Fluctuation in electrolyte solutions: The self energy

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(Received 12 August 2009; published 9 February 2010)

We address the issue of the self energy of the mobile ions in electrolyte solutions within a general Gaussian renormalized fluctuation theory using a field-theoretic approach. We introduce the Born radii of the ions in the form of a charge distribution allowing for different Born radii between the cations and anions. The model thus automatically yields a theory free of divergences and accounts for the solvation of the ions at the level of continuous dielectric media. In an inhomogeneous dielectric medium, the self energy is in general position dependent and differences in the self energy between cations and anions can give rise to local charge separation in a macroscopically neutral system. Treating the Born radius a as a smallness parameter, we show that the self energy can be split into an $O(a^{-1})$ nonuniversal contribution and an $O(a^0)$ universal contribution that depends only on the ion concentration, valency, and the spatially varying dielectric constant. For a weakly inhomogeneous dielectric medium, the nonuniversal part of the self energy is shown to have the form of the Born energy with the local dielectric constant. This self energy is incorporated into the Poisson-Boltzmann equation as a simple means of including this local fluctuation effect in a mean-field theory. We illustrate the phenomenon of charge separation by considering cations and anions of difference sizes and valencies in a periodic dielectric medium.

I. INTRODUCTION

The Poisson-Boltzmann (PB) equation is the most common theoretical approach for studying electrostatic effects in the presence of salt ions [1] and is used to describe a wide variety of phenomena in soft-matter physics and biomolecular systems [2–8]. The PB equation determines the electrostatic potential ψ in a dielectric medium due to the presence of some fixed charge density $\rho_{ex}(\mathbf{r})$ and mobile cations and anions. In SI units, the PB equation reads

$$-\nabla \cdot (\varepsilon \nabla \psi) = \rho_{ex} + c_+^{(0)} e z_+ \exp(-\beta e z_+ \psi)$$
$$- c_-^{(0)} e z_- \exp(\beta e z_- \psi). \quad (1.1)$$

In Eq. (1.1), ε is the permittivity of the medium which can be spatially varying, e is the value of the elementary charge, z_+ and z_- are, respectively, the (absolute value of the) valency of the cations and anions, and $c_+^{(0)}$ and $c_-^{(0)}$ are the number concentration of the cations and anions far away from the fixed charges.

The PB theory is a mean-field theory that describes a system in terms of the average electrostatic potential and average concentration of mobile ions. Furthermore, in the most popular version of the PB theory, the cations and anions are considered to be volumeless point charges, although excluded volume effects can be accounted for either through an incompressibility constraint [9], in a virial expansion [10], or in the form of an exclusion zone [11]. In recent years, there has been a growing interest in both the specific ion effects (manifested for example in the Hofmeister series [12]) and fluctuation effects (manifested, for example, in attraction of like-charged macroions [13]) in charged systems. While the explanation of the specific ion effects involve a multiplicity

of factors, such as the finite polarizability of the ions [14,15] and the dispersion forces [16], an obvious effect that is missing in the PB treatment is the Born solvation energy or more generally the self energy of the small ions. (In conformation with the use of the field-theoretic description in the rest of this paper, we will henceforth use the term self energy.) For an ion of radius a of valency z in a dielectric medium of permittivity ε, the self energy in the Born model [17] is

$$u = \frac{z^2 e^2}{8 \pi \varepsilon a}. \quad (1.2)$$

In a spatially uniform system, the self energy is a constant, which can usually be absorbed into a redefinition of the reference chemical potential of the ion. However, for a spatially varying dielectric medium, the self energy will be spatially dependent, and since the self energy depends on the valency and ion radius, the spatial dependence will in general be different for the cations and anions and this difference can lead to local charge separation. Such an effect is completely missed by the PB equation, Eq. (1.1). Indeed, in the absence of any fixed charges, the PB equation yields the trivial solution $\psi=0$ (or some constant), which implies complete local charge neutrality *and* uniform salt concentration.

The self energy of an ion includes both the Born solvation effects and other longer-range effects. A well-known example is the depletion of ions near the water-air interface. Again, in the absence of any external fixed charges, the PB equation, as applied to the entire system, would predict $\psi=0$, leading to the trivial and erroneous solution of a uniform distribution for both cations and anions. A nontrivial solution was obtained first by Wagner [18] and later more systematically by Onsager and Samaras [19], by focusing on a test ion and solving the linearized PB equation (the Debye-Hückel approximation [20]) for the test ion. The repulsion from the image charge gives rise to a self energy that amounts to a

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surface repulsive potential for the ions leading to their depletion from the interface. The interplay between the image forces (what will be termed the universal part of the self energy in this work) and the Born solvation (what will be termed the nonuniversal part of the self energy) has been shown to partially explain the Hofmeister series in the surface tension of salt solutions when a finite interfacial width is assumed [21].

The self energy is closely related to fluctuation in a charged system: it is the energy associated with a highly localized charge fluctuation—that of gathering a finite amount of infinitely dispersed charges into a small space. Indeed, in a strict mean-field formulation as embodied by the PB equation, the issue of self energy does not rise. It should be emphasized that, in spite of its namesake, the self energy is not just a single-ion effect, but includes interaction effects with other ions. In field-theoretic approaches, the self energy is the same-point Green's function, which is infinite for point-charge models without a microscopic cutoff. The divergent part is usually either discarded, absorbed into a redefined reference state, or regularized through some renormalization procedure [22–25]. These procedures are permissible as long as the discarded infinity is a constant. Such is generally not the case when the dielectric constant is position dependent. Other authors introduce an *ad hoc* mesoscopic cutoff [26,27] following an argument similar to the Debye frequency for the density of states in the calculation of the heat capacity of solids [28]. Still others introduce a projection operator to project out the local part of the self energy effectively introducing a cutoff. We will show that it is possible—in fact more natural—to explicitly allow a finite charge distribution that can be different for the cations and anions, which automatically yields a theory free of divergences and accounts for the Born solvation of the ions.

In this work, we develop a fluctuation theory that explicitly incorporates the Born solvation energy of the ions in a generally spatially varying dielectric medium using a field-theoretic approach. Field-theoretical methods have been used by several groups in studying various aspects of the electrostatic interactions [22,24,25,29–32]. While a natural approach to studying fluctuation is to perform a systematic loop expansion, as in the work of Refs. [22–24], we adopt a variational approach in this work using the Gibbs-Feynman-Bogoliubov bound [33,34], which has been used in various contexts by a number of authors [32,35–37]. With a Gaussian reference action, the variational approach amounts to a self-consistent Hartree approximation [38], which includes a subset of infinite diagrams. Therefore, the result of this work is a nonperturbative fluctuation theory for mobile ions in an inhomogeneous medium that also accounts for the ion solvation effects.

The rest of the paper is organized as follows. In Sec. II, we introduce the model and formulate the exact partition function starting from the field-theoretical representation. Then we apply a variational approach based on the Gibbs-Feynman-Bogoliubov variational principle by using a Gaussian reference action functional. The variational procedure leads to a modified Poisson-Boltzmann equation and an equation for the Green's function. In Sec. III, we examine the self energy for the simple case of a bulk electrolyte solution highlighting the effects due to the difference in the self energy between the cations and anions. In Sec. IV, we examine the general structure of the self energy in a weakly inhomogeneous dielectric medium. We show that the self energy can be split into a nonuniversal piece that depends inversely on the ion radius and a universal piece that is independent of this microscopic length scale. The nonuniversal part takes the form of a Born energy with the *local* dielectric constant. In Sec. V, we propose an augmented PB equation with the nonuniversal part of the self energy incorporated, as a simple mean-field approach for capturing the leading effects due to dielectric inhomogeneity. We demonstrate the phenomenon of charge separation resulting from differences in self energy for the anions and cations in Sec. VI by considering mobile ions in a periodically varying dielectric medium. Section VII summarizes our key results with some concluding remarks.

II. GENERAL THEORY

We formulate our theory by considering a fixed charge distribution $e\rho_{ex}(\mathbf{r})$ in the presence of small mobile cations of valency z_+ and anions of valency z_-, in a dielectric medium of permittivity $\varepsilon(\mathbf{r})$. e is the elementary charge, and for convenience of notation, we have written the charge density as a (signed) number density times the elementary charge. The ions are otherwise taken to be point particles; however, the charge on an ion is assumed to have a finite spread around the position of the particle given by a short-ranged distribution function $h_\pm(\mathbf{r}-\mathbf{r}_i)$ for the ith ion. (In this work, the subscript $\pm$ in an expression means that the expression applies for both cations and anions.) We may think of the role of the function $h_\pm(\mathbf{r}-\mathbf{r}_i)$ as introducing a finite radius for the ions (not in the sense of excluded volume, but in the sense of charge distribution). The point-charge model corresponds to setting $h_\pm(\mathbf{r}-\mathbf{r}_i)=\delta(\mathbf{r}-\mathbf{r}_i)$. The point-charge limit will be invoked for any properties that are well behaved in this limit. However, for the self energy, it is crucial to keep the distribution function with a finite range.

As our interest in this work is in a coarse-grained description, it is not our concern to have a microscopically accurate model for the charge distribution. For our purpose, the only requirement is that the charge distribution model reproduces the Born solvation energy. This single constraint leaves considerable freedom in the choice of the function $h_\pm$; the choice can therefore be made purely based on mathematical convenience. A convenient choice is the Gaussian distribution of the form

$$h_\pm = \left(\frac{1}{2a_\pm^2}\right)^{3/2} \exp\left[-\frac{\pi(\mathbf{r}-\mathbf{r}')^2}{2a_\pm^2}\right]. \quad (2.1)$$

It will be easily seen that this distribution yields the Born energy of a single ion, Eq. (1.2). We will henceforth refer to $a_\pm$ as the Born radius.

Introducing the particle density operator for the ions

$$\hat{c}_\pm(\mathbf{r}) = \sum_{i=1}^{n_\pm} \delta(\mathbf{r}-\mathbf{r}_i) \quad (2.2)$$

the total charge density is then

$$e\rho(\mathbf{r}) = e\rho_{ex}(\mathbf{r}) + e \int d\mathbf{r}'[z_+ h_+(\mathbf{r}' - \mathbf{r})\hat{c}_+(\mathbf{r}')$$
$$- z_- h_-(\mathbf{r}' - \mathbf{r})\hat{c}_-(\mathbf{r}')]. \tag{2.3}$$

The Coulomb energy of the system, including the self energy, is

$$H = \frac{e^2}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) C(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}'), \tag{2.4}$$

where $C(\mathbf{r}, \mathbf{r}')$ is the Coulomb operator given by

$$-\nabla \cdot [\varepsilon \nabla C(\mathbf{r}, \mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}'). \tag{2.5}$$

The canonical partition function of the system is

$$Q = \frac{1}{n_+! n_-! v_+^{n_+} v_-^{n_-}} \int \prod_{i=1}^{n_+} d\mathbf{r}_i \prod_{j=1}^{n_-} d\mathbf{r}_j \exp(-\beta H), \tag{2.6}$$

where $v_\pm$ is some volume scale which can be taken, for example, to be the cube of the de Broglie wavelength, but the choice can be arbitrary as it merely shifts the value of the chemical potential.

We transform the partition function into a field-theoretic representation by the usual Hubbard-Stratonovich transformation via the introduction of a field variable $\xi(\mathbf{r})$ to decouple the quadratic interaction in Eq. (2.4). This gives

$$Q = \frac{1}{n_+! n_-! v_+^{n_+} v_-^{n_-}} \frac{1}{Z_C} \int \prod_{i=1}^{n_+} d\mathbf{r}_i \prod_{j=1}^{n_-} d\mathbf{r}_j \int D\xi$$
$$\times \exp\left\{ -\beta \int d\mathbf{r} \left[\frac{1}{2}\varepsilon(\nabla\xi)^2 + i\rho e \xi \right] \right\}, \tag{2.7}$$

where Z_C is the normalization factor given by

$$Z_C = \int D\xi \exp\left[-\frac{1}{2}\beta \int d\mathbf{r} \varepsilon(\nabla\xi)^2 \right] = [\det(\beta^{-1}C)]^{1/2}. \tag{2.8}$$

To economize notation, we introduce nondimensionalized and scaled quantities. We define a dimensionless field ϕ by

$$\phi = \beta e \xi \tag{2.9}$$

and a scaled permittivity

$$\epsilon = \varepsilon/(\beta e^2). \tag{2.10}$$

Furthermore, we choose $k_B T$ as the unit of energy, so that we may set $\beta = 1$. Note that the scaled permittivity ϵ has the dimension of an inverse length; it is related to the Bjerrum length l_b via

$$l_b = \frac{1}{4\pi\epsilon}. \tag{2.11}$$

For an inhomogeneous dielectric medium, ϵ will turn out to be more convenient than l_b. With these scalings, the only quantities in our theory that have dimensions are those related to length such as the position, the screening length, and the density (concentration).

It is convenient to work with the grand canonical ensemble with chemical potentials μ_+ and μ_- for the cations

and anions, respectively. The grand partition function is

$$\Xi = \sum_{n_+=0}^{\infty} \sum_{n_-=0}^{\infty} Q(n_+, n_-) e^{n_+\mu_+} e^{n_-\mu_-}. \tag{2.12}$$

The integration and summation over the degrees of freedom of the mobile ions can be easily performed and we obtain

$$\Xi = \frac{1}{Z_C} \int D\phi \exp\{-L[\phi]\}, \tag{2.13}$$

where the "action" L is

$$L = \int d\mathbf{r} \left[\frac{1}{2}\epsilon(\nabla\phi)^2 + i\rho_{ex}\phi - \lambda_+ e^{-iz_+\hat{h}_+\phi} - \lambda_- e^{iz_-\hat{h}_-\phi} \right]. \tag{2.14}$$

In Eq. (2.14), $\lambda_\pm$ is the fugacity of the ions defined as

$$\lambda_\pm = \frac{e^{\mu_\pm}}{v_\pm} \tag{2.15}$$

and we have used the short-hand notation $\hat{h}_\pm\phi$ to represent the local spatial averaging of ϕ by the charge distribution function:

$$\hat{h}_\pm\phi = \int d\mathbf{r}' h_\pm(\mathbf{r}' - \mathbf{r})\phi(\mathbf{r}'). \tag{2.16}$$

From the partition function, Eq. (2.13), we obtain the (dimensionless) grand free energy as

$$W = -\ln \Xi \tag{2.17}$$

and the average number of mobile ions is obtained from

$$\langle n_\pm \rangle = \frac{\partial \ln \Xi}{\partial \mu_\pm} = \lambda_\pm \int d\mathbf{r} \langle e^{\mp iz_\pm\hat{h}_\pm\phi} \rangle, \tag{2.18}$$

which identifies the local density of the ions as

$$c_\pm = \lambda_\pm \langle e^{\mp iz_\pm\hat{h}_\pm\phi} \rangle. \tag{2.19}$$

The average appearing in Eqs. (2.18) and (2.19) refers to an average over the field ϕ with the weight $\exp(-L)$. We note that a more systematic way to obtain the local density as well as any correlation functions is by introducing a generating field and take appropriate functional derivatives of the grand free energy with respect to the generating field [10]. However, the density correlation functions are not the main focus of this work and so we shall not pursue such a procedure.

Equation (2.13) together with Eq. (2.14) forms the starting point of the field-theoretic approach. As the action is nonlinear, the partition function cannot be evaluated exactly. The lowest-order approximation corresponds to taking the saddle-point contribution of the functional integral; this results in the Poisson-Boltzmann equation Eq. (1.1) with $c_\pm^{(0)} = \lambda_\pm$ and $\psi = i\phi^*$ where ϕ^* is the saddle-point value of the fluctuating field ϕ. As no divergence appears in the saddle-point approximation, we may take the point-charge limit. A perturbative systematic expansion can be performed by expanding the action around the saddle point and taking successively higher order corrections into account [22–24]. Af-

ter eliminating the one-particle reducible contributions in the thermodynamic potential, the result is a systematic loop expansion. In practice, only the one-loop correction is kept; the validity of such a one-loop approach is controlled by some smallness parameter [24].

To develop a nonperturbative theory, we perform a variational calculation of Eq. (2.13) using the Gibbs-Feynman-Bogoliubov bound. We use a Gaussian reference action of the form [35,37]

$$L_{ref} = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' [\phi(\mathbf{r}) + i\psi(\mathbf{r})] G^{-1}(\mathbf{r},\mathbf{r}')[\phi(\mathbf{r}') + i\psi(\mathbf{r}')],$$

$$(2.20)$$

where the average electrostatic field ψ and the Green's function G are taken to be variational parameters. G^{-1} is the functional inverse of the Green's function defined through

$$\int d\mathbf{r}'' G^{-1}(\mathbf{r},\mathbf{r}'')G(\mathbf{r}'',\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'). \qquad (2.21)$$

Applying the Gibbs-Feynman-Bogoliubov inequality, we have for Eq. (2.13)

$$\Xi = \Xi_{ref}\langle \exp\{-L[\phi] + L_{ref}[\phi]\}\rangle_{ref} \geq \Xi_{ref}$$
$$\times \exp\{-\langle L[\phi] - L_{ref}[\phi]\rangle_{ref}\}, \qquad (2.22)$$

where

$$\Xi_{ref} = \frac{1}{Z_C} \int D\phi \exp\{-L_{ref}[\phi]\} = \frac{(\det G)^{1/2}}{(\det C)^{1/2}}, \quad (2.23)$$

the average $\langle \cdots \rangle_{ref}$ is taken in the reference ensemble with action L_{ref}. For notational clarity, we will henceforth denote $\langle \cdots \rangle_{ref}$ simply as $\langle \cdots \rangle$.

We approximate the partition function by the upper bound of the right-hand side of Eq. (2.22) or equivalently by minimizing the variational grand free energy

$$W = W_{ref} + \langle L[\phi] - L_{ref}[\phi]\rangle = -\frac{1}{2}\ln\left(\frac{\det G}{\det C}\right)$$

$$- \frac{1}{2}\int d\mathbf{r} d\mathbf{r}'\{\delta(\mathbf{r}' - \mathbf{r})[\epsilon(\nabla\psi)^2 - \epsilon\langle(\nabla\chi)^2\rangle] + G^{-1}(\mathbf{r},\mathbf{r}')$$

$$\times \langle \chi(\mathbf{r})\chi(\mathbf{r}')\rangle\} + \int d\mathbf{r}[\rho_{ex}\psi - \lambda_+ e^{-z_+\psi}\langle e^{-iz_+\hat{h}_+\chi}\rangle$$

$$- \lambda_- e^{z_-\psi}\langle e^{iz_-\hat{h}_-\chi}\rangle], \qquad (2.24)$$

where $\chi \equiv \phi + i\psi$. Because the distribution of χ is Gaussian by our ansatz, the averages in Eq. (2.24) can be evaluated exactly. Noting that

$$\langle \chi(\mathbf{r})\chi(\mathbf{r}')\rangle = G(\mathbf{r},\mathbf{r}'), \qquad (2.25)$$

we have

$$\int d\mathbf{r} d\mathbf{r}' \, \delta(\mathbf{r} - \mathbf{r}')\epsilon\langle(\nabla\chi)^2\rangle$$

$$= \int d\mathbf{r} d\mathbf{r}' \nabla_{\mathbf{r}} \cdot [\epsilon(\mathbf{r})\nabla_{\mathbf{r}'}\delta(\mathbf{r} - \mathbf{r}')]G(\mathbf{r},\mathbf{r}') \quad (2.26)$$

and

$$\langle e^{\mp iz_\pm \hat{h}_\pm \chi}\rangle = \exp\left[-\frac{1}{2}z_\pm^2 \int d\mathbf{r}' d\mathbf{r}'' h_\pm(\mathbf{r}' - \mathbf{r})\right.$$

$$\left. \times G(\mathbf{r}',\mathbf{r}'')h_\pm(\mathbf{r}'' - \mathbf{r})\right]. \qquad (2.27)$$

From Eq. (2.27), we obtain the density of the ions:

$$c_\pm(\mathbf{r}) = \lambda_\pm \exp[\mp z_\pm \psi(\mathbf{r}) - u_\pm(\mathbf{r})], \qquad (2.28)$$

where $u_\pm$ is the self energy

$$u_\pm(\mathbf{r}) = \frac{1}{2}z_\pm^2 \int d\mathbf{r}' d\mathbf{r}'' h_\pm(\mathbf{r} - \mathbf{r}')G(\mathbf{r}',\mathbf{r}'')h_\pm(\mathbf{r}'' - \mathbf{r}).$$

$$(2.29)$$

Minimizing W with respect to ψ and G, yields, respectively,

$$-\nabla \cdot (\epsilon \nabla \psi) = \rho_{ex} + \lambda_+ z_+ e^{-z_+\psi - u_+} - \lambda_- z_- e^{z_-\psi - u_-} \quad (2.30)$$

and

$$-\nabla \cdot [\epsilon \nabla G(\mathbf{r},\mathbf{r}')] + 2I(\mathbf{r})G(\mathbf{r},\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \quad (2.31)$$

where $I(\mathbf{r})$ is the local ionic strength,

$$I(\mathbf{r}) = \frac{1}{2}(\lambda_+ z_+^2 e^{-z_+\psi - u_+} + \lambda_- z_-^2 e^{z_-\psi - u_-}). \qquad (2.32)$$

The detailed derivation of these equations is given in Appendix A. We note that these equations were given in the work of Netz and Orland [35] for point charges in their study of surface charge renormalization. However, the consequences of these equations were not discussed and their theory contained an infinite self energy that needed to be renormalized.

Equations (2.29)–(2.31) are the key results of this work. Equation (2.30) has the same form as the PB equation, but now with the self energy of the ions appearing in the Boltzmann factor. When the self energy is constant, it can be absorbed into a redefined fugacity. In that case Eq. (2.30) reduces to the usual PB equation and the Green's function in Eq. (2.31) simply reflects the Gaussian fluctuation around the saddle point. If in addition the electrostatic potential is also constant, Eq. (2.31) yields the Debye-Hückel correlation function [20]. In general, however, Eqs. (2.30) and (2.31) are coupled through the self energy, Eq. (2.29), and Eq. (2.31) is nonlinear in G because of the self energy term.

Making use of Eqs. (2.30) and (2.31), we arrive at the expression for the equilibrium grand free energy,

$$W = -\int d\mathbf{r}[c_+(\mathbf{r}) + c_-(\mathbf{r})] + \frac{1}{2}\int d\mathbf{r}\psi(\mathbf{r})[\rho_{ex}(\mathbf{r}) - z_+ c_+(\mathbf{r})$$

$$+ z_- c_-(\mathbf{r})]$$

$$+ \frac{1}{2}\ln\left(\frac{\det C}{\det G}\right) - \int d\mathbf{r} I(\mathbf{r})G(\mathbf{r},\mathbf{r}). \qquad (2.33)$$

The last term in Eq. (2.33) contains a same-point Green's that might appear to be infinite and would seem to require a cutoff to make it finite. If so, an ambiguity would arise as to which Born radius to use. Fortunately, however, a cutoff is not needed, because this term exactly cancels the divergence arising from the penultimate term, as will be shown in Sec. III in the case of a bulk electrolyte solution. Since the divergences in these terms are microscopic in origin, we expect this cancellation to hold for an inhomogeneous system and in the presence of fixed external charges.

III. UNIFORM BULK ELECTROLYTE SOLUTION

We illustrate the application of our theory first to the case of a bulk electrolyte solution with a uniform dielectric constant by showing some nontrivial effects of the self energy. In order to bring out the effects due to size and valency asymmetry, we consider a salt of the form $M_{\nu_+}X_{\nu_-}$. Charge neutrality requires that $\nu_+ z_+ = \nu_- z_-$. For small values of the valency such as $z_\pm = 1, 2$—this will be the most relevant case anyway since ions with higher valencies are more likely to exist as ion pairs rather than free ions [39]—we have simply $\nu_+ = z_-$ and $\nu_- = z_+$.

With a constant density for the ions, Eq. (2.31) yields the Debye-Hückel result for the Green's function, $G(\mathbf{r}-\mathbf{r}') = (4\pi\epsilon|\mathbf{r}-\mathbf{r}'|)^{-1}\exp(-\kappa|\mathbf{r}-\mathbf{r}'|)$, or

$$G(\mathbf{p}) = \frac{1}{\epsilon(p^2 + \kappa^2)} \qquad (3.1)$$

in Fourier space, with κ being the inverse of the Debye screening length given by

$$\kappa^2 = 2I/\epsilon = 4\pi z_+ z_-(z_+ + z_-)c_s l_b, \qquad (3.2)$$

where c_s is the salt concentration, which is related to the cation and anion concentration via $c_+ = z_- c_s$ and $c_- = z_+ c_s$, and l_b is the Bjerrum length defined in Eq. (2.11). Using the Debye-Hückel Green's function in Eq. (2.29) in conjunction with Eq. (2.1), we obtain

$$u_+ = z_+^2\left(\frac{l_b}{2a_+} - \frac{l_b\kappa}{2}\right) \qquad (3.3)$$

and

$$u_- = z_-^2\left(\frac{l_b}{2a_-} - \frac{l_b\kappa}{2}\right). \qquad (3.4)$$

Thus, we see that the self energy contains both a Born solvation term and a term due to interaction with other ions. Substituting Eqs. (3.3) and (3.4) in Eq. (2.28), we obtain the expression for the chemical potential as a function of the ion concentration,

$$\mu_+ = z_+^2\left(\frac{l_b}{2a_+} - \frac{l_b\kappa}{2}\right) + \ln(c_+/c_+^R), \qquad (3.5)$$

$$\mu_- = z_-^2\left(\frac{l_b}{2a_-} - \frac{l_b\kappa}{2}\right) + \ln(c_-/c_-^R), \qquad (3.6)$$

where we have written the inverse of the reference volume in Eq. (2.15) as a reference concentration to be consistent with conventions in solution thermodynamics. It is convenient to write the cation and anion concentration in terms of the salt concentration: $c_+ = \nu_+ c_s = z_- c_s$ and $c_- = \nu_- c_s = z_+ c_s$. Because of charge neutrality, the chemical potentials of the cations and anions are not independent. Following the standard practice in electrochemistry, we define the mean chemical potential of the ions by $\mu = (\nu_+\mu_+ + \nu_-\mu_-)/(\nu_+ + \nu_-)$. Thus,

$$\mu = \frac{z_+ z_-}{z_+ + z_-}\left(\frac{z_+ l_b}{2a_+} + \frac{z_- l_b}{2a_-}\right) - \frac{z_+ z_-}{2}l_b\kappa + \ln\left(\frac{c_s}{c_s^R}\right)$$

$$= \frac{z_+ z_-}{z_+ + z_-}\left(\frac{z_+ l_b}{2a_+} + \frac{z_- l_b}{2a_-}\right) + \ln\left(\gamma\frac{c_s}{c_s^R}\right), \qquad (3.7)$$

where the second line of the equation defines the mean activity coefficient, $\gamma = \exp(-z_+ z_- l_b\kappa/2)$. Using the concentration dependence for κ, we recover the well-known Debye-Hückel limiting law for the activity coefficient [20].

Equation (3.7) can be used to predict the solubility of salt in different solvents and partitioning of salt in two coexisting solvents. While this expression could be obtained by intuitively adding a Born solvation term to the Debye-Hückel theory, in our case it emerges naturally from a unified theory.

The difference in the Born radius and/or valency between the cations and anions will give rise to a finite electrostatic potential difference between two coexisting salt solutions such as water and a polar organic liquid. This is because in addition to charge neutrality in each phase, the chemical potential of the cations and anions must each be equal between the two phases. This can only be satisfied when there is a finite difference in the electrostatic potential between the two phases. This potential difference was first examined theoretically by Verwey and Niessen [40]. The general thermodynamic derivation was given by Hung [41] and a more thorough analysis was provided in a review article by Girault and Schiffrin [42]. With our explicit results for the chemical potential of the ions, Eqs. (3.5) and (3.6), and allowing for an electrostatic potential difference between the coexisting phases, a straightforward calculation gives

$$\Delta\psi = -\frac{1}{z_+ + z_-}(\Delta u_+ - \Delta u_-) = \frac{\Delta l_b}{z_+ + z_-}\left(\frac{z_-^2}{2a_-} - \frac{z_+^2}{2a_+}\right)$$

$$+ \frac{z_- - z_+}{2}\Delta(l_b\kappa), \qquad (3.8)$$

where the difference operator refers to that between the two solution phases. We see that a finite potential difference develops when the cations and anions have unequal Born radii and/or different valencies. We note that this potential difference has also been derived previously by Onuki [43,44] and by Kung et al. [45] using the Born energy alone, which can be seen to be valid when the cations and anions are of equal valency. In that case, the potential difference is independent of the salt concentration. In general, however, difference in

the valency between the cation and anion adds an additional term due to the Debye-Hückel activity correction giving rise to a weak square-root concentration dependence [46].

We close our discussion in this section by examining the equilibrium grand free energy of the system. The last two terms in Eq. (2.33) are fluctuation contributions to the free energy. While each term has a diverging part without a cut-off, the two terms add up to a finite result. Using the Debye-Hückel propagator in Fourier space Eq. (3.1), with a corresponding expression for C, the last two terms can be written as

$$\frac{V}{4\pi^2}\int_0^\infty p^2 dp\left[\ln\left(1+\frac{\kappa^2}{p^2}\right)-\frac{\kappa^2}{p^2+\kappa^2}\right]=\frac{\kappa^3}{24\pi}V$$

$$=\frac{\pi^{1/2}}{3}z_+^{3/2}z_-^{3/2}(z_++z_-)^{3/2}l_b^{3/2}c_s^{3/2}V. \quad (3.9)$$

The osmotic pressure of the solution due to the salt ions is then

$$\Pi=-W/V=(z_++z_-)c_s-\frac{\pi^{1/2}}{3}z_+^{3/2}z_-^{3/2}(z_++z_-)^{3/2}l_b^{3/2}c_s^{3/2}. \quad (3.10)$$

As expected, the Born solvation self energy does not affect the bulk osmotic pressure.

IV. SELF ENERGY OF IONS IN A WEAKLY INHOMOGENEOUS DIELECTRIC MEDIUM

For ions in an inhomogeneous dielectric medium, the self energy becomes position dependent. In this section, we discuss the self energy of ions in a weakly inhomogeneous dielectric medium. Weak inhomogeneity means that the length scale over which the dielectric constant varies is much larger than the Born radii of the ions and that the amplitude of the spatial variation in the dielectric constant is much less than the spatial average. Microphases of weakly segregated block copolymers [47,48] are examples of weakly inhomogeneous dielectric media. The case of a discontinuous change in the dielectric constant will be treated in future work.

For the case of weak dielectric inhomogeneity, we will show that the self energy can be separated into two parts: a "nonuniversal" part that explicitly depends on the Born radius in the same way as the Born energy with the local dielectric constant and a "universal" part that does not explicitly depend on this microscopic length scale. (However, the universal part still depends on the Born radii implicitly through the self energy appearing in the spatially dependent concentration.) We demonstrate this by exploiting the structure of the solution to Eq. (2.31).

We start by rewriting Eq. (2.31) in a matrix form

$$\mathbf{\Gamma}\cdot\mathbf{G}=\mathbf{I}, \quad (4.1)$$

where the notation should be obvious. Note that we use the boldface $\mathbf{I}$ to denote the identity matrix, to distinguish it from the ionic strength I. The matrix element of $\mathbf{\Gamma}$ is $\nabla_\mathbf{r}\cdot\epsilon\nabla_{\mathbf{r}'}\delta(\mathbf{r}-\mathbf{r}')+2I(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')$ in real space or $-\mathbf{p}\cdot\mathbf{p}'\epsilon_{\mathbf{p}+\mathbf{p}'}+2I_{\mathbf{p}+\mathbf{p}'}$ in

reciprocal space where the Fourier transform of a matrix element $B(\mathbf{r},\mathbf{r}')$ is defined as

$$B_{\mathbf{p},\mathbf{p}'}=\int d\mathbf{r}d\mathbf{r}' e^{-i\mathbf{p}\cdot\mathbf{r}-i\mathbf{p}'\cdot\mathbf{r}'}B(\mathbf{r},\mathbf{r}'). \quad (4.2)$$

Equation (4.1) can be written either in real space or in reciprocal space.

Writing the spatially varying dielectric constant as $\epsilon(\mathbf{r})=\epsilon_0+\Delta\epsilon(\mathbf{r})$ and similarly $I(\mathbf{r})=I_0+\Delta I(\mathbf{r})$, we can write the matrix $\mathbf{\Gamma}$ as $\mathbf{\Gamma}^{(0)}$ for a uniform system with permittivity ϵ_0 and ionic strength I_0, plus a correction term $\Delta\mathbf{\Gamma}$ that is due to the spatial variations in the permittivity and spatially varying concentrations [Eq. (2.32)]. In Fourier space, the matrix elements are

$$\Gamma_{\mathbf{p},\mathbf{p}'}=\epsilon_0(p^2+\kappa_0^2)\delta_{\mathbf{p},-\mathbf{p}'}-\mathbf{p}\cdot\mathbf{p}'\Delta\epsilon_{\mathbf{p}+\mathbf{p}'}+2\Delta I_{\mathbf{p}+\mathbf{p}'}$$

$$=\Gamma_{\mathbf{p},\mathbf{p}'}^{(0)}+\Delta\Gamma_{\mathbf{p},\mathbf{p}'}, \quad (4.3)$$

where the identification of $\Gamma_{\mathbf{p},\mathbf{p}'}^{(0)}$ and $\Delta\Gamma_{\mathbf{p},\mathbf{p}'}$ should be obvious. Equation (4.1) can then be formally solved to yield

$$\mathbf{G}=\mathbf{G}^{(0)}-\mathbf{G}^{(0)}\cdot\Delta\mathbf{\Gamma}\cdot\mathbf{G}, \quad (4.4)$$

where $\mathbf{G}^{(0)}$ is the inverse of $\mathbf{\Gamma}^{(0)}$. This equation forms the basis for an iterative solution or a perturbative expansion in $\Delta\mathbf{\Gamma}$, the latter being obtained by repeated use of the expression for $\mathbf{G}$ on the right-hand side:

$$\mathbf{G}=\mathbf{G}^{(0)}-\mathbf{G}^{(0)}\cdot\Delta\mathbf{\Gamma}\cdot\mathbf{G}^{(0)}+\mathbf{G}^{(0)}\cdot\Delta\mathbf{\Gamma}\cdot\mathbf{G}^{(0)}\cdot\Delta\mathbf{\Gamma}\cdot\mathbf{G}^{(0)}-\cdots. \quad (4.5)$$

The self energy is then

$$u_\pm(\mathbf{r})=\frac{z_\pm^2}{2V^2}\sum_{\mathbf{p}_1,\mathbf{p}_2}e^{i(\mathbf{p}_1+\mathbf{p}_2)\cdot\mathbf{r}}G_{\mathbf{p}_1,\mathbf{p}_2}\exp\left(-\frac{a_\pm^2\mathbf{p}_1^2}{2\pi}-\frac{a_\pm^2\mathbf{p}_2^2}{2\pi}\right). \quad (4.6)$$

Using the perturbation expansion for G in Eq. (4.4), we can then evaluate the self energy perturbatively around the uniform state. In Appendix B, we calculate explicitly the first-order correction. To first order in the spatial inhomogeneity, the self energy of an ion is

$$u_\pm(\mathbf{r})=\frac{z_\pm^2}{8\pi a_\pm\epsilon_0}-\frac{z_\pm^2}{8\pi a_\pm\epsilon_0^2}\Delta\epsilon(\mathbf{r})-\frac{z_\pm^2\kappa_0}{8\pi\epsilon_0}$$

$$+\frac{z_\pm^2}{8\pi\epsilon_0^2}\frac{1}{V}\sum_\mathbf{k}e^{i\mathbf{k}\cdot\mathbf{r}}[X(k)\Delta\epsilon_\mathbf{k}-Y(k)\Delta I_\mathbf{k}], \quad (4.7)$$

where

$$X(k)=\kappa_0+\left(\frac{\kappa_0^2}{k}+\frac{k}{2}\right)\arcsin\frac{k}{\sqrt{4\kappa_0^2+k^2}}, \quad (4.8)$$

$$Y(k)=\frac{2}{k}\arcsin\frac{k}{\sqrt{4\kappa_0^2+k^2}}. \quad (4.9)$$

Two points about Eq. (4.7) are worth noting. First, the expression has the general structure of having two kinds of terms, one that is $O(a^{-1})$ which is due to local solvation

effect and one that is independent of the microscopic length scale a. We shall term the first type the nonuniversal part and the second type the universal part of the self energy. The correction term in the nonuniversal part is seen to be the first-order term in the Taylor expansion of $1/[8\pi a(\epsilon_0 + \Delta\epsilon(\mathbf{r})] = 1/[8\pi a\epsilon(\mathbf{r})]$. As demonstrated in Appendix C, each higher-order term in the perturbation expansion results in a nonuniversal contribution that equals the corresponding term in the Taylor expansion of this expression. Therefore, resummation of the perturbation expansion leads to the following general result:

$$u_{\pm}(\mathbf{r}) = \frac{z_{\pm}^2}{8\pi a_{\pm}\epsilon(\mathbf{r})} + z_{\pm}^2 g(\mathbf{r}), \qquad (4.10)$$

where $g(\mathbf{r})$ is a functional (generally nonlocal) of the spatially varying electric permittivity $\epsilon(\mathbf{r})$ and ionic strength $I(\mathbf{r})$ but has no explicit dependence on the microscopic parameters $a_{\pm}$. We note that the split of the self energy into a nonuniversal and a universal part in the form of Eq. (4.10) is similar in spirit to the projection operator approach in Ref. [37]. However, the nonuniversal part in our theory has a clear physical interpretation, i.e., that of a local Born solvation energy, and more importantly it can be different for the cations and anions.

Before we leave this section, we briefly comment on the case of a discontinuous change in the dielectric constant, as in the step-function model for liquid-vapor [18,19] and liquid-liquid [40,45,49] interfaces. With a true mathematical discontinuity in the dielectric constant, the separation of the self energy into a local Born term and a universal term independent of the ion radii is no longer possible—the image interaction will become dependent on the ion radii in the immediate vicinity of the interface. (This situation can be treated with our smeared charge model in the full equations; detailed analysis will be deferred to future work.) Alternatively, one can model the interface with a finite width, as in the work of Onuki [43,44]. As long as the interfacial width is much larger than the ion radii, a perturbation analysis in the inverse power of the ion radii $a_{\pm}^{-1}$ would still yield a self energy in the form of Eq. (4.10), where the universal term accounting for the image interaction will contain a length scale associated with the width of the interface. A leading-order perturbation calculation of this term in the gradient of the interfacial profile was given by Onuki [43,44]; the method we describe here is more general.

V. BORN-ENERGY AUGMENTED POISSON-BOLTZMANN THEORY

The separation of the self energy based on its dependence on the ion radii reflects fluctuation effects on different length scales. The nonuniversal term in Eq. (4.10) reflects local fluctuations on length scales of the size of the ion, whereas the second term arises from fluctuation effects on longer length scales and is a collective effect. When the Born radii $a_{\pm}$ are the smallest length scales (compared to all other length scales in the problem—the Bjerrum length, the Debye screening length, and the length scale of the dielectric varia-

tion), the first term in Eq. (4.10) dominates. As this term is independent of the collective variables, such as the concentration and electrostatic potential, it is natural to incorporate this part of the self energy into the mean-field description when such a description is appropriate. We term such a theory the Born-energy augmented PB theory. The PB equation now reads

$$-\nabla \cdot [\epsilon(\mathbf{r})\nabla\psi(\mathbf{r})] = \rho_{ex} + \lambda_+ z_+ \exp\left[-z_+\psi(\mathbf{r}) - \frac{z_+^2}{8\pi a_+\epsilon(\mathbf{r})}\right]$$
$$-\lambda_- z_- \exp\left[z_-\psi(\mathbf{r}) - \frac{z_-^2}{8\pi a_-\epsilon(\mathbf{r})}\right]. \qquad (5.1)$$

Consistent with the neglect of longer-length scale fluctuations, only the mean-field part of the equilibrium free energy—the terms in the first line of Eq. (2.33)—need to be retained.

While still a mean-field theory in nature, such a modified PB theory can already capture some important effects missed in the simplest PB approach such as the difference in solubility of salts in different solvents and charge separation in inhomogeneous dielectric media. Several authors have in essence adopted such a modified PB approach in their study of various effects associated with the ion size effects [21,43–45,50]. The early work of Verwey and Niessen [40] and the more recent work of Bier *et al.* [49] on electrolytes near liquid-liquid interfaces, while not explicitly invoking the Born energy, are also equivalent to a modified PB theory in which the cations and anions experience different one-body potentials in the different phases. Our analysis provides the theoretical basis for such an approach [51] and the means for including correlation effects neglected in this level of mean-field theory.

The inclusion of the Born solvation energy into the PB theory is analogous to recent strategies in incorporating local fluctuation effects into a mean-field description for polymer blends and block copolymers. In that case, it was shown that a literal interpretation of the mean-field theory as the result of a saddle-point approximation can be qualitatively incorrect in predicting the phase behavior of polymer mixtures and block copolymers. For example, conformation asymmetry between two different polymers can lead to phase separation in polymer mixtures or microphase separation in block copolymers [52,53]. A qualitatively correct mean-field theory must incorporate such small-length-scale correlation effects in a coarse-grained pseudopotential [54,55].

VI. CHARGE SEPARATION IN A PERIODIC DIELECTRIC MEDIUM

As alluded to in Sec. I, a qualitative failure of the PB equation in the absence of fixed external charges is its erroneous prediction of complete local charge neutrality and uniform salt concentration in an inhomogeneous dielectric medium. Our fluctuation renormalized PB equation, Eq. (2.30), on the other hand, shows that unless the self energies of the cations and anions are everywhere the same, local charge

neutrality will not be maintained. In this section, we examine the issue of charge separation in a periodic dielectric medium, which can mimic, for example, ordered block copolymer phases. Self energy effects of the small ions have been completely neglected in existing theoretical treatment of microphase separation in ion-containing block copolymers [56]. To include the full fluctuation effects would require numerical solutions to Eqs. (2.30) and (2.31). However, in order to highlight some key effects, we opt for a more analytical approach using the simpler Born-energy augmented PB equation, Eq. (5.1). Furthermore, to facilitate the analysis, we assume that the variation in the dielectric constant is sufficiently weak that a first-order expansion suffices.

Consider a sinusoidally varying dielectric medium of the form

$$\epsilon(\mathbf{r}) = \epsilon_0[1 + A\cos(kz)]. \qquad (6.1)$$

The local Born energy can be written as

$$u_\pm = \frac{z_\pm^2}{8\pi a_\pm \epsilon(\mathbf{r})} = u_\pm^{(0)}[1 - A\cos(kz) + A^2\cos^2(kz) - \cdots]. \qquad (6.2)$$

We seek a perturbative solution of the electrostatic potential of the form

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \psi_1(\mathbf{r})A + \psi_2(\mathbf{r})A^2 + \cdots. \qquad (6.3)$$

The zeroth order solution is $\psi_0 = $ const and $\lambda_+ z_+ \exp[-u_+^{(0)}] = \lambda_- z_- \exp[-u_-^{(0)}]$, which is a statement of overall charge neutrality $c_+^{(0)} z_+ = c_-^{(0)} z_- = c_s^{(0)} z_+ z_-$, where $c_s^{(0)}$ is the average concentration of dissolved salt and we again have used the relationship between the stoichiometric coefficients and the valencies of the ions, assuming small valencies and full dissociation of the salt ions. At the first order, the equation reads

$$-\epsilon_0 \nabla^2 \psi_1 + 2I_0 \psi_1 = (c_+^{(0)} z_+ u_+^{(0)} - c_-^{(0)} z_- u_-^{(0)})\cos(kz)$$
$$= z_+ z_- c_s^{(0)}(u_+^{(0)} - u_-^{(0)})\cos(kz). \qquad (6.4)$$

The equation is trivially solved to yield

$$\psi_1 = \frac{z_+ z_- c_s^{(0)}}{\epsilon_0(k^2 + \kappa_0^2)}(u_+^{(0)} - u_-^{(0)})\cos(kz). \qquad (6.5)$$

Using the expression for $u_\pm^{(0)}$, we obtain

$$\psi = \frac{z_+ z_- c_s^{(0)}}{2\epsilon_0(k^2 + \kappa_0^2)}\left(\frac{z_+^2 l_{b,0}}{a_+} - \frac{z_-^2 l_{b,0}}{a_-}\right)A\cos(kz). \qquad (6.6)$$

The local charge density is obtained straightforwardly from the Poisson equation, and to first order, and the result is

$$\rho = \frac{z_+ z_- c_s^{(0)} k^2}{2(k^2 + \kappa_0^2)}\left(\frac{z_+^2 l_{b,0}}{a_+} - \frac{z_-^2 l_{b,0}}{a_-}\right)A\cos(kz). \qquad (6.7)$$

This expression predicts an interesting dependence on the salt concentration and on the wavelength of the dielectric constant variation. We examine two limiting cases $k \gg \kappa_0$ and $k \ll \kappa_0$. For $\kappa_0 \ll k$, which corresponds to low salt concentration and/or short wavelength modulation in the dielectric constant, Eq. (6.7) predicts a charge separation with an amplitude that is proportional to the overall salt concentration

and independent of the wavelength of the dielectric variation:

$$\rho = \frac{1}{2} z_+ z_- c_s^{(0)}\left(\frac{z_+^2 l_{b,0}}{a_+} - \frac{z_-^2 l_{b,0}}{a_-}\right)A\cos(kz). \qquad (6.8)$$

In the opposite limit, the screening length is shorter than the wavelength and we obtain a result that increases with the wave number but becomes independent of the salt concentration:

$$\rho = \frac{\epsilon_0 k^2}{2(z_+ + z_-)}\left(\frac{z_+^2 l_{b,0}}{a_+} - \frac{z_-^2 l_{b,0}}{a_-}\right)A\cos(kz). \qquad (6.9)$$

VII. CONCLUSIONS

In this work, we have developed a systematic theory for fluctuation in electrolyte solutions with an emphasis on the proper treatment of the self energy in an inhomogeneous dielectric medium. By introducing a finite charge distribution for the ions, allowing for different Born radii for the cations and anions, the theory naturally incorporates the Born solvation effect while simultaneously frees itself of divergences in a field-theoretic formulation. At the level of treatment in which the solvent is taken as a linear dielectric medium and in which the volume exclusion of the ions are ignored (which is justified for low ion concentrations), the theory presented here represents the most comprehensive treatment of fluctuation effects at both long and short length scales and opens the way to treating a number of phenomena where the self energy plays a key role such as ions near a liquid-liquid interface.

For weakly inhomogeneous media, using the Born radius as a natural smallness parameter, we show that the self energy of an ion can be written as a nonuniversal term in the form of the Born energy with the local dielectric constant plus a universal term that is independent of this microscopic length scale. This analysis motivates a Born-energy augmented Poisson-Boltzmann theory as a simple mean-field theory to capture the self energy effect in weakly inhomogeneous dielectric media. In many cases, the nonzero mean-field electrostatic potential produced by the differential relative solubility of the cations and anions (due to the local Born energy—the nonuniversal part of the self energy) are the dominant effects, and effects due to the universal part of the self-energy may be neglected. Such is the case for the $c^{1/2}$ dependence in salt concentration in the liquid-liquid interfacial tension of electrolyte solutions [49,57]. On the other hand, the Onsager-Samaras result, which predicts a $c \ln c$ dependence in the surface tension of an aqueous solution, is solely based on a (random phase level) fluctuation effect—the universal part of the self energy. As first pointed out by Nichols and Pratt [57] and elaborated more recently by Bier *et al.* [49], whether the mean-field effect or the fluctuation effect dominates depends on the local interactions of the ions near the interface and the width of the interfacial region, and in some cases, both are important. While we are not examining the issue of interfacial tension in electrolyte solutions in this paper, the framework developed here is naturally applicable to that problem.

For many applications of the theory involving dielectric inhomogeneity, numerical solutions will be required. While the task is not a trivial one, we note that both Eqs. (2.30) and (2.31) have the structure of the Poisson-Boltzmann equation, for which a number of efficient numerical schemes exist [58]. Furthermore, the variational origin of these equations makes it possible in some cases to construct physically motivated trial functions for the electrostatic field and the Green's function by using a small number of variational parameters, thus, reducing the point-wise solution of differential equations to that of a small set of algebraic equations. These efforts will be reserved for future work.

We note that for specific systems, it is often possible to construct simpler and more physically intuitive approximate theories for treating strongly correlated/fluctuating charged systems. For example, in the case of macroion screening by multivalent small ions, the scheme of matching a strong coupling region with a weak coupling region has been shown to accurately reproduce computer simulation data [59,60]. Such approaches have the virtue of being easier to implement and providing physical insight in simpler terms. On the other hand, the variational formulation of the field-theoretical approach has the advantage of being more systematic and generally applicable. For example, Ref. [35] shows that with a single variational parameter, the field-theoretical variational approach is capable of capturing the surface charge renormalization near a charged surface and describing the full crossover between the strong and weak coupling regimes. The advantage of a more general and systematic approach will become more transparent when dealing systems with dielectric inhomogeneity. There, it will be more challenging to identify the dominant effects and construct simple approximate theories, since there can often be several competing effects and the balance between them is often not obvious, as in the salt-concentration dependence in the liquid-liquid interfacial tension of electrolyte solutions [49,57].

We end this paper by offering some perspectives of our work. Our work employs the field-theoretical approach, a common approach employed in several previous studies of electrostatic interactions [22,24,25,29–32]. For an electrostatic system, the field-theoretical formulation is a natural one: indeed, field theory was born from studies of electromagnetism. Furthermore, in recent years, field-theoretical methods have been used in studies of a wide range of physical and nonphysical systems [34]. In the area of polymers, including polyelectrolytes, it is often the method of choice [61]. In addition to the systematicness of the field-theoretical approach, interactions involving the fields are usually of the "soft" type, which offers computational advantages over particle-based models with hard interactions. The approach adopted in our work is naturally compatible with the field-theoretical description of these soft-matter systems. Once one adopts a field-theoretical description of a statistical mechanical system, the problem of a microscopic cutoff becomes unavoidable when treating fluctuation effects. Our work suggests a physically based recipe for properly treating the cutoff effects in the form of Born radii, which simultaneously cures the unpleasant divergences plaguing any field-theoretical treatments of fluctuation effects and offers a systematic framework for treating both long-range and short-

range effects in problems involving dielectric inhomogeneity. In a broader sense, it is often the interplay between specific local interactions with the long-range nature of Coulomb interactions that make studies of charged systems interesting and challenging; our work serves as a step forward in this respect.

APPENDIX A: DERIVATION OF THE KEY EQUATIONS IN SEC. II

We note that the variational free energy can be written as

$$
W = -\frac{1}{2}\ln\left(\frac{\det G}{\det C}\right) - \frac{1}{2}\int d\mathbf{r}\,\epsilon(\nabla\psi)^2 - \frac{1}{2}\int d\mathbf{r}d\mathbf{r}'[G^{-1}(\mathbf{r},\mathbf{r}')
$$
$$
- C^{-1}(\mathbf{r},\mathbf{r}')]G(\mathbf{r},\mathbf{r}') - \int d\mathbf{r}[\lambda_+ e^{-z_+\psi - u_+} + \lambda_- e^{z_-\psi - u_-}
$$
$$
- \rho_{ex}\psi], \tag{A1}
$$

where C^{-1} is the Poisson operator $\nabla_\mathbf{r}\cdot[\epsilon(\mathbf{r})\nabla_{\mathbf{r}'}\delta(\mathbf{r}-\mathbf{r}')]$ [the inverse of the Coulomb operator in Eq. (2.5)]. The following relations are useful. First, since $(1/2)\ln\det G$ is the result of a Gaussian functional integral, we have

$$
\frac{1}{2}\frac{\delta\ln\det G}{\delta G^{-1}(\mathbf{r},\mathbf{r}')} = -\frac{1}{2}G(\mathbf{r},\mathbf{r}'). \tag{A2}
$$

Second, we note the following chain rule:

$$
\frac{\delta F}{\delta G(\mathbf{r},\mathbf{r}')} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\delta F}{\delta G^{-1}(\mathbf{r}_1,\mathbf{r}_2)}\frac{\delta G^{-1}(\mathbf{r}_1,\mathbf{r}_2)}{\delta G(\mathbf{r},\mathbf{r}')}
$$
$$
= -\int d\mathbf{r}_1 d\mathbf{r}_2 G^{-1}(\mathbf{r},\mathbf{r}_1)\frac{\delta F}{\delta G^{-1}(\mathbf{r}_1,\mathbf{r}_2)}G^{-1}(\mathbf{r}_2,\mathbf{r}'),
$$
$$
\tag{A3}
$$

where the second part of the equation follows from the relationship between G and G^{-1}, Eq. (2.21). Setting the functional derivative of Eq. (A1) to zero with the aid of the above relations, we obtain

$$
0 = -G^{-1}(\mathbf{r},\mathbf{r}') + \nabla_\mathbf{r}\cdot[\epsilon(\mathbf{r})\nabla_{\mathbf{r}'}\delta(\mathbf{r}-\mathbf{r}')] + \lambda_+ z_+^2
$$
$$
\times \int d\mathbf{r}_1 h_+(\mathbf{r}-\mathbf{r}_1)h_+(\mathbf{r}_1-\mathbf{r}')e^{-z_+\psi(\mathbf{r}_1)-u_+(\mathbf{r}_1)} + \lambda_- z_-^2
$$
$$
\times \int d\mathbf{r}_1 h_-(\mathbf{r}-\mathbf{r}_1)h_-(\mathbf{r}_1-\mathbf{r}')e^{z_-\psi(\mathbf{r}_1)-u_-(\mathbf{r}_1)}. \tag{A4}
$$

Inverting the above matrix equation, we obtain

$$
0 = -\delta(\mathbf{r}-\mathbf{r}') - \nabla_\mathbf{r}\cdot[\epsilon(\mathbf{r})\nabla_\mathbf{r}G(\mathbf{r},\mathbf{r}')]
$$

$$
+ \lambda_+ z_+^2 \int d\mathbf{r}_1 d\mathbf{r}_2 h_+(\mathbf{r}-\mathbf{r}_1)h_+(\mathbf{r}_1-\mathbf{r}_2)
$$
$$
\times e^{-z_+\psi(\mathbf{r}_1)-u_+(\mathbf{r}_1)}G(\mathbf{r}_2,\mathbf{r}')
$$

$$
+ \lambda_- z_-^2 \int d\mathbf{r}_1 d\mathbf{r}_2 h_-(\mathbf{r}-\mathbf{r}_1)h_-(\mathbf{r}_1-\mathbf{r}_2)
$$
$$
\times e^{z_-\psi(\mathbf{r}_1)-u_-(\mathbf{r}_1)}G(\mathbf{r}_2,\mathbf{r}'). \tag{A5}
$$

As the second and third lines are well behaved in the point-

charge limit, we may safely take this limit and replace the distribution function $h_\pm$ by the Dirac δ function. The result is Eq. (2.31).

APPENDIX B: FIRST-ORDER CORRECTION TO THE SELF ENERGY FOR A WEAKLY INHOMOGENEOUS DIELECTRIC MEDIUM

In this appendix, we derive the explicit first-order correction to the self energy for ions in a weakly inhomogeneous dielectric medium. Using Eq. (4.3) and noting that $\mathbf{G}^{(0)}_{\mathbf{p},\mathbf{p}'} = \epsilon_0^{-1}(p^2+\kappa_0^2)^{-1}\delta_{\mathbf{p},-\mathbf{p}'}$, we have for the first-order correction

$$\mathbf{G}_0 \cdot \Delta\Gamma \cdot \mathbf{G}_0 = \frac{-\mathbf{p}\cdot\mathbf{p}'\Delta\epsilon_{\mathbf{p}+\mathbf{p}'} + 2\Delta I_{\mathbf{p}+\mathbf{p}'}}{\epsilon_0^2(p^2+\kappa_0^2)(p'^2+\kappa_0^2)}. \tag{B1}$$

Using this in Eq. (4.6), we have for the first-order correction to the self energy,

$$u_{1,\pm}(\mathbf{r}) = \frac{z_\pm^2}{2V^2}\sum_{\mathbf{p}_1,\mathbf{p}_2} e^{i(\mathbf{p}+\mathbf{p}')\cdot\mathbf{r}} \frac{-\mathbf{p}\cdot\mathbf{p}'\Delta\epsilon_{\mathbf{p}+\mathbf{p}} + 2\Delta I_{\mathbf{p}+\mathbf{p}'}}{\epsilon_0^2(p^2+\kappa_0^2)(p'^2+\kappa_0^2)}$$
$$\times \exp\left(-\frac{a_\pm^2\mathbf{p}^2}{2\pi} - \frac{a_\pm^2\mathbf{p}'^2}{2\pi}\right). \tag{B2}$$

Defining $\mathbf{k}=\mathbf{p}+\mathbf{p}'$, the above equation can be written as

$$u_{1,\pm}(\mathbf{r}) = \frac{z_\pm^2}{2\epsilon_0^2 V}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}} Q_\pm(\mathbf{k}), \tag{B3}$$

where

$$Q_\pm(\mathbf{k}) = \frac{1}{V}\sum_{\mathbf{p}} \frac{\mathbf{p}\cdot(\mathbf{p}-\mathbf{k})\Delta\epsilon_{\mathbf{k}} + 2\Delta I_{\mathbf{k}}}{(p^2+\kappa_0^2)[(\mathbf{p}-\mathbf{k})^2+\kappa_0^2]}$$
$$\times \exp\left[-\frac{a_\pm^2\mathbf{p}^2}{2\pi} - \frac{a_\pm^2(\mathbf{p}-\mathbf{k})^2}{2\pi}\right]. \tag{B4}$$

We now evaluate this expression by going to the continuum limit. First, we note that

$$\exp\left[-\frac{a_\pm^2(\mathbf{p}-\mathbf{k})^2}{2\pi}\right] = \exp\left(-\frac{a_\pm^2\mathbf{p}^2}{2\pi}\right)(1 + \pi^{-1}a_\pm^2\mathbf{p}\cdot\mathbf{k} + \cdots). \tag{B5}$$

Because of the Gaussian factor, each power of p in the expansion corresponds to a factor of a^{-1}. The leading-order term of the integral is $O(a^{-1})$, so the second term in the expansion above is of $O(a^0)$. However, this term vanishes by symmetry. Higher order terms in the expansion give terms that are $O(a)$ or higher, which can be ignored upon taking the $a\to 0$ limit. Therefore, to order $O(a^0)$, we may replace $\exp[-a^2(\mathbf{p}-\mathbf{k})^2/(2\pi)]$ by $\exp[-a^2\mathbf{p}^2/(2\pi)]$ and Eq. (B4) becomes

$$Q_\pm(\mathbf{k}) = \frac{1}{(2\pi)^3}\int d\mathbf{p} \frac{\mathbf{p}\cdot(\mathbf{p}-\mathbf{k})\Delta\epsilon_{\mathbf{k}} + 2\Delta I_{\mathbf{k}}}{(p^2+\kappa_0^2)[(\mathbf{p}-\mathbf{k})^2+\kappa_0^2]}\exp\left[-\frac{a_\pm^2\mathbf{p}^2}{\pi}\right]$$

$$= \frac{1}{(2\pi)^3}\int d\mathbf{p}\left\{\frac{e^{-a_\pm^2 p^2/\pi}}{p^2+\kappa_0^2}\Delta\epsilon_{\mathbf{k}} + \frac{[\mathbf{k}\cdot(\mathbf{p}-\mathbf{k}) - \kappa_0^2]\Delta\epsilon_{\mathbf{k}} + 2\Delta I_{\mathbf{k}}}{(p^2+\kappa_0^2)[(\mathbf{p}-\mathbf{k})^2+\kappa_0^2]}\right\}, \tag{B6}$$

where the Gaussian weight is omitted in the second term of the second line of the equation since this term is convergent without a cutoff. The final result for Q is

$$Q_\pm(\mathbf{k}) = \frac{1}{4\pi a_\pm}\Delta\epsilon_{\mathbf{k}} - \frac{1}{4\pi}\left[\kappa_0 + \left(\frac{\kappa_0^2}{k} + \frac{k}{2}\right)\arcsin\frac{k}{\sqrt{4\kappa_0^2+k^2}}\right]$$
$$\times\Delta\epsilon_{\mathbf{k}} + \frac{\Delta I_{\mathbf{k}}}{2\pi k}\arcsin\frac{k}{\sqrt{4\kappa_0^2+k^2}}. \tag{B7}$$

APPENDIX C: THE NONUNIVERSAL PART OF THE SELF ENERGY

We show that the nonuniversal part of the self energy takes the form of a Born energy with the local dielectric constant. Consider, for example, the contribution from the third order term $\mathbf{G}^{(0)}\cdot\Delta\Gamma\cdot\mathbf{G}^{(0)}\cdot\Delta\Gamma\cdot\mathbf{G}^{(0)}\cdot\Delta\Gamma\cdot\mathbf{G}^{(0)}$. The most ultraviolet divergent term in the self energy is

$$u_{3,\pm}(\mathbf{r}) = \frac{z_\pm^2}{2\epsilon_0^4 V^2}\sum_{\mathbf{p}_1,\mathbf{p}_2,\mathbf{p}_3,\mathbf{p}_4} e^{i(\mathbf{p}_1+\mathbf{p}_4)\cdot\mathbf{r}}\exp\left(-\frac{a_\pm^2\mathbf{p}_1^2}{2\pi} - \frac{a_\pm^2\mathbf{p}_4^2}{2\pi}\right)\frac{(-\mathbf{p}_1\cdot\mathbf{p}_2)\Delta\epsilon_{\mathbf{p}_1+\mathbf{p}_2}(\mathbf{p}_2\cdot\mathbf{p}_3)\Delta\epsilon_{-\mathbf{p}_2+\mathbf{p}_3}(\mathbf{p}_3\cdot\mathbf{p}_4)\Delta\epsilon_{-\mathbf{p}_3+\mathbf{p}_4}}{(p_1^2+\kappa_0^2)(p_2^2+\kappa_0^2)(p_3^2+\kappa_0^2)(p_4^2+\kappa_0^2)}. \tag{C1}$$

Changing variables to $\mathbf{k}=\mathbf{p}_1+\mathbf{p}_2$, $\mathbf{k}'=\mathbf{p}_3-\mathbf{p}_2$, $\mathbf{k}''=\mathbf{p}_4-\mathbf{p}_3$, and renaming the variable $\mathbf{p}_1$ simply $\mathbf{p}$, we have

$$u_{3,\pm}(\mathbf{r}) = \frac{z_\pm^2}{2\epsilon_0^4 V^3}\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''} e^{i(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')\cdot\mathbf{r}}\Delta\epsilon_{\mathbf{k}}\Delta\epsilon_{\mathbf{k}'}\Delta\epsilon_{\mathbf{k}''}J(\mathbf{k},\mathbf{k}',\mathbf{k}''), \tag{C2}$$

where

$$J(\mathbf{k},\mathbf{k}',\mathbf{k}'') = \frac{1}{V}\sum_{\mathbf{p}}\exp\left(-\frac{a_\pm^2\mathbf{p}^2}{2\pi} - \frac{a_\pm^2(\mathbf{p}-\mathbf{k}-\mathbf{k}'-\mathbf{k}'')^2}{2\pi}\right)\frac{[\mathbf{p}\cdot(\mathbf{p}-\mathbf{k})][(\mathbf{p}-\mathbf{k})\cdot(\mathbf{p}-\mathbf{k}-\mathbf{k}')][(\mathbf{p}-\mathbf{k}-\mathbf{k}')\cdot(\mathbf{p}-\mathbf{k}-\mathbf{k}'-\mathbf{k}'')]}{(p^2+\kappa_0^2)[(\mathbf{p}-\mathbf{k})^2+\kappa_0^2][(\mathbf{p}-\mathbf{k}-\mathbf{k}')^2+\kappa_0^2][(\mathbf{p}-\mathbf{k}-\mathbf{k}'-\mathbf{k}'')^2+\kappa_0^2]}. \tag{C3}$$

Evaluating the summation over **p** by converting to an integral and keeping the most divergent term, we have simply

$$J(\mathbf{k}, \mathbf{k}', \mathbf{k}'') \approx \frac{1}{(2\pi)^3} \int d\mathbf{p} \, \exp\left(-\frac{a_\pm^2 \mathbf{p}^2}{\pi}\right) \frac{p^6}{p^8} = \frac{1}{4\pi a_\pm}. \tag{C4}$$

Therefore, the term has the form

$$u_{3,\pm} = -\frac{z_\pm^2}{8\pi a_\pm \epsilon_0^4} [\Delta\epsilon(\mathbf{r})]^3. \tag{C5}$$

More generally, the order n term has the form

$$u_{n,\pm} = (-1)^n \frac{z_\pm^2}{8\pi a_\pm \epsilon_0^{(n+1)}} [\Delta\epsilon(\mathbf{r})]^n. \tag{C6}$$

Summing over n, we obtain

$$u_\pm = \frac{z_\pm^2}{8\pi a_\pm \epsilon(\mathbf{r})}. \tag{C7}$$

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