Effective attractions between like-charged objects are quite common and have been extensively studied. For example, highly charged DNA is densely packed in cell nuclei via positively-charged intermediaries, and, in vitro, DNA may be condensed into toroids by adding sufficient concentrations of divalent or trivalent counterions. In this paper we use local molecular field (LMF) theory to study one of the simplest models that exhibits like-charged attraction — two uniformly-charged walls with neutralizing point counterions, as shown in Fig. 1(a) with length scales that will be discussed later.

LMF theory defines a general mapping that relates the structure and thermodynamics of a nonuniform system with long-ranged intermolecular interactions in an external field \( \phi \) to those of a simpler “mimic system” with short-ranged interactions in the presence of an effective field \( \phi_R \), as qualitatively shown in Fig. 1(b). \( \phi_R \) accounts for the averaged effects of the long-ranged interactions and self-consistently depends on the nonuniform density the field induces. This approach is particularly useful for systems with Coulomb interactions, because one can choose specific slowly-varying, long-ranged components of the Coulomb interactions that are especially well-suited for the mean-field average. The remaining short-ranged “Coulomb core” components combine with other existing short-ranged interactions to define the intermolecular interactions in the Coulomb mimic system. Thus the theory is not restricted to point counterions and very accurate results have already been found for uniform fluids with charged hard cores.

However, additional approximations were made in these earlier applications of LMF theory. In particular the Boltzmann approximation for the density response to the effective field was used for the charged wall system. Here we use Monte Carlo (MC) simulations to accurately determine the density response. We believe that such simulations of the mimic system will often be needed to obtain quantitative results from LMF theory in more realistic models of biophysical interest.

Then the only remaining errors are those inherent in the LMF mapping itself. The results provide a critical test of LMF theory in a nonuniform Coulomb system where the basic physics of the counterion-mediated attraction is highly nontrivial but well-understood, and where extensive benchmark simulations are available.

Before giving details of the model and the LMF map-
Simulations from [9]. For results of the LMF theory for two system couplings, osmotic pressure define the thermodynamic state of this system. Effective core size \( \sigma \) defines using the Lekner-Sperb method; our simulations agree very well with full simulations from\[3\]. For \( d = 20 \) and \( \xi = 20 \), the effective core size \( \sigma_{\text{min}} \) is 18 and for \( d = 20 \) and \( \xi = 100 \), \( \sigma_{\text{min}} \) is 34.

**FIG. 2:** Pressure vs. distance curves for two couplings, \( \xi = 20 \) and \( \xi = 100 \). LMF simulations agree very well with full simulations from \[3\]. For \( d = 20 \) and \( \xi = 20 \), the effective core size \( \sigma_{\text{min}} \) is 18 and for \( d = 20 \) and \( \xi = 100 \), \( \sigma_{\text{min}} \) is 34.

ping, the quantitative accuracy achieved in practice is illustrated in Fig. 2 which compares the dimensionless osmotic pressure \( P \) for the full Coulomb system \[2\] to results of the LMF theory for two system couplings, \( \xi \). Depending on the separation \( d \), either coupling can result in a net attractive force on the walls as indicated by negative values of \( P \). Simulations of the full Coulomb system required careful and costly treatment of periodic boundary conditions using the Lekner-Sperb method; our simulations of the short-ranged mimic system used only a simple minimum image method.

In the model two infinite hard walls with a negative charge density \( q_w \) are located at \( z = 0 \) and \( z = d \). Positive neutralizing point counterions with valence \( Z \) and charge \( Z q_0 \) are contained in \( 0 \leq z \leq d \) and there is a uniform dielectric constant \( \epsilon \) everywhere. The three length scales shown in Fig. 1(a) can be motivated by an examination of the energetics of one uniformly charged wall at \( z_w \). The potential energy between the wall and a counterion at \( z \) is \(-2\pi q_w Z e_0 |z - z_w|/\epsilon \). The Bjerrum length \( L_B \) is defined using the potential energy between a pair of ions: \( L_B = Z^2 e_0^2/(k_B T) \). The third length scale, \( L_w \), is determined from the surface area of the wall neutralized by one counterion: \( L_w^2 = Z e_0 / |q_w| = 2\pi L_B L_G \).

We will use dimensionless variables where lengths are measured in units of \( L_B \) and energy in units of \( k_B T \). Specifying \( d \) and the coupling strength \( \xi \equiv L_B/L_G \) fully defines the thermodynamic state of this system. Effective attractions can arise for strong-coupling states with \( \xi \gtrsim 12 \) [2]. Since the total force on a counterion from both walls exactly cancels, the bare external potential \( \phi = 0 \) for \( 0 \leq z \leq d \). However due to the long-ranged Coulomb repulsion, counterions will organize next to the walls into either one or two layers, based on a complex balance between coupling strength \( \xi \) and the width \( d \) available.

This equation can be derived by integrating the first equation of the exact Yvon-Born-Green hierarchy relating intermolecular forces and conditional singlet densities in the full and mimic systems after making two interconnections and physically reasonable approximations [2][8]. First, when Eq. (1) holds, the conditional singlet density \( \rho_R(r; \phi_R) \) in the mimic system should also approximately equal that in the full system, provided that \( u_0 \) gives a good representation of the short-ranged core interactions between particles. Second, the force from the
slowly-varying \( u_1(\mathbf{r}' - \mathbf{r}) \) should be very small over the range \( \bar{a} \) of characteristic nearest neighbor distances where \( \rho_R(\mathbf{r}'; \phi_R) \) differs significantly from \( \rho_R(\mathbf{r}'; \phi_R) \). Then \( \rho_R(\mathbf{r}'; \phi_R) \) may be reasonably replaced by \( \rho_R(\mathbf{r}'; \phi_R) \) in the integration of the force that yields Eq. (2).

For Coulomb systems we can control the accuracy of the second (mean field) approximation by convoluting the dimensionless Coulomb potential \( w(\mathbf{r}) = \xi/r \) with a Gaussian whose width \( \sigma \) is a parameter at our disposal. This yields a long-ranged component \( u_1(r) = \xi \exp(\sigma/r) \) that remains slowly varying at distances less than \( \sigma \) as illustrated in Fig. 3(a) and the associated core component \( u_0(r) = \xi \exp(\sigma/r) \). When \( \sigma \) is too small, results of the LMF theory will be poor and will vary rapidly as \( \sigma \) increases. But when \( \sigma \geq \sigma_{min} \), with \( \sigma_{min} \) of order the characteristic neighbor spacing \( \bar{a} \), we expect that \( u_1 \) is sufficiently slowly-varying that the LMF averaging is consistent and there will be little change in results as \( \sigma \) increases beyond \( \sigma_{min} \).

Using this choice of \( u_1 \), and noting that \( \phi = 0 \), we can integrate exactly over lateral coordinates in Eq. (2) and obtain the two-wall LMF equation:

\[
\phi_R(z) = \int_0^d dz' n_R(z'; [\phi_R])G(z', z).
\]  

(3)

Here \( n_R(z) = 2\pi \xi \rho_R(z) \) is a dimensionless rescaled density and \( G(z', z) \equiv [-z - z' \exp(\sigma) - \sigma \xi^{-1/2} \exp(\sigma z'^2/\sigma^2)] \), which can be interpreted as the potential at \( z \) due to a Gaussian charge density \( \sigma \xi^{-1/2} \exp(\sigma z'^2/\sigma^2) \), with \( G(z', 0) = 0 \). As explained earlier, \( \phi_R(z) \) plays an important role in this nonuniform mimic system. The bare field \( \phi(z) = 0 \) must be replaced by \( \phi_R(z) \) in simulations of the mimic system for the particles to separate correctly into two layers, as shown in Fig. 3(b).

LMF theory gives exact results both as \( \xi \rightarrow 0 \), where it reduces to the Poisson-Boltzmann (PB) theory, and in the strong coupling limit \( \xi \rightarrow \infty \). To assess its performance for intermediate \( \xi \), canonical MC simulations of the nonuniform mimic system were carried out in a simulation cell of volume \( L \times L \times d \). Particle number \( N \) was chosen so that the wall length \( L \) dictated by neutrality is large enough to justify the minimum image convention. We used the simplest self-consistent simulation closure of the LMF equation by explicitly iterating solutions indexed by \( i \) of Eq. (3) with converged MC values for \( n_R(z) \) until the self-consistency criterion \( \int dz \left| \phi_R^{(i)}(z) - \phi_R^{(i-1)}(z) \right| / d < 0.001 \) was met. Properties were averaged over 5 \( \times 10^5 \) to \( 2 \times 10^6 \) simulation sweeps. \( n_R(z) \) and \( \phi_R(z) \) were calculated on a grid with spacing \( \Delta z = \min\{0.1, 0.01 d\} \). The reduced osmotic pressure was calculated by an accurate method that uses the well-converged density at the midplane and the force between particles and walls on the left and right of the midplane.

\[
F = n(z_{midplane}) + 2\pi \xi \langle F_{LR} \rangle / A.
\]

Crucial for the success of the theory is the proper choice of \( \sigma_{min} \), which should scale with the characteristic neighbor spacing \( \bar{a} \) at strong coupling. The discussion above suggests a simple criterion that uses the consistency of the theory itself to determine a precise value for \( \sigma_{min} \). During a simulation with a given \( \sigma \), we measure the nearest-neighbor distance averaged over particles, \( \langle L_{nn} \rangle \). As \( \sigma \) increases from small values by steps \( j \), we expect initially that \( \langle L_{nn} \rangle \) will increase as the core repulsions in \( u_0(r) \) becomes larger. But for \( \sigma \geq \sigma_{min} \), the variation in \( \langle L_{nn} \rangle \) should level off. As a numerical criterion that gives very reasonable results we choose the first \( \sigma \) such that \( (\langle L_{nn} \rangle - \langle L_{nn}^{-1} \rangle) / (\sigma - \sigma_{min}^{-1}) < 0.005 \).

Figure 4 illustrates the application of this convergence criterion to a strongly-coupled system with \( \xi = 10 \). In Fig. 4(a) the smoothed curves qualitatively represent the limits of \( \sigma_{min} \) determined for two separate layers at large \( d \) and for a single layer at small \( d \). Between those curves lie data for specific \( d \), ranging from two weakly correlated separate layers with weak attraction (\( d = 20 \)) to a single layer configuration where attraction is maximal (\( d = 6 \)). As the walls are pushed closer together and the counterions shift from two layers to one layer, the characteristic neighbor spacing \( \bar{a} \) decreases by a factor of \( \sqrt{2} \). In the \( \sigma_{min} \) convergence plots, we see the expected corresponding factor of \( \sqrt{2} \) as \( \sigma_{min} \) shifts from 36 to 26.

FIG. 3: Potentials and densities for \( \xi = 10 \) with \( \sigma = 14 \). In (a) \( \xi/r \) is split into \( u_0 \) and \( u_1 \). As shown in (b) for \( d = 20 \), when simulating mimic particles that interact only via \( u_0 \), the inclusion of \( \phi_R \), which here has well depths greater than \( 5k_B T \) (scale on right) rather than the flat \( \phi \), is crucial. \( n_0(z; \phi_R) \) is quite different than the accurate \( n_R(z; [\phi_R]) \) as shown by the contact densities (scale on left).
the average (effectively choosing includes the rapidly varying Coulomb core components in effective field resulting from a mean-field average of the implicit in the classical PB or Gouy-Chapman theory is an explicit in the classical PB approach is greatly improved by averaging only over the slowly-varying \( u_1 \) as dictated by LMF theory \(^5\) and can even predict attraction for the two-wall system \(^5\). We have shown here that simulations of the short-ranged cores in conjunction with the \( \phi_R \) given by LMF theory give quantitative agreement with simulations of the full Coulomb system. Further results for this system including analysis of the 2D correlation functions during the formation of a single or two layers, the scaling of \( \sigma_{\text{min}} \), and more realistic descriptions of counterions and co-ions will be reported elsewhere. This work was supported by NSF through grant CHE05-17818. JMR was supported by an NDSEG fellowship.

\[ \sigma_{\text{min}} = \frac{1}{10} \sqrt{\frac{\xi L}{\Delta \sigma}} \]

\[ \langle g_{2D} \rangle \text{min} = 1.18\left( \frac{L}{w} \right)^{0.509} \]

\[ \text{Attractive} \]

\[ \text{Repulsive} \]

FIG. 4: Determination of the consistency parameter \( \sigma_{\text{min}} \). The criterion is applied for \( \xi = 100 \) and varying \( d \) in (a) the horizontal line indicates the convergence threshold of 0.005. The smooth curves schematically represent the upper and lower limits for \( \sigma \) convergence; once a single layer or two layers unambiguously form, the neighbor distance \( \bar{a} \) and hence \( \sigma_{\text{min}} \) should not vary further. \( (L_{\text{nn}}) \) (dotted lines) and \( \sigma_{\text{min}} \) (dashed lines) are related to \( g_{2D} \) pair correlation curves in (b).

FIG. 5: Points where \( P(\xi, d) = 0 \) from LMF simulations are compared to full system simulations in \(^9\). In addition, separations \( d_{\text{min}} \) where the maximum attractive force is found are fit by a power law to \( L_W \propto \sqrt{\xi} \) \( (d_{\text{min}} = 1.18 L_W^{0.509}) \). This agrees very well with an LMF scaling prediction \(^5\).
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