
- ⁵⁹S. May, *Curr. Opin. Electrochem.* **13**, 125–131 (2019).
- ⁶⁰P. Cats and R. van Roij, *J. Chem. Phys.* **155**, 104702 (2021).
- ⁶¹Y. Georgievskii, C.-P. Hsu, and R. A. Marcus, *J. Chem. Phys.* **110**, 5307 (1999).
- ⁶²L. Blum, *Theoretical Chemistry: Advances and Perspectives* (Academic, New York, 1980), Vol. 5, pp. 1–66.
- ⁶³J. Høye, J. L. Lebowitz, and G. Stell, *J. Chem. Phys.* **61**, 3253 (1974).
- ⁶⁴G. Stell and S. F. Sun, *J. Chem. Phys.* **63**, 5333 (1975).