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Phase diagram of charged dumbbells: A random phase approximation approach

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The phase diagram of the charged hard dumbbell system (hard spheres of opposite unit charge fixed at contact) is obtained with the use of the random phase approximation (RPA). The effect of the impenetrability of charged spheres on charge-charge fluctuations is described by introduction of a modified electrostatic potential. The correlations of ions in a pair are included via a correlation function in the RPA. The coexistence curve is in good agreement with Monte Carlo simulations. The relevance of the theory to the restricted primitive model is discussed.

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I. INTRODUCTION

The criticality of simple electrolytes has been a subject of intense research for decades. The two defining features of electrolytes were already captured by Debye and Hückel [1] who pointed out the essential role of charge fluctuations, and Bjerrum [2] who noted that for large charges/concentrations strongly nonlinear interactions would lead to effective pairing of oppositely charged ions. The simplest theoretical model which received most attention is the restricted primitive model (RPM), which consists of an equal number of positively and negatively charged spheres, all of diameter a. Recent interest in the phase diagram of the RPM has been stimulated by appearance of reliable results from Monte Carlo simulations [3–8].

Most of the theories of phase separation in the RPM concentrate on calculating the properties of clusters [9] and obtaining the estimates for the association constant for dimer formation [10] or the free energies of higher order clusters [11]. However, the interactions between different clusters have not received due consideration. They are either neglected [9], considered as interactions between charged spheres of the size of the clusters [11], or only dimer-ion interactions are considered [12,13]. Fisher and Levin [10,13] emphasized the necessity of a correct description of intercluster interactions. They incorporated dimer-ion interactions into the Debye-Hückel theory (DH) and thus obtained a good estimate of the coexistence curve. (We avoid the use of the term "dipole" here to avoid confusion between point-like dipoles and related systems of dipolar spheres, in which no phase separation is found [14,15] unless van der Waals interactions are included [16].) The fairly simple theory of Fisher and Levin [10,13] yields better results when compared with Monte Carlo (MC) simulations than those obtained with the use of the mean-spherical approximation (MSA) [11,12] for simple electrolytes. This demonstrates that correct account of charge correlations is more important than a correct description (as in the MSA) of the hardcore of the spheres.

Recent computer simulations have conclusively demonstrated that the phase coexistence in RPM is driven by interactions between dimers [17]. Camp and Patey [5] found that the number of free ions at the critical temperature of the RPM is "essentially zero." Actually, the phase coexistence curve of the charged hard dumbbell (CHD) system is found to be very close to that of the RPM [18,19]. Most recent [20] MC calculations of the critical point of the CHD system give T_c^* almost identical to that of the RPM, while ρ_c^* is found to be approximately 25% higher. They also conclude that the CHD system belongs to the same universality class (Ising) as the RPM [7], the general features upon approach to the critical point were found to be similar. A recent binding mean-spherical approximation theory of Jiang *et al.* [21] yields the best results when ions are assumed to be fully paired.

We construct here a theory of phase coexistence in charged hard dumbbells using the RPA. We use the RPA (which for point-like ions is equivalent to the DH theory [22]) to account on a linear level for collective fluctuations of charge density due to linearizable long-range electrostatic interactions. The strong short-range correlations that bind the $+$ and $-$ charges are described via molecular correlation functions. We consider the simplest case when all ions form ionic dimers or dumbbells. In principle, the form of the correlation function between ions in a pair can be arbitrary in the theory. We construct the phase diagram using different forms for the molecular correlations of the ionic pairs and compare the results; we also compare the RPA phase diagrams of dumbbells with the phase diagrams obtained by using the binding MSA and MC simulations for dumbbells and for the RPM. Our RPA approach is closely related to the theory of Fisher and Levin [10,13], who used a DH-like approach to calculate the fluctuation contribution from dimer-ion interactions. We use instead a RPA formulation of the DH theory to calculate the contribution from dimer-dimer interactions.

The random phase approximation is a well-established theoretical method extensively used in polymer physics [23–25]. It successfully describes collective fluctuations in polymer blends [24,26,27] and polyelectrolyte solutions [22]. The applicability of the RPA in polymer blends is based on the presence of long-range structural correlations due to the connectedness of monomers in a polymer chain. This results in the Ginzburg region being vanishingly small [24] $t=|T-T_c|/T_c\sim N^{-1}$ (where N is the number of polymers in a chain, typically $N\sim 10^3$). For simple electrolytes long-range

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correlations are due to the long-range nature of the bare Coulomb potential, which could be expected to ensure similarly small t. However, although the Ising criticality for RPM and CHD has been confirmed in MC simulations [6,7,20], at present no agreement exists concerning the Ginzburg number of RPM, with reported values varying from $t \sim 10^{-4}$ (Refs. [28–30]) to the values $t \sim 10^{-1}$ found for neutral van der Waals fluids [31–34].

II. THEORY AND RESULTS

We consider a system of dumbbells composed of two hard spheres of opposite unit charges $+e$ and $-e$ fixed at the contact point. The diameters of all spheres are a which constitutes the only molecular scale of the system. The number concentration of all charges (spheres) is ρ (thus the concentration of dumbbell molecules is $\rho/2$). It is convenient to construct the phase diagram in terms of reduced concentration $\rho^* = \rho a^3$ and temperature $T^* = k_B T \varepsilon a / e^2 = a / l_B$ (here ε is the dielectric constant of the medium and l_B is the Bjerrum length).

We use the random phase approximation [23,24] to calculate the fluctuation contribution to the free energy arising from charge-charge fluctuations. The expression for the general case when structural correlations are present between different components reads (below all energies are reduced by $k_B T$ and all lengths and wavevectors by a):

$$\frac{F_{\mathrm{RPA}}}{V/a^3} = \frac{1}{2} \int \left(\ln\{\det[\mathbf{I} + \mathbf{g}(q)\mathbf{U}(q)]\} - \sum_i \rho_i U_{ii}(q) \right) \frac{d^3 q}{(2\pi)^3}. \tag{1}$$

Here $\mathbf{U}(q) = z_i z_j U(q)$ is the interaction matrix, with z_i being the valences, and $U(q)$ the Fourier transform: $U(q) = \int dr e^{iqr} U(r)$. For the bare Coulomb potential we obtain

$$U_{\mathrm{Coul}}(r) = \frac{l_B}{r}, \quad U_{\mathrm{Coul}}(q) = \frac{4\pi l_B}{q^2}. \tag{2}$$

Structural bonding (either chemical or thermoreversible) is described in the structure matrix $\mathbf{g}(q)$ the elements of which are molecular correlation functions [35]. Given that the components of the matrix $\mathbf{U}(q)$ have the form $U_{ij}(q) = z_i z_j \varphi(q)$, where $\varphi(q)$ does not depend on i or j, we can rewrite (1) as [35]:

$$f_{\mathrm{RPA}} = \frac{F_{\mathrm{RPA}}}{V/a^3} = \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} (\ln\{1 + \mathrm{Tr}[\mathbf{g}(q)\mathbf{U}(q)]\} - \mathrm{Tr}[\mathbf{g}(q = \infty)\mathbf{U}(q)]). \tag{3}$$

We start by considering the case of point-like positive and negative ions each having a number concentration $\rho/2$. The Coulomb interaction is given by Eq. (2) with the vector of valences $z_i = \{+1, -1\}$. The structural correlation matrix is diagonal and for point-like ions is given by the concentrations

$$\mathbf{g}(q) = \begin{pmatrix} \rho/2 & 0 \\ 0 & \rho/2 \end{pmatrix}, \tag{4}$$

which corresponds to no structural correlations between ions, or no ionic internal structure. Substituting $\mathbf{U}(q)$ and $\mathbf{g}(q)$ into Eq. (3) we obtain the free energy correction

$$f_{\mathrm{RPA}} = \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} \left(\ln\left[1 + \frac{4\pi l_B \rho^*}{q^2} \right] - \frac{4\pi l_B \rho^*}{q^2} \right) = -\frac{\kappa^3}{12\pi}, \tag{5}$$

where $\kappa = (4\pi l_B \rho^*)^{1/2}$. This is exactly the Debye-Hückel result for point-like ions.

As mentioned earlier, the RPA by its construction cannot describe the effects of impenetrability of ions. To incorporate these effects into the RPA we phenomenologically modify the electrostatic potential $U(q)$. The modification should be carried out at $q \gg 1$, given that at large distances we should have unscreened Coulomb potential (2). Since the potential is isotropic, it must be a function of q^2. Thus, we naturally arrive at

$$U_{\mathrm{cut}}(q) = \frac{4\pi l_B}{q^2} \frac{1}{1 + q^2}, \tag{6}$$

$$U_{\mathrm{cut}}(r) = \frac{l_B}{r} [1 - e^{-r}], \tag{7}$$

which removes the singularity of the Coulomb potential at $r = 0$. In particular, this potential has been shown previously [36] to correctly describe the qualitative features of the κ-transition in simple electrolytes [37–39]. It also has proved successful in the description of phase separation in polyelectrolyte solutions [40]. However, until now no quantitative comparison has been attempted. Given the phenomenological nature of the potential to achieve a quantitative description we need to introduce a fitting parameter. We do it here by adjusting the abruptness of the cutoff

$$U_{\alpha}(q) = \frac{4\pi l_B}{q^2} \frac{1}{(1 + q^2)^{\alpha}}. \tag{8}$$

We find the value of α by numerically fitting the free energy of the RPM obtained from using this potential in the RPA expression (3):

$$f_{\mathrm{RPA}}^{(\mathrm{RPM})} = \frac{1}{2} \int \frac{d^3 q}{(2\pi)^3} \left\{ \ln\left[1 + \frac{\kappa^2}{q^2} \frac{1}{(1 + q^2)^{\alpha}} \right] - \frac{\kappa^2}{q^2} \frac{1}{(1 + q^2)^{\alpha}} \right\} \tag{9}$$

with the well-known solution [41] of the linearized Poisson-Boltzmann equation for hard charged spheres, which takes correctly into account the boundary conditions for electrostatic potential

$$f_{\mathrm{PB}} = -\frac{1}{4\pi} \left[\ln \kappa - \kappa + \frac{\kappa^2}{2} \right]. \tag{10}$$

Considering the fact that the free energy is used to construct the phase diagram, we attempt to fit simultaneously the free energy and its first derivative. Plots of $-4\pi f_{\mathrm{PB}}(\kappa)$ and

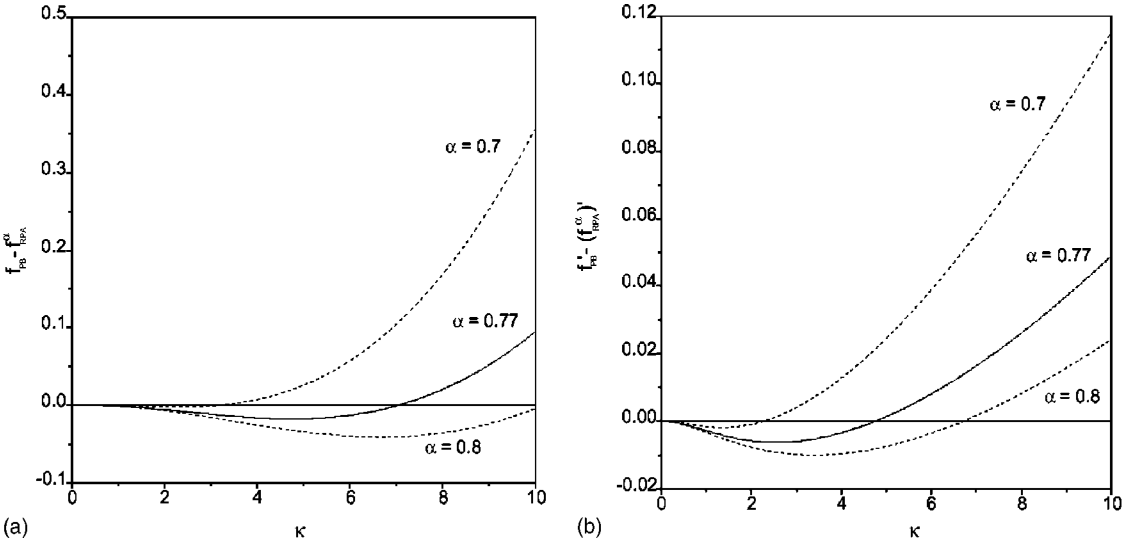

FIG. 1. Plots of the differences of the free energies (a) and the first derivatives of the free energy (b) relative to those of linearized PB. $\alpha=0.7$ and $\alpha=0.8$ (dashed lines). $\alpha=0.77$ (solid line) represents the best fit to the PB free energy.

$-4\pi f_{\mathrm{RPA}}(\kappa)$ and their first derivatives $-4\pi f'_{\mathrm{PB}}(\kappa)$ and $-4\pi f'_{\mathrm{RPA}}(\kappa)$ are presented in Fig. 1. The solid lines corresponds to f_{PB}, two dotted lines are for f_{RPA} with $\alpha=0.7$ and $\alpha=0.8$ as indicated, and the dashed line is for $\alpha=0.77$. As expected, using just α we cannot fit both $f_{\mathrm{RPA}}(\kappa)$ and $f'_{\mathrm{RPA}}(\kappa)$ for all values of κ. In order to obtain certain value for α we fit the values of the first derivatives $f'_{\mathrm{RPA}}(\kappa)$ and $f'_{\mathrm{PB}}(\kappa)$ at $\kappa\approx 5$, corresponding to $\kappa\approx 5.1$ of the critical point of charged dumbbells $(\rho^*=0.101\pm 0.003, T^*=0.049\,11\pm 0.000\,03)$ obtained in MC simulations [20] (which is also very close to $\kappa\approx 4.4$ of the critical point of the RPM [7]). The best fit is obtained for $\alpha=0.77$ which is depicted with a dashed curve. We see that the overall fit of $f_{\mathrm{RPA}}(\kappa)$ and $f'_{\mathrm{RPA}}(\kappa)$ is sufficiently good.

Note, that we choose the potential in the form (3) based only on the fact that we can obtain a good fit of the resulting free energy (9) to the linearized PB one (10). We can also try to adjust the effective radius of the cutoff by introducing the following potential:

$$U_\beta(q)=\frac{4\pi l_B}{q^2}\frac{1}{[1+(\beta q)^2]}. \tag{11}$$

However, we have found that the simultaneous fits of the free energy and its first derivative using this potential (adjusting β) are inferior to those obtained employing the potential (8). In principle, one could improve the fits by using a more elaborate potential than (8), however, given the overall approximations of the theory, the accuracy provided by $U_\alpha(q)$ (combined with its simplicity) is satisfactory.

In order to find the RPA free energy of dumbbells we need to introduce the structural correlations between positive and negative ions via the structure matrix

$$\mathbf{g}(q)=\begin{bmatrix}\frac{\rho}{2} & \frac{\rho}{2}p(q)\\ \frac{\rho}{2}p(q) & \frac{\rho}{2}\end{bmatrix} \tag{12}$$

with $p(q)$ describing the correlations between ions in a dumbbell. We use here the natural first approximation that fixes ions at contact, i.e., $p(\mathbf{r})=\delta(|\mathbf{r}|-1)$ or in Fourier space

$$p(q)=\frac{\sin q}{q}. \tag{13}$$

Substituting the matrix (12) with the effective potential $U_\alpha(q)$ into Eq. (3) we obtain the electrostatic contribution for dumbbells with finite size effects

$$f^{(\mathrm{db})}_{\mathrm{RPA}}=\frac{1}{2}\int\frac{d^3q}{(2\pi)^3}\left\{\ln\left[1+\frac{\kappa^2}{q^2}\frac{1-p(q)}{(1+q^2)^\alpha}\right]-\frac{\kappa^2}{q^2}\frac{1}{(1+q^2)^\alpha}\right\}. \tag{14}$$

The full free energy is a sum of the free energy of the neutral system and the electrostatic input

$$f=f_{\mathrm{TS}}+f^{(\mathrm{db})}_{\mathrm{RPA}}. \tag{15}$$

The free energy of neutral dumbbells is given by the Tildesley-Streett form [42] (we give here the formula for the particular case when the distance between ions $l^*=1$, which corresponds to our assumption)

$$f_{\mathrm{TS}}=\frac{\rho^*}{2}\ln\rho^*+\frac{A\eta-B\eta^2}{(1-\eta)^2}+C\ln(1-\eta), \tag{16}$$

$$A=8.211\,99,\quad B=6.3090\,95,\quad C=2.755\,03,$$

where $\eta=\pi\rho^*/6$.

The coexistence curve of charged dumbbells calculated from the free energy (15) using $\alpha=0.77$ is plotted in Fig. 2 as

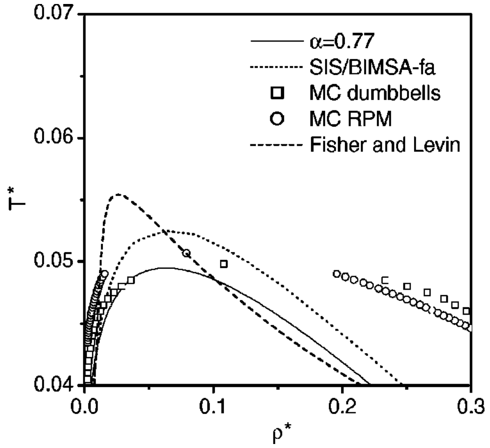

FIG. 2. Comparison of the phase coexistence curves obtained from our theory (solid line) and the model of Jiang *et al.* [21] (dots), Fisher and Levin [13] (dashes). Circles are MC results of Luijten *et al.* [7] for RPM, and squares are MC for dumbbells [19].

a solid line. For comparison we also plot the MC simulations results for the RPM [7] (circles) and for CHD [19] (squares), and the theoretical predictions of Fisher and Levin [13] (dashed curve) and Jiang *et al.* [21] (dotted curve). The critical point is located at $(\rho^* = 0.063, T^* = 0.0495)$ which is to be compared with MC results $(\rho^* = 0.101 \pm 0.003, T^* = 0.049\,11 \pm 0.000\,03)$ for CHD [20] and $[\rho^* = 0.0790(25), T^* = 0.050\,69(2)]$ for the RPM [7]. We conclude that our approach yields the best available theoretical prediction for the critical point. Our coexistence curve has a shape very similar to that obtained by Jiang *et al.* [21]. In fact, we can fit the two curves adjusting the value of α.

An important issue that needs to be addressed is how robust our results are to changes in different inputs of the free energy. Since we lack any alternative expression for hardcore contribution of electroneutral dumbbells, the sensitivity to choosing the appropriate term due to density-density correlations is checked for the RPM. The phase diagrams for this case are calculated using the potential $U_\alpha(q)$. We compare the coexistence curves obtained using the Carnahan-Starling free energy of hard spheres [43] with the curve obtained with a simpler Flory-Huggins approximation $[(1-\rho^*)\ln(1-\rho^*)]$. The difference in the critical temperature is approximately 2%, which indicates robustness of the results to the choice of hardcore free energy. (Guillot and Guissani [44] investigated the Fisher-Levin model [13] and reached a similar conclusion.) This suggests that hard core density effects are minor in the phase segregation induced by charge fluctuations.

The robustness of our RPA dumbbell model to the choice of the fitting parameter α is illustrated in Fig. 3. We plot the CHD coexistence curves using $\alpha = 0.77$ (solid) and $\alpha = 0.8$ and $\alpha = 0.7$ (dashed) (the equivalent free energies for the simple electrolyte for these values of α are given in Fig. 1). For these different values of α there is practically no change in the ρ_c^*, while the temperature changes noticeably. However, comparing these plots with each other, we can conclude that the results are sufficiently stable with respect to the choice of the value of α. For $\alpha = 0.7$ (which clearly does not fit the PB curve for a simple electrolyte in Fig. 1) the temperature is $T_c^* = 0.058$ which is not very high (e.g., it is very close to the result of Fisher and Levin [13] $T_c^* = 0.057$). For $\alpha = 0.8$ we obtain $T_c^* = 0.047$ which is to be compared with $T_c^* = 0.049$ for $\alpha = 0.77$. Note that our choice of $\alpha = 0.77$ is based on the fact that for a simple electrolyte $f'_{\mathrm{RPA}}(x) = f'_{\mathrm{PB}}$ at $\kappa = 4.7$, which corresponds to $\kappa = 4.4$ for the RPM obtained from MC [20,7]. The difference in T_c^* when α is varied from 0.77 to 0.8 for the dumbbell is acceptable, if we take into account that for $\alpha = 0.8$ the fit of the simple electrolyte free energies $f'_{\mathrm{RPA}}(x) = f'_{\mathrm{PB}}$ occurs at $\kappa = 6.7$ which is much larger than the value for $\alpha = 0.77$.

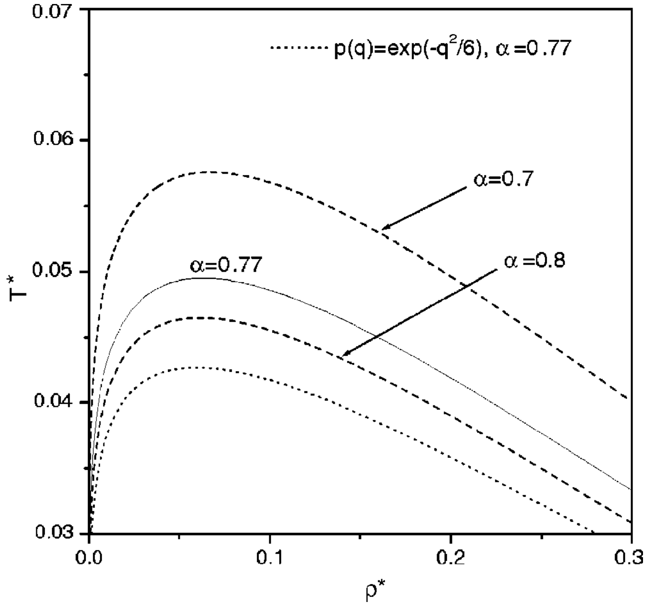

FIG. 3. Phase coexistence curves for $\alpha = 0.77$ (solid line), $\alpha = 0.7$ and $\alpha = 0.8$ (dashed lines as indicated). The dotted line is for $\alpha = 0.77$ and a Gaussian correlator between the ions in a pair.

It is also important to determine the sensitivity of the dumbbell RPA theory to the details of the molecular correlation of the ionic pairs, i.e., to the exact form of the correlation function $p(q)$ used in Eq. (14). In Fig. 3 the dotted curve corresponds to the coexistence curve of a system in which the ions in a pair have Gaussian correlations: $p(q) = \exp(-q^2/6)$ (for this curve $\alpha = 0.77$). In this case $T_c^* = 0.043$, while ρ_c^* changes negligibly. Given a significantly different nature of correlations the shift of the critical point is not large. Note that the case of a Gaussian correlator is of particular interest for polymer physics, since for flexible polymer chains covalent bonds between monomers are theoretically described by Gaussian correlations. The assumption of the same Gaussian correlations between thermoreversibly associated ions (such as charged ions in associating polyelectrolytes) and covalent bonds considerably simplifies a theoretical description [35].

As mentioned earlier, MC simulations yield a value of ρ_c^* for the CHD that is approximately 25% higher [20] than that of the RPM [7]. As we see from Fig. 3 a rather significant change of short-range correlations between ions in a pair, shifts ρ_c^* only negligibly. Therefore, the observed difference between the CHD and the RPM critical point must be attributed to other effects not accounted here such as clustering differences between the RPM and the CHD. That is, in the RPM there may be ions associated into nonelectroneutral clusters which may be elongated. Instead, in the CHD the clusters are always electroneutral, and, therefore, they are compact. Clustering at higher densities may also explain the differences in the dense branch of the coexistence curve between the RPA dumbbell model and the MC results.

III. CONCLUSIONS

We have calculated the phase diagram of charged hard-core dumbbells using the random phase approximation. It has long been recognized [2] that a linearized Debye-Hückel approach by itself is inadequate for description of phase coexistence of simple ions due to strong (and thus nonlinearizable) interactions between neighboring ions. The idea of our approach is to include short-range nonlinear interactions via a correlation function, while the remaining long-range part (leading to collective fluctuations of charge) is well accounted for by the RPA. In fact, the RPA is a formulation of the Debye-Hückel theory that allows natural introduction of structural correlations. (In this sense our work can be viewed as an extension of the Fisher-Levin theory [13] in which they used DH approach to take into account dimer-ion interactions [45].) The disadvantage of using the RPA to calculate charge-charge correlations is that we cannot take into account the finite size of the charged particles; that is, to account correctly for electrostatic boundary conditions [41]. We overcome this difficulty by introducing a phenomenological electrostatic potential which is adjusted at length-scales of the order of the sphere diameter.

Our theory gives a very good prediction for the location of the critical point, however, the coexistence curve is too narrow when compared with MC simulations [19,20]. This may be due to a neglect of all higher clusters, which must be particularly important in the dense phase. Indeed, calculations of cluster distributions in RPM have found non-negligible amount of higher mers, in particular tetramers [9,4]. In principle, we can include higher order clusters into our theory by higher order correlation functions and considering thermal equilibrium between different clusters.

An important wider implication of the presented work is that the modified random phase approximation quantitatively describes strongly interacting Coulomb systems. The method developed here can be easily applied for description of more complex electrostatic systems with strong interactions, such as associating polyelectrolytes [35].

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