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The study of the electrical double layer lies at the heart of soft matter physics and biophysics. Here, we address the effects of the image charges on the double layer structure and forces. For electrolyte solutions between two neutral plates, we show that depletion of the salt ions by the image charge repulsion results in short-range attractive and long-range repulsive forces. If cations and anions are of different valency, the asymmetric depletion leads to the formation of an induced electrical double layer. In comparison to a 1:1 electrolyte solution, both the attractive and the repulsive parts of the interaction are stronger for the 2:1 electrolyte solution. For two charged plates, the competition between the surface charge and the image charge effect can give rise to like-charge attraction and charge inversion. These results are in stark contrast with predictions from the Poisson-Boltzmann theory. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4821636>]

I. INTRODUCTION

The study of the electrical double layer resulting from a charged surface is at the heart of colloid and interface sciences.^{1–8} Standard textbook theories of the electrical double layer are based on the Poisson-Boltzmann (PB) theory, a mean-field theory that describes a system in terms of the mean electrostatic potential and the average concentration of the mobile ions. At large surface-charge density, high counterion valency, and high ion concentration – the so-called strong coupling limit – the PB theory fails to capture a number of qualitative effects observed in experiments and simulation, such as like-charge attraction^{9–13} and charge inversion.^{14–18} In this regime, integral-equation methods^{19,20} and other strong-coupling theories²⁴ have been employed to account for the strong interionic correlations. Under weak-coupling conditions, it is generally accepted that the electrical double layer is well described by the PB theory.^{21–26} However, a number of phenomena involving double layers under the weak-coupling conditions, such as the long-range electrostatic attraction between two neutral plates,²⁷ the slow ion transport in the ion channels,^{28,29} and salt effects on bubble coalescence in water,^{30,31} cannot be explained, even qualitatively, by the PB theory.

An obvious effect missing in the PB theory is the self energy of the mobile ions.³² The self energy consists of a local contribution due to the interaction between the ion and the local dielectric medium and a long-range contribution arising from the fluctuation in the electrostatic potential around the test ion. For systems with dielectric discontinuity, which is commonplace because of the much lower dielectric constant of air, lipid membranes, and colloidal particles ($\epsilon \sim 1$) than that of the aqueous solution ($\epsilon \sim 80$), the distortion of the electrostatic potential at the interface known as the image charge effect is an important component of the self energy. The image charge effect plays a key role in the surface tension of electrolyte solutions^{33–37} and the adsorption of polyelectrolytes.³⁸

Here, we examine the electrical double layer structure and forces between two neutral or like-charged plates by accounting for the image charge effects under weak-coupling conditions. For neutral surfaces, we show that the image charge effect results in depletion of the ions near the surface, which gives rise to short-range attraction and long-range repulsion between the plates. If cations and anions are of different valency, the unequal depletion induces charge separation and generates an electrostatic potential. For two like-charged plates, we predict like-charge attraction and charge inversion as a result of the competition between the surface charge and the image charge effect. All these results are in stark contrast with predictions from the usual PB theory.

We considered two parallel plates of infinite thickness of dielectric constant ϵ_P , immersed in an electrolyte solution, of dielectric constant ϵ_S , separated by a distance D . We set $x = 0$ at the mid-plane between the two plates, so the two plate surfaces are located at $x = \pm D/2$. Following the standard model for electrical double layer, the surfaces of the two plates are taken to have a smeared-out charge density σ ($\sigma = 0$ for a neutral surface). Mobile cations and anions are taken as point particles with charge z_+e and z_-e , respectively. The electrolyte solution between the two plates (referred to as the “inner solution” hereafter) is connected with an “outer” bulk reservoir of concentration $c_{\pm}^b$. Each mobile ion in the solution generates an infinite series of image charges because of the dielectric discontinuity as illustrated in Figure 1.

II. THEORY

We treat the electrostatics of our system in the framework of the weak-coupling theory,^{32,39–41} which accounts for the leading fluctuation effects in an electrolyte solution. This theory treats the *physical* weak-coupling condition (low surface charge density, low valency of ions, and low ion concentrations), which can be derived either through a cluster expansion³⁹ or a variational approach.³² We comment that

FIG. 1. Schematic of mobile ions between two charged plates. The purple sphere represents a test ion; white spheres represent its image charges.

the term “weak-coupling theory” used in this work is different from the meaning associated by some researchers in the electrolyte community with that in the work of Netz.²³ Netz considered the counterion-only system by treating the fluctuation effects through a systematic perturbation expansion using the coupling parameter $\Xi \equiv 2\pi z^3 l_B^2 \sigma_s$, where z is the counterion valency, l_B is the Bjerrum length, and σ_s is the surface charge density. Netz showed that the mean-field PB theory is the leading order theory for small Ξ and becomes exact in the limit of $\Xi \rightarrow 0$. Applying the Netz approach explicitly to a surface with dielectric discontinuity, Kanduč and Podgornik²⁶ arrived at a similar result, concluding that the image force only enters as a correction to the leading PB theory. In the weak-coupling theory we employ here, the fluctuation effect on the ion distribution and free energy is treated self-consistently and nonperturbatively, leading to the appearance of the image force effect in the Boltzmann factor. In our theory, we find no limiting condition for which PB theory is valid for the system we consider.

The weak-coupling theory used in this work involves two approximations: First, the hierarchy of multi-ion correlation functions is closed at the two-body level, known as the Loeb closure,⁴² and second, the fluctuation part of the electrostatic potential treated at the Debye-Hückel level⁴³—the interaction between a test charge with its own fluctuation part of the electrostatic potential gives rise to a self-energy that includes the image charge interaction. The weak-coupling theory has also been formulated more systematically using field-theoretical method by a renormalized Gaussian-fluctuation variational approach,^{32,44} which yields a set of self-consistent equations for the mean electrostatic potential $\psi(\mathbf{r})$, the correlation function (Green function) $G(\mathbf{r}, \mathbf{r}')$, and the self energy $u_{\pm}(\mathbf{r})$ of mobile ions. These self-consistent equations are derived in Ref. 32 for a general system of ions with charge distribution function $h_{\pm}(\mathbf{r} - \mathbf{r}')$ in a spatially varying dielectric medium, which, for the present two-plate system, takes the following form:

$$-\nabla \cdot [\varepsilon_0 \varepsilon(\mathbf{r}) \nabla \psi(\mathbf{r})] = \rho_{ex}(\mathbf{r}) + \Gamma(\mathbf{r})(e\lambda_{+z_+} e^{-\beta z_+ e\psi - \beta u_{+}} - e\lambda_{-z_-} e^{\beta z_- e\psi - \beta u_{-}}), \quad (1)$$

$$-\nabla \cdot [\varepsilon_0 \varepsilon(\mathbf{r}) \nabla G(\mathbf{r}, \mathbf{r}')] + 2\Gamma(\mathbf{r})I(\mathbf{r})G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (2)$$

$$u_{\pm}(\mathbf{r}) = \frac{z_{\pm}^2 e^2}{2} \int d\mathbf{r}' d\mathbf{r}'' h_{\pm}(\mathbf{r} - \mathbf{r}') G(\mathbf{r}', \mathbf{r}'') h_{\pm}(\mathbf{r} - \mathbf{r}''), \quad (3)$$

where the spatially varying $\varepsilon(\mathbf{r})$ is

$$\varepsilon(\mathbf{r}) = \begin{cases} \varepsilon_S & \text{for } |x| < \frac{D}{2} \\ \varepsilon_P & \text{for } |x| > \frac{D}{2} \end{cases}.$$

$\rho_{ex}(\mathbf{r}) = \sigma \delta(x \pm D/2)$ denotes the surface charge density at the two plate surfaces and $\Gamma(\mathbf{r})$ is a step-like function to confine the mobile ions within the region between two plates:

$$\Gamma(\mathbf{r}) = \begin{cases} 1 & \text{for } |x| < \frac{D}{2} \\ 0 & \text{for } |x| \geq \frac{D}{2} \end{cases}$$

and $\lambda_{\pm}$ is the fugacity of cations and anions determined from the salt concentration in the outer bulk reservoir. $I(\mathbf{r})$ in Eq. (2) is the local ionic strength,

$$I(\mathbf{r}) = \frac{\beta e^2}{2} [z_+^2 c_+(\mathbf{r}) + z_-^2 c_-(\mathbf{r})], \quad (4)$$

with the number concentration of cations and anions $c_{\pm}(\mathbf{r})$ given by

$$c_{\pm}(\mathbf{r}) = \lambda_{\pm} e^{\mp \beta z_{\pm} e\psi(\mathbf{r}) - \beta u_{\pm}(\mathbf{r})}. \quad (5)$$

The appearance of the self energy in the Boltzmann factor reflects the nonlinear feedback effects of the fluctuation in the renormalized Gaussian variational approach, an aspect that was missing in a perturbation expansion.^{21–23,26} A detailed and in-depth discussion of this point will be given in a future publication.

Inside the semi-infinite plate ($|x| > \frac{D}{2}$), Eq. (1) is simplified to the Laplace equation $\varepsilon_0 \varepsilon_P \nabla^2 \psi(\mathbf{r}) = 0$, which yields a constant ψ in this region due to the requirement that ψ remain finite as $x \rightarrow \pm\infty$. Integrating Eq. (1) across an infinitesimally thin region enclosing the dielectric interface generates the boundary condition as $\mathbf{n} \cdot \nabla \psi = -\sigma/\varepsilon_0 \varepsilon_S$ where $\mathbf{n}$ is the unit outward normal of the plate surface.

The self energy given by Eq. (3) is the reversible work required to assemble the given charge distribution on an ion at the spatial location $\mathbf{r}$ by bringing in the constituent charges from an infinitely dispersed state, where the interaction is zero. This is a unified expression that includes the Born energy of the ion, the interaction between the ion and its ionic atmosphere, as well as self-interaction due to the distortion of the electric field by a spatially varying dielectric function, the latter taking the form of image charge interaction near a sharp dielectric discontinuity. For a spatially inhomogeneous medium, a finite charge distribution in the ion results in a finite value for the short-range part of the self energy in the form of a local Born solvation energy.³² Since the solvent in the gap has a uniform dielectric constant, the Born energy amounts to a constant shift in the reference chemical potential. It is then more convenient to take the point-charge limit $h_{\pm}(\mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. Then Eq. (3) is simplified to

$$u_{\pm}(\mathbf{r}) = \frac{z_{\pm}^2 e^2}{2} G(\mathbf{r}, \mathbf{r}).$$

The point-charge limit produces a diverging self energy of the ion, which can be regularized by subtracting the same-point Green function in the bulk, as done in Ref. 44. The finite part

of the self energy that only includes the image charge and interaction with other ions is now

$$u_{\pm}(\mathbf{r}) = \frac{z_{\pm}^2 e^2}{2} \lim_{\mathbf{r}' \rightarrow \mathbf{r}} \left[G(\mathbf{r}, \mathbf{r}') - \frac{1}{4\pi\epsilon_0\epsilon_S |\mathbf{r} - \mathbf{r}'|} \right]. \quad (6)$$

Equations (1)–(3) constitute a complete set of equations for describing the electrostatics of our system, the general solution of which requires extensive numerical calculation. To avoid solving the high-dimensional Green function, Buff and Stillinger⁴⁰ proposed an approximate solution to Eq. (2) based on the WKB (Wentzel-Kramers-Brillouin) approximation: the Green function is first solved for a constant ionic strength, but in the resulting expression the ionic strength is replaced by its local value that depends on the local ion concentrations. With the approximate $G(\mathbf{r}, \mathbf{r}')$, the self energy can be written as a function of the one-dimensional coordinate x along the normal of the plate surface in the following form:

$$u_{\pm}(x) = \frac{e^2 z_{\pm}^2}{8\pi\epsilon_0\epsilon_S} [-\kappa(x) + J(x, \kappa(x))],$$

where

$$J(x, \kappa(x)) = \sum_{m=2,4,6,\dots} \frac{2f^m e^{-\kappa(x)(mD)}}{mD} + \sum_{m=1,3,5,\dots} f^m \left[\frac{e^{-\kappa(x)(mD+2x)}}{mD+2x} + \frac{e^{-\kappa(x)(mD-2x)}}{mD-2x} \right], \quad (7)$$

with $f = (\epsilon_S - \epsilon_P)/(\epsilon_S + \epsilon_P)$ representing the dielectric discontinuity. $\kappa(\mathbf{r}) = [2I(\mathbf{r})/\epsilon_0\epsilon_S]^{1/2}$ is the inverse of the local screening length. The first term in the self energy accounts for the local ionic atmosphere surrounding the test ion at the level of the Debye-Hückel theory.⁴³ The second term represents the accumulated effects of interaction from all the image charges

generated by a test ion. In our case $f > 0$, so all image-charge interactions are repulsive.

In the outer bulk reservoir, ψ is set to zero. From Eq. (5), the fugacity of the ions is related to the bulk salt concentration via $\lambda_{\pm} = c_{\pm}^b e^{-\beta z_{\pm}^2 e^2 \kappa_b / 8\pi\epsilon_0\epsilon_S}$, where κ_b is the inverse screening length in the bulk. By solving Eqs. (1), (5), and (7) iteratively, we obtain the mean electrostatic potential $\psi(x)$ and the ion distribution $c_{\pm}(x)$. Finally, the grand potential per area is constructed as

$$\beta G = \int dx \left[\frac{\beta\epsilon_0\epsilon_S}{2} (\nabla\psi)^2 + c_+ \ln \frac{c_+}{\lambda_+} - c_+ + c_- \ln \frac{c_-}{\lambda_-} - c_- + F_{fl} \right], \quad (8)$$

where $F_{fl} = \kappa^2 \int_0^1 [\alpha J(\alpha\kappa) - \alpha\kappa] d\alpha / 4\pi$ is the fluctuation contribution obtained by the charging method.^{41,45} The force per unit area between the two plates is given by $p = -(\partial G / \partial D)_{\lambda_{\pm}} - p_b$, where p_b is the bulk osmotic pressure.

III. ION DEPLETION AND DEPLETION FORCE

We first study the behavior of equal-valency cations and anions ($z_+ = z_-$) between two neutral plates. Because the cation and anion have equal self energy in this case, there is no charge separation, and the mean electrostatic potential is everywhere zero. However, from Eq. (7), the image charge repulsion increases the self energy of ions in the inner solution, and consequently ions are depleted to the outer bulk solution (i.e., $c(x) < c^b$). The image charge effect is stronger near the interface and as the separation distance D decreases; see Figures 2(a)–2(c). The depletion is nearly complete close to the interface and when the gap is sufficiently small. In contrast, the PB theory predicts a trivial uniform ion concentration of the bulk value.

FIG. 2. Ion depletion and depletion force between two neutral plates with $\epsilon_P = 2.5$, $z_+ = z_- = 1$. ((a)–(c)) Effect of varying D on the ion concentration profile, $\epsilon_S = 80$ and $c^b = 0.01$ M. ((d) and (e)) Mid-plane value $c(0)/c^b$ as a function of D for several values of c^b and ϵ_S , respectively. (f) Pressure between two plates as a function of D (in units of the osmotic pressure of a 1 mM ideal solution). The inset shows the change from attraction to repulsion.

The mid-plane value of the ion concentration $c(0)$ as a function of the separation is shown in Figures 2(d) and 2(e), which follows the analytical relation $c(0)/c^b = (1 - f e^{-\kappa(0)D}) z_{\pm}^2 l_B / D$, where l_B is the Bjerrum length of the liquid and is approximately 0.7 nm for water. For small separations, nearly all the ions are depleted from the inner solution as shown by Figure 2(a) and the initial plateau of the curves in Figures 2(d) and 2(e). A length scale D_1 for the onset of this regime can be obtained by the location of the fastest rise from the plateau (i.e., maximum of $\partial^2 c(0)/\partial D^2$) with the result $D_1 = -z_{\pm}^2 l_B \ln(1 - f)/(3 + \sqrt{3})$ ($\kappa_b D_1 \ll 1$). Note that D_1 increases with decreasing ϵ_S and is independent of the salt concentration. In the limit of large separation, the higher order image charge effect from the opposing surface becomes negligible compared to the first image charge of the ion; this defines a length scale D_2 , which to leading order is given by the screening length $D_2 = \kappa_b^{-1}$. For $D > D_2$, the image charge effect is restricted to a depletion layer of thickness $D_2/2$ from the plate surface (see Figure 2(c)), and the mid-plane concentration approaches the bulk value. Intermediate separation is defined by $D_1 < D < D_2$, where the image charge interaction affects the entire region between the two plates but the mid-plane concentration is not too much lower than the bulk value; see Figure 2(b).

Ion depletion leads to an attractive well at short distances. The bottom of the well, of depth $2c^b$ extends to separation D_1 , beyond which the attraction decays with the scale of the screening length; see Figure 2(f). Interestingly, on this length scale and beyond, the interaction becomes repulsive as shown

in the inset. This phenomenon can be understood from the ion profile at large separation: while the middle portion of the profile has reached the bulk plateau, the thickness of the depletion layer still shrinks slightly with increasing separation because of the decaying influence of higher order image charges. Thus, increasing D by δD in plate separation brings more than $2c^b \delta D$ ions per plate area to the inner solution from the reservoir, which gives rise to the repulsive force between the two plates. We note that a similar behavior and explanation were given in the work of Tamashiro and Pincus⁵⁷ who pointed out that the transition of the depletion force from short-range attraction to long-range repulsion is a result of the disappearance of the overlapping of the depletion layer. However, their work used the PB theory; the depletion free energy used in their work was introduced artificially and extraneously without resorting to an explicit physical origin. The force profile shown in Figure 2(f) has also previously been reported by Bell and Levine.⁴¹ Our work provides the first study of the ion profiles and analysis of the length scales for the image-charge induced depletion.

IV. ASYMMETRIC DEPLETION AND INDUCED ELECTRICAL DOUBLE LAYER

The image charge contribution to the self energy is quadratic in the valency of the ions. Thus, for an asymmetric salt with unequal valency, the distribution of the cations and anions will be different, leading to charge separation near the wall. Figure 3(a) shows charge separation for a 2:1 electrolyte solution. The divalent cations are pushed further away

FIG. 3. The induced electrical double layer of 2:1 electrolyte solution between two neutral plates. ((a) and (b)) Ion concentration profile and dimensionless electrostatic potential profile for $D = 2$ nm, $\epsilon_S = 80$, $\epsilon_P = 2.5$, and $c^b = 0.01$ M. (c) Induced electrostatic potential at the plate surface ψ_s as a function of D . (d) Pressure as a function of D (in units of the osmotic pressure of a 1 mM ideal solution) for a 0.01 M 2:1 electrolyte solution (solid line) in comparison with a 0.015 M 1:1 electrolyte solution (dashed line). The comparison is made under condition of equal amount of ions in bulk.

FIG. 4. Concentration profiles for monovalent (blue) and divalent (red) cations. (a) Cation profiles for 0.01 M 1:1 electrolyte alone and 0.01 M 2:1 electrolyte alone in the reservoir. (b) Cation profiles when both 1:1 electrolyte and 2:1 electrolyte are present with the same respective concentration in the reservoir as in (a).

from the wall than the monovalent anions, resulting in the formation of an effective double layer with a finite induced surface potential, even though there is no fixed surface charge. The induced electrostatic potential in the electric double layer (Figure 3(b)), with the sign determined by $z_-^2 - z_+^2$, can be understood as a response of the system to the difference in the self energy between the cations and anions so as to maintain overall charge neutrality. The situation is similar to the Galvani potential across the interface between two co-existing salt solutions and the local charge separation at the interface,^{32,48,49} which are induced by the solvation energy difference between the cations and the anions. As shown in Figure 3(c), the potential is stronger at smaller separation D and approaches an asymptotic value of the single surface for large D . The induced electrostatic potential depends primarily on the dielectric constants of the media and valency of the ions; it depends weakly on the bulk concentration c^b as a result of screening. In comparison to a 1:1 electrolyte solution, both the attractive and the repulsive parts of the interaction are stronger for the 2:1 electrolyte solution with the same total number of ions.

Reference 57 considered unequal depletion of the cations and anions by artificially choosing two different depletion potentials respectively for the cations and anions near the surface. Although their system is for 1:1 salts, and these depletion potentials were not given an explicit physical origin, inasmuch as unequal depletion of cations and anions leads to charge separation and generates an induced surface potential, and the interaction force is attractive at short range but repulsive at long range, their results are similar to ours reported in this section.

Complex ion depletion behavior arises when the salt solution is a mixture of 1:1 electrolyte and 2:1 electrolyte. Cations of different valency are strongly correlated and their distributions markedly differ from the profiles when each electrolyte is present alone; see Figure 4. Compared to the profiles of when each electrolyte is present alone, the concentration of monovalent cations in the gap increases while the concentration of divalent cations is considerably reduced; a large portion of divalent cations are replaced by the monovalent cations which have lower self energy.

V. LIKE-CHARGE ATTRACTION AND CHARGE INVERSION

We now consider plates whose surfaces are weakly charged. For concreteness, we take the surface charges to be positive. Here, the counterions are attracted to the surface due to Coulomb forces; however, image force repulsion is always operative and tends to exclude the counterions from the surface. The co-ions are more strongly repelled by the surface since both the surface charge and the image charge act in the same direction. The interplay between these factors leads to rich and complex behavior in the double layer structure and the interaction forces between two like-charged plates. The role of surface charge becomes more important as the surface charge density increases, while the image charge effect gets stronger with the increase of salt concentration and counterion valency.

Figures 5(a) and 5(b) show the double layer structure for a 1:1 electrolyte solution between two weakly charged surfaces at two separation distances. For small separation distances ($D = 1$ nm), the ion concentration profiles calculated by our theory drastically differ from the PB mean-field results and are dominated by the image charge effect. Excess counterions are not accumulated at the plate surface but are instead pushed to the middle of the gap. For large D , the dominance of the image charge effect is confined to a depletion layer near the plate surface (see Figure 5(b)). Due to the image repulsion, counterions cannot accumulate within the depletion layer, which significantly reduces the screening of the surface charge on this length scale. Beyond the depletion layer, the ion concentration profiles approach the PB mean-field results.

The PB mean-field theory predicts purely repulsive force between two like-charged plates for all separation distances.^{1,2,25} However, by incorporating the image charge effect, the force profile (see Figures 5(c) and 5(d)) develops an attractive well at small plate separations under conditions of small surface charge density or high salt concentration, as a consequence of the depletion of the mobile ions. Attraction between like-charged surfaces observed in experiments and simulations⁹⁻¹³ have previously been explained by the correlation effects in the strong coupling regime due to the formation of 2D crystal-like layer of multivalent counterions in the

FIG. 5. Electrical double layer structure and force for 1:1 electrolyte solution between two charged plates. ((a) and (b)) Ion concentration profiles for $D = 1$ nm and $D = 10$ nm, respectively. $\sigma = 1e/50 \text{ nm}^2$ and $c^b = 0.1$ M. Pressure as a function of D (in units of the osmotic pressure of a 1 M ideal solution) for (c) effects of surface charge density σ at $c^b = 0.1$ M and (d) effects of c^b at $\sigma = 1e/100 \text{ nm}^2$.

vicinity of highly charged surfaces.²⁴ However, here we show that attraction can also appear under the weak-coupling condition with monovalent ions.

The competition between the surface charge and the image charge effect can give rise to another counter-intuitive phenomenon known as charge inversion. In the diffuse electrical double layer predicted by the PB mean-field theory, the local charge in the inner solution is always of the opposite sign to the surface charge regardless of the ion valency. However, if the co-ions have higher valency than the counterions, the stronger image charge repulsion for the co-ions pushes them farther away from the surface, necessitating a greater amount of counterions to fill the space in between. With the increase of salt concentration, the accumulated counterions near the plate surface may exceed the amount that is required to neutralize the surface charge, giving rise to a sign change in the local electrostatic potential. We define $\tau(x) = \sigma + \int_{-D/2}^x \rho(x')dx'$ as the local accumulative charge density (integrated from the surface) ($\tau(-D/2) = \sigma$ and $\tau(0) = 0$). The double layer structures for 2:1 electrolyte solutions of different salt concentrations are shown in Figures 6(a) and 6(b). At low salt concentration ($c^b = 0.015$ M), the electrostatic potential profile is positive and convex everywhere; $\tau(x)/\sigma$ decays monotonously from the plate surface to the mid-plane, indicating the normal neutralization of the surface charge. As the salt concentration increases to a critical value ($c_{cr}^b = 0.022$ M for the given surface charge and plate separation), ψ shows a plateau in the middle region as $\tau(x)$ approaches zero. For salt concentrations exceeding this critical value, charge inversion occurs: ψ is convex near the plate surface but becomes concave in the middle region. Excess coun-

terions overcharge the plate surface as reflected by the negative $\tau(x)$. The co-ions accumulate outside this diffuse layer of inverted surface charge and serve to screen it. The critical salt concentration c_{cr}^b for charge inversion increases with the increase of σ as shown in Figure 6(c). In addition, c_{cr}^b decreases as D increases and approaches the asymptotic value of an isolated charged plate for large separation. The phenomenon elucidated here as a result of image charge effects offers an alternative explanation of charge inversion based on either counterion adsorption to the surface or the correlation effects.^{15–18}

VI. APPLICATIONS

The image charge effects elucidated in this work affect a wealth of structural and dynamic behaviors in physical chemistry, colloidal science, soft-matter, and biophysics. The increase of self energy caused by the image repulsion at small separations is closely related to the slow ion transport in ion channels where the lipid constituting the channel wall has a much lower dielectric constant than the aqueous solution.^{28,29} However, previous theories either ignore the screening effects by considering a single ion, or include the image force only on the test ion thus overestimating the screening effect.^{46,47} The dramatic suppression of divalent ion concentration in the dielectric gap in the presence of monovalent ions demonstrated in our work suggests that (1) the study of the transport of the divalent ions must consider the presence of the monovalent ions; and (2) in channels that specifically transport divalent ions, such as the calcium channel,^{50,51} there must be strong surface charge or specific ion-surface interaction to counter

FIG. 6. Charge inversion for 2:1 electrolyte solution between two charged plates of $\sigma = 1e/100 \text{ nm}^2$. (a) Dimensionless electrostatic potential profile and (b) local accumulative charge density at $D = 5 \text{ nm}$ for three different values of c^b . (c) Critical salt concentration for charge inversion c_{cr}^b versus σ . The dashed line shows c_{cr}^b for an isolated charged plate.

the image repulsion to make it favorable for the divalent ions to enter the channel. Furthermore, the image force is an important factor in any systematic theory for understanding the Jones-Ray^{52,53} and Hofmeister series^{35,54} effects for the surface tension of electrolyte solutions. In addition, the long-range repulsion between two neutral surfaces predicted by our theory provides a possible explanation to the long-standing puzzle: the effect of salts in suppressing bubble coalescence that leads to the foaminess of ocean waves.³⁰ Because the image force is proportional to $z_{\pm}^2$, our theory also predicts that the inhibition of bubble coalescence is more effective with the ions of high valency, in agreement with the experiment results.³¹

The image charge effect on the double layer of a charged surface is twofold: depletion of the ions near the surface, giving rise to an attractive component in the interaction, and reduced screening of the surface charge, leading to increased electrostatic repulsion. Neither of these effects are captured by the PB theory. However, many important model parameters in colloidal and surface sciences such as the surface charge density and Hamaker constants are obtained by fitting the experiment data to the PB theory.¹ The surface force measurements of Kekicheff and Spalla²⁷ raised doubt about this procedure. In light of our results, we propose that these parameters be re-examined using our improved theory to incorporate the image charge effects. Our theory also indicates that the zeta potential predicted by the PB theory is qualitatively wrong under conditions of charge inversion. The charge-inversed double layer structure should lead to reversal in the direction

of the electroosmotic flow and qualitatively change the electrophoretic mobility of charged particles.^{55,56}

- ¹J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, London, 1992).
- ²D. Andelman, in *Soft Condensed Matter Physics in Molecular and Cell Biology*, edited by W. C. K. Poon and D. Andelman (Taylor and Francis, Boca Raton, Florida, 2000).
- ³B. Honig and A. Nicholls, *Science* **268**, 1144–1149 (1995).
- ⁴V. Dahirel and M. Jardat, *Curr. Opin. Colloid Interface Sci.* **15**, 2–7 (2010).
- ⁵Y. Levin, *Rep. Prog. Phys.* **65**, 1577–1632 (2002).
- ⁶P. Attard, *Curr. Opin. Colloid Interface Sci.* **6**, 366–371 (2001).
- ⁷G. M. Luo, S. Malkova, J. Yoon, D. G. Schultz, B. H. Lin, M. Meron, I. Benjamin, P. Vanysek, and M. L. Schlossman, *Science* **311**, 216–218 (2006).
- ⁸E. M. Knipping, M. J. Lakin, K. L. Foster, P. Jungwirth, D. J. Tobias, R. B. Gerber, D. Dabdub, and B. J. Finlayson-Pitts, *Science* **288**, 301–306 (2000).
- ⁹W. R. Bowen and A. Q. Sharif, *Nature* **393**, 663–665 (1998).
- ¹⁰W. M. Gelbart, R. F. Bruinsma, P. A. Pincus, and V. A. Parsegian, *Phys. Today* **53**, 38–44 (2000).
- ¹¹P. Linse and V. Lobaskin, *Phys. Rev. Lett.* **83**, 4208–4211 (1999).
- ¹²R. Kjellander, S. Marelja, R. M. Pashley, and J. P. A. Quirk, *J. Chem. Phys.* **92**, 4399–4407 (1990).
- ¹³Y. S. Jho, M. Kanduc, A. Naji, R. Podgornik, M. W. Kim, and P. A. Pincus, *Phys. Rev. Lett.* **101**, 188101 (2008).
- ¹⁴R. Messina, C. Holm, and K. Kremer, *Phys. Rev. Lett.* **85**, 872–875 (2000).
- ¹⁵K. Besteman, M. A. G. Zevenbergen, H. A. Heering, and S. G. Lemay, *Phys. Rev. Lett.* **93**, 17082 (2004).
- ¹⁶T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, *Phys. Rev. Lett.* **85**, 1568–1571 (2000).
- ¹⁷A. Y. Grosberg, T. T. Nguyen, and B. I. Shklovskii, *Rev. Mod. Phys.* **74**, 329–345 (2002).
- ¹⁸P. Kekicheff, S. Marcelja, T. J. Senden, and V. E. Shubin, *J. Chem. Phys.* **99**, 6098–6113 (1993).

- ¹⁹R. Kjellander, T. Akesson, B. Jonsson, and S. Marelja, *J. Chem. Phys.* **97**, 1424–1431 (1992).
- ²⁰J. W. Zwanikken and M. Olvera de la Cruz, *Proc. Natl. Acad. Sci. U.S.A.* **110**, 5301–5308 (2013).
- ²¹P. Attard, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.* **88**, 4987–4996 (1988).
- ²²P. Attard, D. J. Mitchell, and B. W. Ninham, *J. Chem. Phys.* **89**, 4358–4367 (1988).
- ²³R. R. Netz, *Eur. Phys. J. E* **5**, 557–574 (2001).
- ²⁴A. Naji, S. Jungblut, A. G. Moreirac, and R. R. Netz, *Physica A* **352**, 131–170 (2005).
- ²⁵J. C. Neu, *Phys. Rev. Lett.* **82**, 1072–1074 (1999).
- ²⁶M. Kanduč and R. Podgornik, *Eur. Phys. J. E* **23**, 265–274 (2007).
- ²⁷P. Kekicheff and O. Spalla, *Phys. Rev. Lett.* **75**, 1851–1855 (1995).
- ²⁸A. Parsegian, *Nature* **221**, 844–846 (1969).
- ²⁹T. Bastug and S. Kuyucak, *Biophys. J.* **84**, 2871–2882 (2003).
- ³⁰V. S. J. Craig, B. W. Ninham, and R. M. Pashley, *Nature* **364**, 317–319 (1993).
- ³¹V. S. J. Craig, B. W. Ninham, and R. M. Pashley, *J. Phys. Chem.* **97**, 10192–10197 (1993).
- ³²Z.-G. Wang, *Phys. Rev. E* **81**, 021501 (2010).
- ³³B. C. Garret, *Science* **303**, 1146–1147 (2004).
- ³⁴L. Onsager and N. N. T. Samaras, *J. Chem. Phys.* **2**, 528–536 (1934).
- ³⁵Y. Levin, A. P. dos Santos, and A. Diehl, *Phys. Rev. Lett.* **103**, 257802 (2009).
- ³⁶Y. Levin, *Phys. Rev. Lett.* **102**, 147803 (2009).
- ³⁷A. Onuki, *J. Chem. Phys.* **128**, 224704 (2008).
- ³⁸R. R. Netz and J. F. Joanny, *Macromolecules* **32**, 9013–9025 (1999).
- ³⁹S. L. Carnie and G. M. Torrie, *Adv. Chem. Phys.* **56**, 141–253 (1984).
- ⁴⁰F. P. Buff and F. H. Stillinger, *J. Chem. Phys.* **39**, 1911–1923 (1963).
- ⁴¹G. M. Bell and S. Levine, *J. Chem. Phys.* **49**, 4584–4599 (1968).
- ⁴²A. L. Loeb, *J. Colloid Sci.* **6**, 75–91 (1951).
- ⁴³P. Debye and E. Hückel, *Phys. Z.* **24**, 185–206 (1923).
- ⁴⁴R. R. Netz and H. Orland, *Eur. Phys. J. E* **11**, 301–311 (2003).
- ⁴⁵R. A. Marcus, *J. Chem. Phys.* **24**, 979–989 (1956).
- ⁴⁶P. C. Jordan, R. G. Bacquet, J. A. McCammon, and P. Tran, *Biophys. J.* **55**, 1041–1052 (1989).
- ⁴⁷G. Moy, B. Corry, S. Kuyucak, and S. H. Chung, *Biophys. J.* **78**, 2349–2363 (2000).
- ⁴⁸R. Wang and Z.-G. Wang, *J. Chem. Phys.* **135**, 014707 (2011).
- ⁴⁹W. Kung, F. J. Solis, and M. O. de la Cruz, *J. Chem. Phys.* **130**, 044502 (2009).
- ⁵⁰E. Gouaux and R. MacKinnon, *Science* **310**, 1461–1465 (2005).
- ⁵¹D. Boda, M. Valisko, B. Eisenberg, W. Nonner, D. Henderson, and D. Gillespie, *J. Chem. Phys.* **125**, 034901 (2006).
- ⁵²G. Jones and W. A. Ray, *J. Am. Chem. Soc.* **59**, 187–198 (1937).
- ⁵³P. B. Petersen and R. J. Saykally, *J. Am. Chem. Soc.* **127**, 15446–15452 (2005).
- ⁵⁴F. Hofmeister, *Arch. Exp. Pathol. Pharmacol.* **24**, 247–260 (1888).
- ⁵⁵A. Martin-Molina, M. Quesada-Perez, F. Galisteo-Gonzalez, and R. Hidalgo-Alvarez, *J. Chem. Phys.* **118**, 4183–4189 (2003).
- ⁵⁶A. Kubickova, T. Krizek, P. Coufal, M. Vazdar, E. Wernersson, J. Heyda, and P. Jungwirth, *Phys. Rev. Lett.* **108**, 186106 (2012).
- ⁵⁷M. N. Tamashiro and P. Pincus, *Phys. Rev. E* **60**, 6549–6559 (1999).