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# A new approach for efficient simulation of Coulomb interactions in ionic fluids

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We propose a simplified version of local molecular field (LMF) theory to treat Coulomb interactions in simulations of ionic fluids. LMF theory relies on splitting the Coulomb potential into a short-ranged part that combines with other short-ranged core interactions and is simulated explicitly. The averaged effects of the remaining long-ranged part are taken into account through a self-consistently determined effective external field. The theory contains an adjustable length parameter  $\sigma$  that specifies the cutoff distance for the short-ranged interaction. This can be chosen to minimize the errors resulting from the mean-field treatment of the complementary long-ranged part. Here we suggest that in many cases an accurate approximation to the effective field can be obtained directly from the equilibrium charge density given by the Debye theory of screening, thus eliminating the need for a self-consistent treatment. In the limit  $\sigma \rightarrow 0$ , this assumption reduces to the classical Debye approximation. We examine the numerical performance of this approximation for a simple model of a symmetric ionic mixture. Our results for thermodynamic and structural properties of uniform ionic mixtures agree well with similar results of Ewald simulations of the full ionic system. In addition, we have used the simplified theory in a grand-canonical simulation of a nonuniform ionic mixture where an ion has been fixed at the origin. Simulations using short-ranged truncations of the Coulomb interactions alone do not satisfy the exact condition of complete screening of the fixed ion, but this condition is recovered when the effective field is taken into account. We argue that this simplified approach can also be used in the simulations of more complex nonuniform systems. © 2008 American Institute of Physics. [DOI: 10.1063/1.2894478]

## I. INTRODUCTION

The long-ranged nature of the Coulomb interaction often causes problems in computer simulations.<sup>1</sup> Although in some cases direct truncation of Coulomb interactions, e.g., by reaction field methods<sup>2</sup> or shifted force truncation<sup>3</sup> can give accurate results,<sup>4</sup> such methods have suffered from significant errors in many other physically relevant cases.<sup>5–7</sup> Truncation schemes tend to work best in dense uniform systems, where there is considerable cancellation of the long-ranged electrostatic forces, and they often perform poorly in inhomogeneous systems.<sup>5–9</sup> At the same time, the Ewald sum method<sup>10,11</sup>—which does not truncate Coulomb interactions and accurately accounts for all images generated by periodic boundary conditions—is generally complex and computationally demanding when applied to inhomogeneous systems,<sup>12</sup> although considerable simplification is possible in reduced geometries such as a two-dimensional slab.<sup>13–17</sup> Finally, the strict periodicity of the Ewald sum method has been known to introduce artifacts in some biologically relevant studies.<sup>18</sup>

In this paper, we examine the performance of an alternative treatment of inhomogeneous Coulomb systems, local

molecular field (LMF) theory,<sup>19</sup> when applied to a simple model for an ionic solution. This theory accounts for the averaged effects of slowly varying long-ranged components of the intermolecular interactions by using a self-consistently determined effective field. LMF theory provides a general framework for treating both uniform and nonuniform systems. We show for the ionic system considered in this paper that analytic results from the Debye theory of screening can be used to greatly simplify the theory and find very good agreement with results of conventional simulations using Ewald sums.

The derivation of LMF theory and its application to general Coulombic systems are given in detail elsewhere.<sup>8,9,20–23</sup> The ideas behind the theory are best understood by considering a nonuniform one component system with long-ranged intermolecular interactions  $w(r)$  in an external field  $\phi(r)$ , which can represent the interactions with fixed objects such as walls or solutes. LMF theory relates structural and thermodynamic properties of the original system to those of a “mimic system” with short-ranged interactions  $u_0(r)$  in a renormalized effective field  $\phi_R(r)$  that accounts for the averaged effects of the remaining long-ranged component  $u_1(r) \equiv w(r) - u_0(r)$  of the intermolecular interactions. A key idea in LMF theory is that  $u_1(r)$  should be properly chosen to be slowly varying so that the averaging can give accurate results.

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For such a  $u_1(r)$ , the effective field is determined in principle by the condition that the nonuniform singlet density in the mimic system (denoted by the subscript  $R$ ) equals that in the original system,

$$\rho_R(\mathbf{r};[\phi_R]) = \rho(\mathbf{r};[\phi]). \quad (1)$$

An explicit equation for  $\phi_R(\mathbf{r})$  can be derived by subtracting the first equations of the exact Yvon–Born–Green hierarchy that relate the gradient of the singlet density to forces in the full and mimic systems. As argued in Refs. 8, 9, and 20–23, when  $u_1$  is chosen to be slowly varying over the range of pair correlations between neighboring molecules, the effective field  $\phi_R(\mathbf{r})$  is accurately given by the self-consistent LMF equation,

$$\phi_R(\mathbf{r}) = \phi(\mathbf{r}) + \int d\mathbf{r}' \rho_R(\mathbf{r}';[\phi_R]) u_1(|\mathbf{r}' - \mathbf{r}|) + C, \quad (2)$$

where  $C$  is a constant of integration. Equation (1) then relates structure in the original and mimic systems; thermodynamic properties can be similarly related by integration over the structure. Finally, uniform systems are treated in LMF theory by choosing  $\phi(\mathbf{r})$  to be the field arising from a fixed fluid particle, i.e., by taking  $\phi(\mathbf{r}) = w(r)$ . This field will induce a nonuniform singlet density that can be directly related to the pair distribution function in the uniform fluid.<sup>24</sup>

LMF theory has many ideas in common with earlier methods, but they are implemented in new ways that avoid most of the limitations of those methods. As can be seen from Eq. (2), LMF theory uses a mean-field average of the long-ranged interactions, similar in spirit to the random-phase approximation (RPA) of density functional theory<sup>25</sup> or to the Debye theory of screening for ionic systems.<sup>1</sup> However, crucially, the average in LMF theory is taken only over particular slowly varying components  $u_1$ , chosen precisely so that their averaged effects can be accurately described by an effective field.

The general idea of separating intermolecular interactions into short-ranged and long-ranged parts has also proved useful in many different contexts, particularly for uniform systems where long-ranged forces largely cancel and thus can be treated as a weak perturbation or by standard integral equation closures.<sup>1,25–29</sup> For historical reasons the intermolecular potential  $w$  was often split so that the properties of the reference system with the intermolecular potential  $u_0$  would be well known, e.g., a hard sphere fluid or an ideal gas. However, these choices do not generally guarantee that the remaining interactions  $u_1$  can, in fact, be accurately treated by perturbation or diagrammatic methods.

With present day computers, complex short-ranged systems can be simulated efficiently and so the nature of the reference system is no longer an overriding issue. Therefore, the split of the intermolecular potential  $w$  in LMF theory can be optimized to minimize the errors associated with the approximate mean-field treatment of its long-ranged part  $u_1$ . The mimic system is then defined as the special short-ranged reference system resulting from this optimal split of  $w$ , and we can use the simulations to accurately determine its properties.

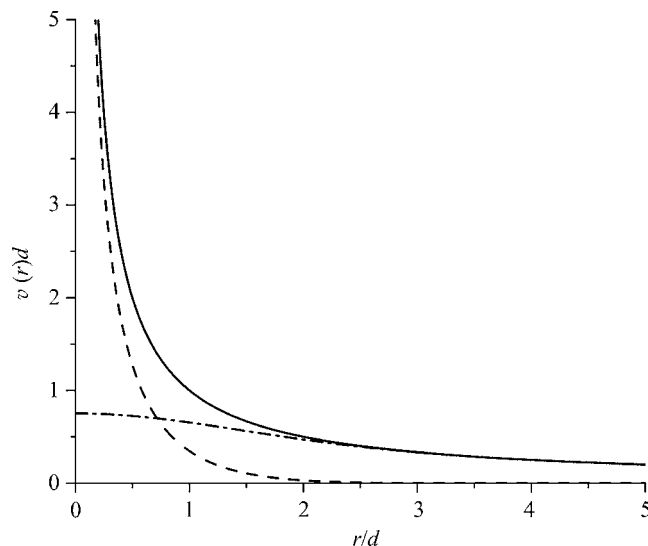


FIG. 1. Separation of the Coulomb potential  $v(r) = r^{-1}$  (solid) into a short-ranged part  $v_0(r, \sigma) = r^{-1} \text{erfc}(r/\sigma)$  (dash) and a long-ranged part  $v_1(r, \sigma) = r^{-1} \text{erf}(r/\sigma)$  (dash-dot). The cutoff length  $\sigma = 1.5d$  shown here is also used in Fig. 2(a), as discussed below in Sec. III.

LMF theory thus corrects the two major shortcomings of the classical Debye theory of ionic systems, namely, its inaccurate mean-field averaging of the entire Coulomb potential and the highly approximate Boltzmann form of the density response to the effective field. However, as discussed below the (linearized) Debye theory satisfies the exact Stillinger–Lovett moment conditions<sup>30</sup> and therefore correctly describes the asymptotic behavior of the charge correlation function. These features of the Debye theory can be exploited to greatly simplify the determination of the effective field in LMF theory while still giving accurate results, as we now show.

## II. APPLICATION OF LMF THEORY TO A SYMMETRIC IONIC FLUID MODEL

We consider a uniform mixture of  $N$  positive and  $N$  negative ions with charges  $+q$  and  $-q$ . The molecular cores are described by the repulsive part of the Lennard–Jones (LJ) potential  $u_0^{\text{LJ}}(r)$ .<sup>27</sup> The total intermolecular potential between ions with charges  $q_i$  and  $q_j$  ( $= \pm q$ ) is taken to be

$$w_{ij}(r) = u_0^{\text{LJ}}(r) + \frac{q_i q_j}{r}, \quad (3)$$

where  $r$  is the distance between the ion centers.

The strength of the Coulomb interactions can be characterized by the ratio  $\Gamma = l_B/d$  of the Bjerrum length  $l_B = q^2/k_B T$  (the distance where the Coulomb energy between two positive ions equals  $k_B T$ ) to the “ion diameter”  $d \equiv \sigma^{\text{LJ}}$ , where  $\sigma^{\text{LJ}}$  is the length parameter in the repulsive LJ potential.  $\Gamma \geq 1$  characterizes the “strong coupling” regime.

Previous studies<sup>8,9,23,31</sup> have shown that it is advantageous to divide the Coulomb interaction  $v(r) \equiv 1/r$  into short-ranged and long-ranged parts in the following way (see Fig. 1),

$$\frac{1}{r} = \frac{\text{erfc}(r/\sigma)}{r} + \frac{\text{erf}(r/\sigma)}{r} \equiv v_0(r, \sigma) + v_1(r, \sigma), \quad (4)$$

where  $\sigma$  is a length scale at our disposal. The idea behind this separation is best understood by considering the Fourier transform of the long-ranged component  $v_1(r, \sigma) = \text{erf}(r/\sigma)/r$ ,

$$\hat{v}_1(k, \sigma) = \frac{4\pi}{k^2} \exp\left(-\frac{k^2\sigma^2}{4}\right). \quad (5)$$

The function  $\hat{v}_1(k, \sigma)$  differs significantly from zero only at small wave vectors  $k\sigma \lesssim 2$ . As a result,  $v_1(r, \sigma)$  remains finite as  $r \rightarrow 0$  and is slowly varying for  $r \lesssim \sigma$ , while still decaying asymptotically as  $1/r$ . This makes it much more suitable for a mean-field averaging than the full Coulomb potential  $v(r)$  used in the classical Debye theory.

This generates a separation of the intermolecular potentials  $w_{ij}(r) \equiv u_{0,ij}(r) + u_{1,ij}(r)$  into short-ranged and long-ranged components, respectively, where

$$u_{0,ij}(r) = u_0^{\text{LJ}}(r) + q_i q_j v_0(r, \sigma) \quad (6)$$

and

$$u_{1,ij}(r) = q_i q_j v_1(r, \sigma). \quad (7)$$

As mentioned above, LMF theory for a uniform system focuses on the density response to a fixed fluid particle. For the symmetric ionic system considered here, we can assume without loss of generality that a positive ion is fixed at the origin. This yields a single particle field  $\phi_j(\mathbf{r}) = w_{+,j}(r)$  acting on an ion with charge  $q_j$ . Using Eqs. (6) and (7),  $\phi_j(\mathbf{r})$  naturally separates into a short-ranged core part  $u_{0,+,j}(r)$  and the long-ranged remainder  $u_{1,+,j}(r)$ .

The fixed ion induces a nonuniform singlet density  $\rho_j(\mathbf{r}) = \rho g_{+,j}(r)$ , proportional to the radial distribution function  $g_{+,j}(r)$  in the uniform fluid.<sup>24</sup> Here  $\rho = N/V$  is the number density of positive or negative ions. Similarly, the induced charge density  $\rho^q(\mathbf{r}) \equiv q\rho_+(\mathbf{r}) - q\rho_-(\mathbf{r})$  satisfies

$$\rho^q(\mathbf{r}) = q\rho[g_{++}(r) - g_{+-}(r)] \equiv q\rho h^q(r). \quad (8)$$

The electrostatic energy per ion in the uniform ionic fluid can be written exactly in terms of the charge density as

$$\frac{U}{2N} = \frac{q}{2} \int d\mathbf{r}' \rho^q(\mathbf{r}') v(r'). \quad (9)$$

LMF theory models the original uniform system by a nonuniform mimic system comprised of “solvent” mimic ions with short-ranged intermolecular interactions  $u_{0,ij}(r)$  in an effective field  $\phi_{R,j}(\mathbf{r})$ , which we can picture as arising from a modified “solute” ion fixed at the origin. According to Eq. (1), when LMF theory is accurate, the solute-induced densities in the mimic system should equal the analogous densities in the original system. Using Eqs. (6) and (7), the LMF equation for  $\phi_{R,j}(\mathbf{r})$  can be written as [cf. Eq. (2)]

$$\begin{aligned} \phi_{R,j}(\mathbf{r}) = & u_{0,+,j}(r) + q_j \int d\mathbf{r}' [q\delta(\mathbf{r}') + \rho_R^q(\mathbf{r}')] \\ & \times v_1(|\mathbf{r} - \mathbf{r}'|, \sigma), \end{aligned} \quad (10)$$

where  $\rho_R^q(\mathbf{r}) = q\rho_{R,+}(\mathbf{r}) - q\rho_{R,-}(\mathbf{r})$  is the induced charge density in the nonuniform mimic system.

The form of the effective field in Eq. (10) clearly depends on  $\sigma$ . There are two criteria that help determine an optimal choice of  $\sigma$ . For the LMF method to be quantitatively valid,  $\sigma$  should be large enough that  $v_1(r, \sigma)$  remains slowly varying on the scale of short-ranged pair correlations. At the same time, it is desirable to keep  $\sigma$  small in order to reduce simulation times of the mimic system. Thus  $\sigma$  is generally chosen near its minimal accurate value  $\sigma_{\text{min}}$ , which is state dependent and of the order of a characteristic neighbor spacing.<sup>8,9,23</sup>

In principle, Eq. (10) has to be solved self-consistently since the effective field  $\phi_{R,j}(\mathbf{r})$  depends on the charge density  $\rho_R^q(\mathbf{r})$  in the presence of the field itself. During an iterative solution of Eq. (10), the density induced by a given field can be accurately determined from the simulation of the nonuniform mimic system. This procedure has been successfully carried out for models of ions<sup>9</sup> or water<sup>32</sup> confined between charged and uncharged hard walls. Once the self-consistent charge density  $\rho_R^q(\mathbf{r})$  has been determined, it can be used in Eq. (9) to calculate the electrostatic energy of the original ionic system.

However, self-consistent simulations of the nonuniform mimic system can be computationally demanding and may not always be required to obtain accurate results. In the following we introduce a simplified version of LMF theory that avoids the need for full self-consistency. We show that both the local structure and the electrostatic energy of the uniform ionic system can be accurately reproduced by combining results of straightforward simulations of the *uniform* mimic system with  $\phi_{R,j}(\mathbf{r}) = 0$  along with analytic results from the Debye theory of screening for corrections arising from the long-ranged forces. Similar ideas have also proved useful in simulations of more complex systems of charged polymers, as will be described elsewhere.<sup>33</sup>

### III. LOCAL STRUCTURE FROM SHORT-RANGED SIMULATIONS

#### A. Strong-coupling approximation

At high density in the uniform ionic system we expect considerable cancellation of the forces from the slowly varying part  $v_1(r, \sigma)$  of the Coulomb interaction when  $\sigma$  is chosen properly. In the simplest “strong-coupling approximation” (SCA) to the full LMF theory,<sup>8,9,23</sup> we ignore all effects of  $v_1(r, \sigma)$  on the fluid structure, i.e., neglect the integral in Eq. (10). Note that the strong short-ranged part  $v_0(r, \sigma)$  of the Coulomb interaction as well as the LJ core is still taken into account in the SCA. This part of the interaction would be expected to dominate local structural arrangements at lower densities as well, provided that  $\sigma$  is chosen large enough.

In the SCA the self-consistent field  $\phi_{R,j}(\mathbf{r})$  in Eq. (10) is approximated by  $\phi_{0,j}(\mathbf{r}) \equiv u_{0,+,j}(r)$ , the known field of a sol-



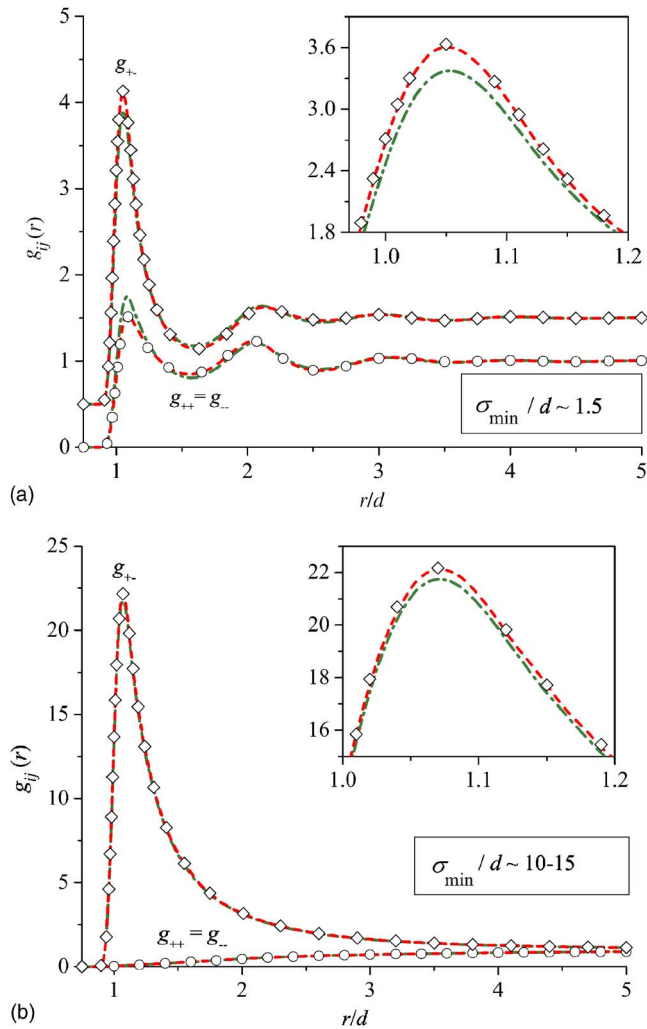


FIG. 2. (Color online) The ion-ion distribution functions  $g_{ij}(r)$  in two uniform symmetric ionic mixtures with  $\Gamma=5$ ,  $\rho d^3=0.3816$  (a), and  $\Gamma=5$ ,  $\rho d^3=0.0012$  (b). The open symbols are the ion pair distribution functions in the full Coulomb systems, obtained using Ewald simulations. The curves are the same functions in the mimic systems with (a)  $\sigma/d=1.5$  (dash) and 1 (dash-dot), (b)  $\sigma/d=15$  (dash) and 10 (dash-dot). The  $g_{+-}(r)$  functions in (a) are vertically displaced by 0.5. The insets show a zoom of the first peak of  $g_{+-}(r)$ .

vent mimic ion. In this case, the induced charge density  $\rho_0^q(\mathbf{r})$  can be determined directly and more efficiently from the radial distribution functions  $g_{0,+j}(r)$  in the *uniform* mimic system [cf. Eq. (8)],

$$\rho_0^q(\mathbf{r}) = q\rho[g_{0,++}(r) - g_{0,+,-}(r)] \equiv q\rho h_0^q(r). \quad (11)$$

Thus the SCA can be viewed as a particularly useful direct truncation scheme,<sup>3</sup> whose accuracy can be justified in certain limits and corrected, if necessary, by the full LMF theory. Note that we use the subscript 0 to refer both to pair correlation functions in the uniform mimic system with  $\phi_{R,j}=0$  and to the equivalent singlet densities in the nonuniform system when  $\phi_{R,j}$  is approximated using the SCA by  $\phi_{0,j}$ . The subscript  $R$  refers to the nonuniform mimic system in the presence of the full renormalized field given by Eq. (10).

Figure 2 gives representative results of Langevin dynamics simulations using the Ewald sum method for the present

ionic fluid model at states with fixed temperature  $k_B T / \epsilon^{LJ} = 1$  and charge  $q$  chosen so that the system is at moderately strong coupling with  $\Gamma=5$ . These are compared to simulations of the uniform mimic system, as described by the SCA, where the cutoff radius for the short-ranged potential  $v_0(r, \sigma)$  is  $2.5\sigma$ .

Figure 2(a) shows results for a high density state with  $\rho d^3=0.3816$ , where there is substantial cancellation of attractive forces. We find that for  $\sigma/d=1.5$  there is excellent agreement between the distribution functions in the full Coulomb and mimic systems over the range of  $r$  shown. Higher values of  $\sigma$  give equally good results, but smaller  $\sigma$  values cause noticeable errors, as illustrated in the inset for  $\sigma/d=1$ , so  $\sigma_{\min}$  is about  $1.5d$  for this state. This good agreement is consistent with previous work on LMF theory<sup>8,9,23</sup> and with earlier findings that models with truncated Coulomb interactions can often provide a good description of structural features in dense uniform systems.<sup>3,4</sup>

Figure 2(b) makes the same comparison for a very low density state with  $\rho d^3=0.0012$ . Despite this low density the coupling is strong enough that the Debye theory alone would give poor results, and this state presents a major challenge to theory. We find that a much larger value of  $\sigma/d=15$  is needed to achieve comparably good results (the small deviations for  $\sigma/d=10$  are shown in the inset). Large  $\sigma$  is needed since there is essentially no force cancellation at low densities and the characteristic neighbor distances are large, but this also makes simulations of the mimic system much more costly in this regime.

However, despite the excellent agreement between the distribution functions in the original and uniform mimic systems in the range of  $r$  shown, there are fundamental differences in the asymptotic behavior of these functions as  $r \rightarrow \infty$ . This is most easily seen from the small- $k$  behavior of the charge structure factor  $S^q(k)$ , which is simply related to the Fourier transform of the dimensionless charge correlation function  $h^q(r)$  defined in Eq. (8),

$$S^q(k) = 1 + \rho \hat{h}^q(k). \quad (12)$$

As  $k \rightarrow 0$ , the charge structure factor  $S^q(k)$  of any ionic system exhibits the same universal behavior,

$$S^q(k) = k^2 \lambda_D^2 + O(k^4), \quad (13)$$

where

$$\lambda_D = (8\pi l_B \rho)^{-1/2} \quad (14)$$

is the Debye screening length. The exact form in Eq. (13) is independent of any details of the short-ranged core interactions  $u_{0,ij}(r)$  and is a consequence of the Stillinger-Lovett moment conditions.<sup>30</sup> In contrast, the analogous function

$$S_0^q(k) = 1 + \rho \hat{h}_0^q(k) \quad (15)$$

for the uniform short-ranged mimic system, where  $h_0^q(r)$  is defined in Eq. (11), will remain finite as  $k \rightarrow 0$ , with the coefficient of  $k^2$  depending on the details of the intermolecular interactions.

In Fig. 3, we compare  $S_0^q(k)$  and  $S^q(k)$  for the same ionic mixtures whose  $g_{ij}(r)$  are shown in Fig. 2. For  $\sigma \geq \sigma_{\min}$ , the

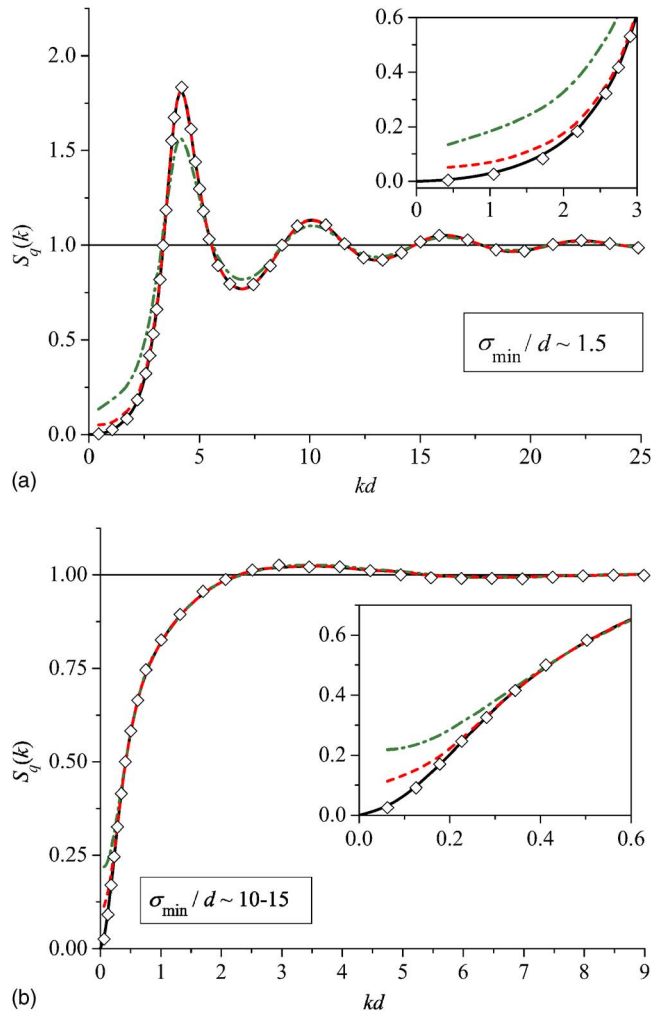


FIG. 3. (Color online) The charge structure factors  $S^q(k)$  for the same systems as in Fig. 2. The insets show a zoom of the small- $k$  region where a discrepancy is seen in the structure factors of the full Coulomb and mimic systems. The solid curves show the results of application of the perturbation Eq. (27) to the dashed curves in (a) and (b).

functions  $S_0^q(k)$  closely follow  $S^q(k)$  everywhere except for small- $k$ , where the differences described above can be seen. If  $\sigma < \sigma_{\min}$ , noticeable discrepancies between  $S_0^q(k)$  and  $S^q(k)$  appear also at larger  $k$ , as illustrated by the dash-dot curve in Fig. 3(a).

## B. Complete screening and the Debye theory

This different behavior at small wave vectors implies that the uniform mimic system will not exactly satisfy the basic “complete screening condition” that true ionic fluids obey. Complete screening (equivalent to the Stillinger–Lovett zeroth moment condition) requires that the exact  $\rho^q$  induced by a fixed positive ion in a grand ensemble will satisfy

$$\int d\mathbf{r} \rho^q(\mathbf{r}) = -q. \quad (16)$$

However, the results above for the simpler SCA imply that Eq. (16) will not hold if  $\rho^q$  is approximated by the  $\rho_0^q$  given by a grand-canonical simulation of the mimic system with a fixed positive solvent mimic ion at the origin.

To verify these conclusions, we have performed grand-canonical ensemble simulations of the nonuniform mimic system in the field  $\phi_{0,j}(\mathbf{r}) = u_{0,+j}(r)$  for a state with  $\Gamma=5$ ,  $\rho d^3=0.0012$  and  $\sigma=10d$ . We find that the mean number of counterions  $\langle N \rangle = 1202.19$  in the simulation box exceeds the mean number of coions by  $\Delta N = 0.68 \pm 0.10$ . This is definitely smaller than the mean difference  $\Delta N = 1$  that should hold in the case of complete screening. We chose a very large simulation box with  $L=100d$  such that this value of  $\Delta N$  is independent of  $L$  and carried out a long 50 ns simulation run to obtain the reported statistical convergence of  $\Delta N$ .

In addition, we ran a similar simulation of the nonuniform mimic system in which the long-ranged part  $v_1(r, \sigma)$  of the Coulomb potential has been taken into account through the LMF Eq. (10). One can show that the density induced by a self-consistent solution of this equation will exactly satisfy the complete screening condition.<sup>23</sup> However, instead of solving Eq. (10) self-consistently, we have replaced the charge density profile  $\rho_R^q(r)$  in this equation by the screening profile of a point charge given by the linearized Debye–Hückel theory,

$$\rho_D^q(r) = -\frac{q}{4\pi\lambda_D^2 r} \exp\left(-\frac{r}{\lambda_D}\right). \quad (17)$$

At first glance this may seem to be a very crude approximation, since the Debye profile is generally accurate only when both  $\Gamma$  and  $\rho$  are very small. Otherwise  $\rho_R^q(r)$  and  $\rho_D^q(r)$  will differ considerably at small  $r$ . However, the Debye profile has the correct asymptotic behavior since it satisfies the exact Stillinger–Lovett zeroth and second moment conditions.<sup>30</sup> Moreover, when integrated over the slowly varying part of the Coulomb potential  $v_1(r, \sigma)$  as in Eq. (10), most of the short-ranged features of this profile on the scale  $r \lesssim \sigma$  become irrelevant, so the resulting estimate for  $\phi_{R,j}(\mathbf{r})$  can still be accurate.

With this approximation, the integration in Eq. (10) can be carried out exactly and we obtain an explicit expression for the effective field  $\phi_{R,j}(\mathbf{r})$ ,

$$\begin{aligned} \phi_{R,j}(\mathbf{r}) \approx & u_{0,+j}(r) + \frac{qj}{2r} \exp\left(\frac{\sigma^2}{4\lambda_D^2}\right) \\ & \times \left[ \exp\left(-\frac{r}{\lambda_D}\right) \operatorname{erfc}\left(\frac{\sigma}{2} - \frac{r}{\sigma}\right) \right. \\ & \left. - \exp\left(\frac{r}{\lambda_D}\right) \operatorname{erfc}\left(\frac{\sigma}{2} + \frac{r}{\sigma}\right) \right]. \end{aligned} \quad (18)$$

The simulation of the nonuniform mimic system, where  $\phi_{R,j}(\mathbf{r})$  is given by Eq. (18), yields  $\Delta N = 1.09 \pm 0.10$ . Thus our simple estimate for the effective field using the Debye theory can reproduce the complete screening behavior seen in the full system or from a complete self-consistent solution of the LMF equation.

## IV. ELECTROSTATIC ENERGY

Thermodynamic properties of ionic systems also require careful attention to contributions from the long-ranged parts of the Coulomb interactions. Again we find that analytic re-

TABLE I. The electrostatic energy  $U$  for the same systems as in Figs. 2 and 3. The errors in the last significant figure are indicated in parentheses. Approximations for the total energy labeled Debye, RPA, and Debye-M are discussed in Eqs. (23), (28), and (29) respectively.

$\frac{\beta U}{2N}$	$\rho d^3=0.0012$		$\rho d^3=0.3816$	
	$\sigma=10$	$\sigma=15$	$\sigma=1$	$\sigma=1.5$
$\frac{\beta U_0}{2N}$	-0.5946(4)	-0.6837(3)	-0.4912(1)	-1.3122(2)
Debye	-0.8487(4)	-0.8622(3)	-3.2068(1)	-3.1597(2)
RPA	-0.8453(5)	-0.8612(3)	-3.0136(2)	-3.1335(2)
Debye-M	-0.8678(4)	-0.8701(3)	-3.2979(1)	-3.1906(2)
$\frac{\beta U_{\text{Ew}}}{2N}$	-0.8708(4)		-3.1880(3)	

sults from the Debye theory can provide simple but accurate corrections to results from the uniform mimic system. In analogy with Eq. (9), the “electrostatic energy” of the uniform mimic system is given by

$$\frac{U_0}{2N} = \frac{q}{2} \int d\mathbf{r}' \rho_0^q(\mathbf{r}') v_0(r', \sigma). \quad (19)$$

As illustrated in Table I,  $U_0$  differs considerably from the full Coulomb energy  $U$ , determined by the Ewald sum method, even for  $\sigma \geq \sigma_{\min}$  when local structural properties of the original and mimic systems closely resemble each other.

To find the needed correction, we note that Eq. (9) can be exactly rewritten as

$$\begin{aligned} \frac{\beta U}{2N} &= \frac{\beta U_0}{2N} + \frac{l_B}{2} \frac{1}{(2\pi)^3} \int d\mathbf{k} [S^q(k) - 1] \hat{v}_1(k, \sigma) \\ &+ \frac{\rho l_B}{2} \int d\mathbf{r}' [h^q(r') - h_0^q(r')] v_0(r', \sigma), \end{aligned} \quad (20)$$

where  $h^q(r)$ ,  $h_0^q(r)$ ,  $S^q(k)$ , and  $U_0$  are defined in Eqs. (8), (11), (12), and (19), respectively.

We expect that the value of the last integral in Eq. (20) is very small, since with proper choice of  $\sigma$ ,  $h^q(r)$  and  $h_0^q(r)$  are very similar over the entire range of  $r$  where  $v_0(r, \sigma)$  differs significantly from zero (see Fig. 2). Hence the energy difference  $\Delta U \equiv U - U_0$  can be accurately estimated as

$$\frac{\beta \Delta U}{2N} \approx \frac{l_B}{2} \frac{1}{(2\pi)^3} \int d\mathbf{k} \hat{v}_1(k, \sigma) [S^q(k) - 1]. \quad (21)$$

Note that the LMF integral in Eq. (10) for  $r=0$  equals  $\Delta U/N$ .

The function  $\hat{v}_1(k, \sigma)$ , given by Eq. (5), is a rapidly decaying function of  $k$  for  $k\sigma \geq 2$ . Thus only the small- $k$  behavior of  $S^q(k)$  is significant in Eq. (21). Similar to our discussion of complete screening in Sec. III B, this suggests that we can accurately use the Debye approximation

$$S_D^q(k) = \frac{k^2}{k^2 + \lambda_D^{-2}} \quad (22)$$

for the charge structure factor  $S^q(k)$  in Eq. (21).

Equation (22) is exact at small enough  $k$  since it satisfies both Stillinger–Lovett moment conditions and, unlike Eq. (13), correctly reduces to unity at large  $k$ . Furthermore it

becomes an exact result for all  $k$  in the limit of very small  $\Gamma$  and  $\rho$ . Substituting Eq. (22) in Eq. (21), we find

$$\frac{\beta \Delta U}{2N} = \frac{\beta U_D}{2N} f_1\left(\frac{\sigma}{\lambda_D}\right), \quad (23)$$

where  $U_D$  is the well known result for the Coulomb energy in the Debye approximation,

$$\frac{\beta U_D}{2N} = -\frac{l_B}{2\lambda_D} \quad (24)$$

and

$$f_1(y) = \exp\left(\frac{y^2}{4}\right) \text{erfc}\left(\frac{y}{2}\right). \quad (25)$$

We expect accurate results from Eq. (23) only when  $\sigma$  is properly chosen to be greater than a state-dependent minimum value  $\sigma_{\min}$ . For strong-coupling states with  $\Gamma \geq 1$ , we note that  $\sigma_{\min} \gg \lambda_D$ . Using the asymptotic expansion of  $\text{erfc}(y/2)$  in Eq. (25), Eq. (23) then reduces to the strong-coupling energy correction

$$\frac{\beta \Delta U}{2N} \approx -\frac{l_B}{\sqrt{\pi}\sigma} \left[ 1 - 2\left(\frac{\lambda_D}{\sigma}\right)^2 \right] \quad (26)$$

derived in Ref. 23, where  $S^q(k)$  was approximated by the second moment term in Eq. (13). However, Eq. (23) also correctly reduces to the exact Debye energy in the limit of very weak coupling and low density where  $\sigma_{\min} \rightarrow 0$  and provides a more generally useful expression.

The resulting energy estimates  $U_0 + \Delta U$  from Eq. (23), labeled “Debye,” are given in Table I and are plotted for more states over a wide range of  $\sigma$  in Fig. 4. We see that the deviations of the Debye corrected energy from the Ewald energies  $U_{\text{Ew}}$  are reduced by approximately an order of magnitude from the uncorrected results given in Table I. Moreover, the accuracy of the correction  $\Delta U$  sharply increases with larger values of the ratio  $\sigma/\lambda_D$ . This allows us to determine appropriate values for  $\sigma_{\min}$  and obtain energy estimates accurate to within 1% when  $\sigma$  is chosen large enough.

In the limit  $\sigma \rightarrow 0$ ,  $U_0$  becomes vanishingly small and Eq. (23) reduces to the classical Debye approximation. Since the Debye theory generally overestimates the absolute value of  $U$ , all the curves in Fig. 4 turn up sharply at small enough  $\sigma < \sigma_{\min}$ .

These results emphasize that LMF theory is an inherently approximate approach and accurate results can be expected only when  $\sigma$  is chosen greater than some state-dependent minimum value  $\sigma_{\min}$ . In the present simplified treatment, errors for a wide range of  $\sigma$  have been determined from comparison with the results of Ewald simulations. These fairly basic simulation studies can be used to devise an estimate of  $\sigma_{\min}$  for an ionic solution of given concentration and ionic strength.

Although the energy correction in Eq. (23) depends only on the ratio  $\sigma/\lambda_D$ , the numerical performance of this correction depends significantly on another length scale, the characteristic neighbor distance between a pair of ions, estimated here by  $r^* = (2\rho)^{-1/3}$ . As can be deduced from Fig. 4, the accuracy of  $\Delta U$  decreases sharply when  $\sigma < r^*$ . When

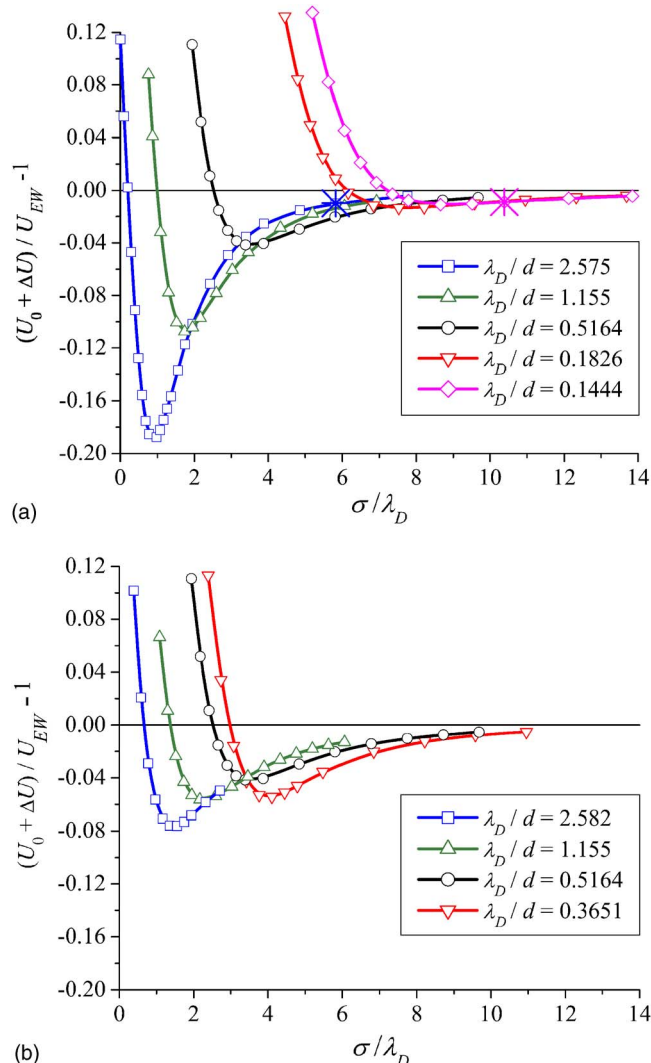


FIG. 4. (Color online) The Debye corrected energies  $U_0 + \Delta U$  from Eq. (23) for a wide range of  $\sigma$  relative to the Ewald energies  $U_{EW}$  of the full Coulomb systems. The data sets, shown from left to right, are for (a)  $\Gamma=5$  and  $\rho d^3 = 0.0012, 0.005\,969, 0.029\,84, 0.2387, 0.3816$ , and for (b)  $\rho d^3 = 0.02984$  and  $\Gamma = 0.2, 1.5, 10$ . The two stars in (a) show the location of  $\sigma_{\min}$  as estimated from the structure shown in Fig. 2 for a low density state with  $\rho d^3 = 0.0012$  and  $\sigma_{\min} = 15$ , and a high density state with  $\rho d^3 = 0.3816$ , and  $\sigma_{\min} = 1.5$ . A spline curve is fitted through each set of data to guide the eye.

$\sigma/r^* > 1$ , the accuracy of  $\Delta U$  is generally acceptable and is higher for larger values of  $\sigma/\lambda_D$ . As a rule of thumb for systems with moderately strong coupling, we suggest that if an ionic solution is simulated as part of a more complex system, the two conditions  $\sigma \gtrsim 2r^*$  and  $\sigma \gtrsim 5\lambda_D$  should be fulfilled simultaneously to yield an accurate description of electrostatic interactions.

## V. INTEGRAL EQUATION METHODS FOR A UNIFORM IONIC FLUID

Integral equation methods that treat the long-ranged part of intermolecular interactions as a weak perturbation<sup>28,29</sup> have long been used to study ionic fluids<sup>1</sup> and could serve as an alternative approach to LMF theory for uniform systems. These equations are usually derived by summing certain classes of diagrams, where individual diagrams represent different terms in the perturbation series for structural and ther-

modynamic quantities. Although it is difficult to develop a physical intuition for what the errors will be in a given application, these methods are expected to work best when the effects of the long-ranged perturbations on the structure of a short-ranged reference system are in some sense small.

Since the local structure is well described by the uniform mimic system, it seems likely that this could serve as a particularly useful reference system for perturbation integral equation methods. This idea was, in fact, suggested long ago by Ceperley and Chester,<sup>31</sup> although they did not discuss the possibility of applying it outside the framework of integral equations. Here we use one of the earliest perturbation approaches, the RPA-like method of Ref. 28, to correct results for the uniform mimic system. In this approach the charge structure factor  $S^q(k)$  of a uniform ionic mixture can be approximately written as

$$S^q(k) = \frac{S_0^q(k)}{1 + 2l_B \rho \hat{v}_1(k, \sigma) S_0^q(k)}, \quad (27)$$

where  $S_0^q(k)$  is the charge structure factor of the uniform mimic system and  $\hat{v}_1(k, \sigma)$  is given in Eq. (5).

The resulting functions  $S^q(k)$  are shown in Fig. 3 where they are compared with  $S_0^q(k)$  obtained from short-ranged simulations. In contrast with  $S_0^q(k)$ , the functions  $S^q(k)$  satisfy both Stillinger–Lovett moment conditions. For  $\sigma \gtrsim \sigma_{\min}$  they are virtually indistinguishable from the results of Ewald simulations.

The perturbation method of Ref. 28 also yields an expression for the energy correction  $\Delta U$ ,

$$\frac{\beta \Delta U}{2N} = \frac{l_B}{2} \frac{1}{(2\pi)^3} \int \left[ \frac{1}{2l_B \rho} \ln \frac{S_0^q(k)}{S^q(k)} - \hat{v}_1(k, \sigma) \right] d\mathbf{k}, \quad (28)$$

where  $S^q(k)$  is given by Eq. (27). The energy estimates resulting from Eq. (28), labeled as “RPA” are given in Table I.

Remarkably, although the calculation based on the Debye profile is much less involved, it gives energy estimates that are equally accurate. We find, however, that yet another energy correction gives even more accurate results,

$$\frac{\beta \Delta U}{2N} = \frac{\beta U_D}{2N} - \frac{\beta U_{0D}}{2N}. \quad (29)$$

Here  $U_{0D}$  is the electrostatic energy of the uniform mimic system in the Debye limit, obtained by summing for “Coulomb cores”  $v_0(r, \sigma)$  the same ring diagrams that lead to the conventional Debye expression  $U_D$  when using the full Coulomb interaction  $v(r)$ . This gives

$$\frac{\beta U_{0D}}{2N} = \frac{\beta U_D}{2N} f_3\left(\frac{\sigma}{\lambda_D}\right), \quad (30)$$

where

$$f_3(y) = \frac{2}{\pi} \int_0^\infty \frac{\left[1 - \exp\left(-\frac{k^2 y^2}{4}\right)\right]^2}{k^2 + 1 - \exp\left(-\frac{k^2 y^2}{4}\right)} dk. \quad (31)$$

The idea behind Eq. (29) is that with a proper choice of  $\sigma$ , the energy correction  $\Delta U$  should be independent of most



details of the short-ranged interactions. Most errors in the Debye treatment of the short-ranged part of the Coulomb interactions are canceled by subtraction of the two terms in Eq. (29). The results in Table I for this “Debye-Mimic” (Debye-M) approximation give best agreement with the Ewald energies  $U_{\text{Ew}}$  of the full Coulomb systems. This seems to indicate that approximations of the RPA type work best if perturbation terms, similar to  $\Delta U$ , contain no information on the short-ranged core structure of the mimic system.

## VI. CONCLUDING REMARKS

In this paper, we have used a simplified version of LMF theory<sup>19</sup> to calculate the structural and thermodynamic properties of a symmetric ionic mixture. LMF theory has already been applied successfully to the description of uniform and nonuniform ionic systems,<sup>8,9,23</sup> where the LMF was either approximated using only the SCA or was determined by a full self-consistent calculation. We have shown for the ionic mixture considered in this paper that we can go beyond the SCA but avoid the necessity of finding a self-consistent solution if we replace the mimic system’s charge density with its Debye analog in the LMF Eq. (10). The resulting effective field, given in Eq. (18), is sufficiently accurate to reproduce the exact complete screening condition in grand-canonical ensemble simulations. Furthermore, the energies of uniform ionic mixtures, obtained under this assumption, agree well with those calculated using diagrammatic techniques and the Ewald sum method.

When applied to complex inhomogeneous systems, this assumption will significantly speed up the simulations of underlying mimic systems since it reduces the simulations in an *a priori* unknown self-consistent field to the simulations in a simpler and well-defined external field. In addition, the Debye charge density is found analytically from the Debye–Hückel equation for an infinite system. For unbounded Coulomb systems this should result in more accurate values of the effective field in Eq. (2) than those obtained by numerical integration using simulation results in a finite volume.

These ideas are being actively applied in our studies of polyelectrolytes in salt solutions.<sup>33</sup> Since the polymer dynamics are slow in comparison with the dynamics of small ions, it is valid to assume that the distribution of salt ions around a polyelectrolyte is always in local equilibrium. In this case, the total effective field of a polyelectrolyte is simply a sum of the effective fields of all its monomer charges, given by Eq. (18). This essentially amounts to replacing the full Coulomb potential of a monomer charge with a screened Coulomb potential, defined as a sum of  $r^{-1} \text{erfc}(r/\sigma)$  and the last term in Eq. (18). We note that the idea of introducing effective Debye–Hückel, or Yukawa, interactions between polyelectrolyte charges has been widely used to account for the screening by small ions.<sup>34,35</sup> The advantage of our approach, however, is that it invokes only the long-ranged fea-

tures of the Debye screening profile, while still explicitly accounting for the strong electrostatic core interactions between charges at small distances in the simulations. This approach should therefore remain accurate for strongly interacting and dense polyelectrolyte systems, where conventional Debye–Hückel interactions are a very crude approximation.

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