Macroion correlation effects in electrostatic screening and thermodynamics of highly charged colloids

R. Castañeda-Priego,[1,*] L. F. Rojas-Ochoa,[1,2] V. Lobaskin,[3] and J. C. Mixteco-Sánchez[1]

[1]*Instituto de Física, Universidad de Guanajuato, Loma del Bosque 103, 37150 León, Mexico*
[2]*Departamento de Física, Cinvestav-IPN, Av. Instituto Politécnico Nacional 2508, 07360 México D. F., Mexico*
[3]*Physik-Department, Technische Universität München, James-Franck-Strasse, D-85747 Garching, Germany*

We study macroion correlation effects on the thermodynamics of highly charged colloidal suspensions using a mean-field theory and primitive model computer simulations. We suggest a simple way to include the macroion correlations into the mean-field theory as an extension of the renormalized jellium model of Trizac and Levin [Phys. Rev. E **69**, 031403 (2004)]. The effective screening parameters extracted from our mean-field approach are then used in a one-component model with macroions interacting via a Yukawa-like potential to predict macroion distributions. We find that inclusion of macroion correlations leads to a weaker screening and hence smaller effective macroion charge and lower osmotic pressure of the colloidal dispersion as compared to other mean-field models. This result is supported by comparison to primitive model simulations and experiments for charged macroions in the low-salt regime, where the macroion correlations are expected to be significant.

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I. INTRODUCTION

Structure and thermodynamics of charged colloidal dispersions became a subject of a renewed interest over the last decades due to the development of experimental and theoretical techniques and accumulation of new data incompatible with classical theories [1–3]. Considerable theoretical efforts have been invested into the upgrade of existing mean-field approaches with inclusion of counterion or macroions correlations, which are missing in the classical Poisson-Boltzmann theory.

Whereas in the aqueous dispersions of micrometer-sized particles the correlations of monovalent counterions are usually negligible, it is known that they might become important for small strongly charged macroions (see [3,4] for review). The role of counterion correlations has been extensively studied by various means, including integral equation theories and molecular simulations starting from the 1980s and is currently well understood [2–4,6–12]. In contrast, macroion correlation effects are usually not explicitly included in mean-field descriptions and therefore not satisfactorily quantified. One can expect these effects to be significant in systems with thick double layers, such as deionized colloidal dispersions.

In order to specify our interest in macroion correlation effects we would like to start from a simple energy argument. Charged colloidal suspensions are composed of a large number of particles of different types. If the molecular details of the solvent and dielectric discontinuities are neglected, one arrives to the primitive electrolyte model. On this level, a charged colloidal dispersion is an asymmetric electrolyte consisting of strongly charged macroions and small counterions. In addition, at least two different species of salt ions are usually present. A straightforward application of the

Debye-Hückel-like mean-field description is usually not successful due to strong spatial correlations of different ionic species. To deal with the correlations, one can attempt to construct a hierarchy of interactions from a quite general viewpoint. If we consider a system of macroions and small ions (including counterions and salt ions) we can classify the contributions to the potential energy into three categories: macroion-macroion (MM), macroion-ion (MI), and ion-ion (II). The relative importance of these terms can be estimated based on simultaneous consideration of their magnitudes and distances, on which they act. Macroions repel each other, so that their interaction energy is of the order of $\beta u_{MM} \approx \lambda_B Z_M^2 \exp(-\kappa d)/d$, the macroion-ion contribution $\beta u_{MI} \approx \lambda_B Z_M Z_I \exp(-\kappa a)/a$, and the ionic part $\beta u_{II} \approx \lambda_B Z_I^2 \exp(-\kappa d_I)/d_I$. Here, $\lambda_B = e^2/(4\pi\varepsilon\varepsilon_0 k_B T)$ is the Bjerrum length, $\beta^{-1} = k_B T$ the thermal energy, k_B the Boltzmann constant, T the temperature, Z_M and Z_I the macroion and ion valence, respectively, and a the macroion radius. Also, $\kappa = [4\pi\lambda_B(nZ_M + 2Z_I^2 n_I)]^{1/2}$ is the Debye-Hückel screening parameter, n and n_I the macroion and ion number densities, respectively, c_s the molar salt concentration, and $d = n^{-1/3}$ and $d_I = n_I^{-1/3} = (1000 N_A c_s + nZ_M)^{-1/3}$ the mean macroion-macroion and ion-ion distance, respectively. Setting $Z_M = 1000$, $Z_I = \pm 1$, $c_s = 1$ mM, $a = 100$ nm, and the macroion volume fraction to 0.01, we get $\beta u_{MM} \approx 3 \times 10^{-30}$, $\beta u_{MI} \approx 3 \times 10^{-4}$, and $\beta u_{II} \approx 3 \times 10^{-2}$. From this quick estimate, one can conclude that for $\kappa a \gg 1$ the two latter contributions dominate the system thermodynamics. When the charge sign is taken into account, the negative MI contribution starts prevailing in the total energy, as the significant part of II contribution; consisting of nearly equal number of terms of opposite signs, cancels itself out. Due to the strong screening, the thermodynamic properties of such dispersion do not differ much from a simple electrolyte, except for a small layer of thickness κ^{-1} around the macroion surface. One observes a very different picture in the regime of thick double layers, $\kappa a \ll 1$. A similar estimate for $c_s = 1$ μM gives

*Electronic address: ramoncp@fisica.ugto.mx

$\beta u_{MM} \approx 80$, $\beta u_{MI} \approx 5$, and $\beta u_{II} \approx 4 \times 10^{-3}$. If this energy per ion is weighted by the corresponding number of species, the MI contribution dominates so that the total Coulomb energy becomes negative [5]. We can also see that the II interactions are unlikely to influence the dispersion properties in case of monovalent ions. The first two contributions, however, have to be taken into account. The natural and common way of dealing with this situation involves (i) solving the Poisson-Boltzmann (PB) equation for ions around a single macroion, (ii) renormalization of the MM interaction parameters based on the Debye-Hückel-like approximation for the long-distance part of the double layer, and (iii) solution of the one-component MM model (OCM) with an effective interaction potential u_{eff} [5,13,14]. This procedure maintains the leading role of the MI interaction, while the effect of MM correlations enters only at the level of the OCM description. The latter approach can be modified in different ways to account for a more pronounced role of the macroion correlations, and the resulting charge inhomogeneities, using the Wigner-Seitz cell model. In this case, the structure of the double layer reflects the inhomogeneous macroion (and hence the counterion) distribution via the cell construction. Numerical schemes based on the cell model and charge renormalization have been successful in describing properties of strongly correlated charged colloidal dispersions [5,13,14].

An alternative route to include the macroionic contribution into the electrostatic screening is based on the jellium approximation for macroions [15,16]. Although the range of validity of the jellium model might be limited to weakly correlated macroion systems, this model can be easily extended to different situations, i.e., rod-like colloids [19] or asymmetric electrolytes and, particularly, its equation of state takes a simple analytical form [see Eq. (3) below].

We further follow the jellium description, which we extend using a simple construction that introduces spatial macroion correlations. Our goal is to study the effect of macroion correlations on the parameters of the OCM for highly charged colloidal dispersions and the corresponding dispersion thermodynamics. We pay special attention to the calculation of the equation of state of such dispersions. It is known that recovering the accurate equation of state basing on the OCM formulation alone is problematic, as the ionic degrees of freedom are omitted from the description. At the same time, information about the ions is contained in the full theory [5,20,21] used for getting the effective parameters for the OCM and one can hope to relate these parameters to the total thermodynamic and structural properties.

II. MACROION CORRELATIONS ON THE MEAN-FIELD LEVEL

Although the PB cell and the renormalized jellium models do not address the macroion degrees of freedom, they implicitly include a model of macroion distribution. The cell model supposes well separated particles, where the role of the neighboring macroions consists of limiting

the volume available for small ions while $g_{MM}(r)$ is simply zero inside this cell. The double layer inside the cell is otherwise unperturbed by the rest of the system. In contrast, the jellium model assumes $g_{MM}(r) = 1$ for $r > 2a$ (diameter of the sphere), i.e., an ideal gas of macroions. As we already noted in the Introduction, this approximation might be unsatisfactory for low-salt colloidal dispersions, where macroions strongly repel each other even at the mean interparticle separation. We therefore will try to avoid considering uniform macroion distributions. On the simplest level, the uniform distribution can be replaced by a $g_{MM}(r)$ taken in the form of a step function. This choice is motivated by the observation that a charge-stabilized colloidal suspension at low salt shows a highly structured $g_{MM}(r)$ with a characteristic length-scale described by the mean interparticle distance $d = n^{-1/3}$ [22]. In particular for $r < d$, $g_{MM}(r)$ is almost zero, a feature that is known as the *correlation hole*. The total charge density in the system at a distance r from the center of a macroion becomes

$$\rho(r) = -Z_{\text{eff}} e n g_{MM}(r) + e\rho_+(r) - e\rho_-(r), \qquad (1)$$

where $g_{MM}(r) = 0$ for $r < d$, and $g_{MM}(r) = 1$ for $r \geq d$; $\rho_\pm(r)$ are the concentrations of salt cations and anions and e is the elementary charge. We should stress that the correlation hole approximation for $g_{MM}(r)$ can be justified only for low-salt systems where the main peak position of $g_{MM}(r)$ scales with $n^{-1/3}$. This results from the fact that the repulsive interaction, $u(r)$, between two colloidal particles approaching each other becomes $u(r) \gg k_B T$ when $r < d$. In a more general case, one should consider a correlation hole of size d^* such that the main peak position scales with it and which should be valid for higher salt concentrations or weakly charged macroions, essentially when $u(d^*) \approx k_B T$. This point will be addressed elsewhere [23].

Our model includes now the dominant part of macroion correlations by placing a macroion at the center of its correlation hole of a size that depends explicitly on the concentration. The macroion distribution outside this hole is still approximated by an ideal gas of macroions, as in the jellium approach [15]. We enforce the smeared-out background charge Z_{back} representing the other macroions around the tagged macroion to coincide with the effective charge Z_{eff}, as in the original work of Trizac and Levin [16]. Then, assuming the solvent as a continuous medium with a dielectric constant ϵ, the Poisson-Boltzmann equation around the tagged macroion reads

$$\nabla^2 \phi(r) = \frac{4\pi e}{\epsilon} [Z_{\text{back}} n g_{MM}(r) - \rho_+(r) + \rho_-(r)]. \qquad (2)$$

The Z_{back} is determined by the electroneutrality condition for the total charge density in the bulk, $2c_s \sinh[e\phi(\infty)/k_B T] = nZ_{\text{back}}$, where $\phi(\infty)$ represents the electrostatic potential at infinity. The electroneutrality condition gives the screening parameter in the form $\kappa_{\text{eff}}^2 = 4\pi\lambda_B \sqrt{Z_{\text{back}}^2 n^2 + 4c_s^2}$ [16]. We, therefore, call our model a modified jellium model (m-jellium).
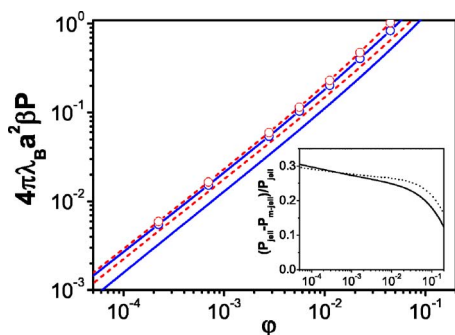
FIG. 1. (Color online) Effect of the macroion correlation correction to the renormalized jellium models on the reduced pressure in a salt-free dispersion. The solid and dashed curves show the pressures in the regime of moderate macroion charges ($Z_{eff}\lambda_B/a=10$) as predicted by the jellium and m-jellium, respectively, and the solid and dashed curves with symbols correspond to saturated effective charges ($Z_{eff}\lambda_B/a=1000$). The inset shows the relative difference between pressures in the renormalized jellium and m-jellium models.

At large distances $(r \to \infty)$ the total charge density given by the right-hand side of Eq. (2) vanishes due to the electroneutrality requirement. It also defines a value of the potential far from the tagged macroion $\phi(\infty)$, which is known as the Donnan potential [17]. Equation (2) with this boundary condition can be solved numerically for $r > d$, where $g(r)=1$. To guarantee the continuity of the electrostatic potential at $r=d$, we impose the conditions $\phi_-(d)=\phi_+(d)$ and $\phi'_-(d)=\phi'_+(d)$, where + indicates the value of the potential obtained from Eq. (2) for $r > d$, which allows us to calculate the potential inside the correlation hole. The bare macroion charge can now be obtained by applying Gauss' law at the particle surface, $(\partial \phi / \partial r)_{r=a}=Z_M\lambda_B/a^2$. We apply this procedure iteratively to compute the bare charge Z_M corresponding to a given effective charge, Z_{eff}.

In the jellium-like models, the pressure in the salt-free case is proportional to the effective charge, Eq. (3). The effect of the introduced macroion correlation hole is illustrated in Fig. 1. Here, one can see that the pressure in a salt-free colloidal dispersion becomes smaller in the m-jellium model as compared to the original jellium result at all macroion volume fractions. For both highly ($Z_{eff}\lambda_B/a=1000$) and moderately ($Z_{eff}\lambda_B/a=10$) charged systems, the relative difference between the two models is maximal (about 0.3) at the lowest volume fraction and decreases as the volume fraction increases (it does not exceed 0.15 at $\varphi=0.1$). The relative differences between pressures from both models are illustrated in the inset of Fig. 1. The difference between both models decreases with density because the size of the correlation hole also scales as $n^{-1/3}$. Therefore, it is expected that results from both models will coincide at higher volume fractions. The variation of the effective charge in both models is also described by the same equation.

When comparing different colloidal systems, it is convenient to present the effective charge in the form $Z_{eff}\lambda_B/a$ [18]. In Fig. 2(a) we compare the effective macroion charge
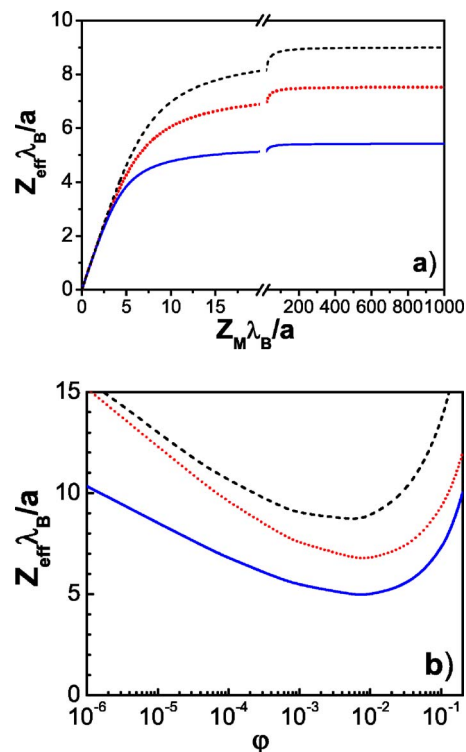

FIG. 2. (Color online) (a) Effective charge for a salt-free suspension at a volume fraction of $\varphi=0.001$ as a function of the bare charge and (b) effective charges at saturation for charge-stabilized colloidal suspensions, salt-free case, as a function of the volume fraction. In both cases, dashed lines are for the PB-cell model, dotted lines for the jellium model, and solid lines for the modified jellium model.

as a function of its bare charge for the PB-cell, jellium, and m-jellium models in the salt-free case. Each model predicts different values of the effective charges at saturation ($Z_M \to \infty$). However, for small bare charges all of them recover the correct limiting behavior $Z_{eff}=Z_M$. It is interesting to note that for the salt-free case at saturation, the system properties are determined by the single parameter: the macroion volume fraction, $\varphi=4\pi a^3 n/3$. In Fig. 2(b) we compare the effective charges at saturation as obtained from each mean-field model.

The behavior of Z_{eff} in the range $\varphi < 10^{-2}$ can be understood from the gradual compression of the ionic double layers on increasing density. At the higher densities, in contrast, the effective charge is increasing because the average electrostatic potential in the bulk (or at least at $r \gtrsim d$) approaches that on the macroion surface, so that the counterion condensation is suppressed. As a result, we observe a minimum in the concentration dependence of Z_{eff} about $\varphi \approx 10^{-2}$. This characteristic behavior can, in fact, be derived from a simple energy-entropy balance reasoning and is known from classical polyelectrolyte literature [18].

The smaller effective charges in the m-jellium model, as compared to the original jellium model of [21], follow from the weaker screening at $r < n^{-1/3}$. In the modified model the macroions are excluded from the internal part of the double layer, which leads to a higher free energy cost of charging
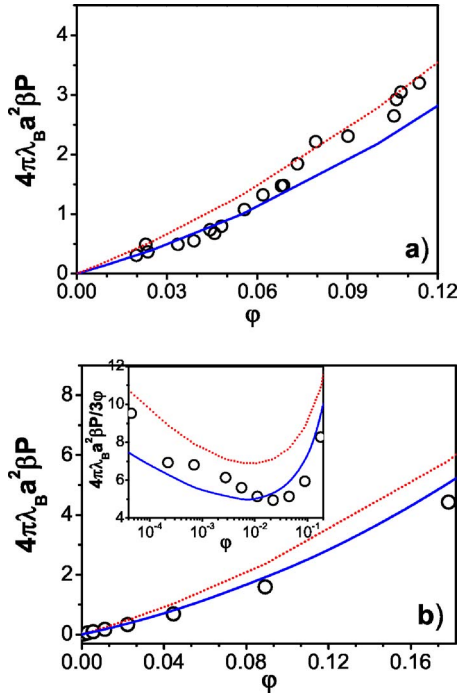
FIG. 3. (Color online) (a) Pressure as a function of the volume fraction obtained from the m-jellium approach (solid line) and the renormalized jellium approximation (dashed line). Symbols correspond to Reus' experiments [24]. No adjustable parameters have been used and the effective charges at saturation are considered. (b) Pressure as a function of the volume fraction obtained from the m-jellium approach (solid line) and from the renormalized jellium approximation (dashed line) with $Z_M \lambda_B / a = 19.47$ and $\lambda_B / a = 0.3245$. Symbols correspond to primitive model simulations. Inset: osmotic coefficient for results in (b).

the macroion. In other words, the weaker screening associated to the m-jellium results in a stronger attraction of the counterions to the macroion surface.

III. PRESSURE

Within the renormalized jellium model, the equation of state reads [16]

$$\beta P = n + \sqrt{Z_{\text{eff}}^2 n^2 + 4c_s^2}. \tag{3}$$

After exclusion of the condensed counterions by the charge renormalization procedure only the free ions contribute to the pressure [18]. In the salt-free case, $c_s = 0$, the equation of state given by Eq. (3) simply reduces to $\beta P = n(1 + Z_{\text{eff}})$. In the low electrostatic coupling regime, where Z_{eff} coincides with Z_M, Eq. (3) recovers the ideal gas pressure $\beta P \simeq n(1 + Z_M)$. In Fig. 3(a) we compare predictions from the renormalized and the m-jellium models for the osmotic pressure data from Reus *et al.* [24], obtained for deionized suspensions of bromopolystyrene particles. Although the overall agreement between experiments and both models is good, for $\varphi < 0.07$ the m-jellium approach performs visibly better, while for higher densities the renormalized jellium model seems to be a better approximation. Further on, in Fig. 3(b)

we compare the results from both jellium-like models with data from primitive model simulations for a salt-free asymmetric electrolyte with an asymmetry in charge 60:1 (we use the same cluster MC simulation protocol and settings as in [5] with 80 macroions). Here we observe that both models reproduce the pressure behavior qualitatively, while the m-jellium seems to give a better quantitative agreement in the wide range of macroion concentrations. An alternative representation of the same data is shown in the inset of Fig. 3(b), where both models are compared to the osmotic coefficients for the same simulated system. This representation confirms the better performance of the m-jellium model. Thus, our model improves the description of the osmotic pressure for suspensions in the counterion-dominated screening regime.

IV. STRUCTURE

The effective charge and the screening parameter computed from mean-field models can be used to calculate the effective pair potential and the structure of charged colloidal suspensions. We assume the effective pair interaction between macroions to have the Yukawa form

$$\beta u_{\text{eff}}(r) = Z_{\text{eff}}^2 \lambda_B \left[\frac{\exp(\kappa_{\text{eff}} a)}{1 + \kappa_{\text{eff}} a} \right]^2 \frac{\exp(-\kappa_{\text{eff}} r)}{r}. \tag{4}$$

The pair distribution of the macroions interacting through the effective pair potential, Eq. (4), can be computed using the Ornstein-Zernike (OZ) equation [25],

$$h_{MM}(r) = c^{\text{eff}}(r) + n \int d^3 r' c^{\text{eff}}(r') h_{MM}(|\mathbf{r} - \mathbf{r}'|), \tag{5}$$

where $h_{MM}(r) = g_{MM}(r) - 1$ and $c^{\text{eff}}(r)$ is the so-called effective direct correlation function [14,26]. An additional closure relation is needed to solve the OZ equation. In particular, the Rogers-Young (RY) closure relation can be used to solve the OZ equation self-consistently [27]. The RY closure enforces both thermodynamic and density fluctuations to be the same in order to calculate both the structure and thermodynamics of a colloidal suspension and it is known to accurately describe Yukawa-like systems [22]. Technically, this is done by computing the isothermal compressibility using the virial route for the OCM, $\chi_v^{-1} = (\partial \beta P_{\text{MM}} / \partial n)_T$, where P_{MM} is the macroion-macroion virial contribution and can be written as

$$\beta P_{\text{MM}} = n - \frac{n^2}{6} \int_{r=2a}^{\infty} g(r) \frac{d\beta u_{\text{eff}}(r)}{dr} r d^3 \mathbf{r}. \tag{6}$$

The isothermal compressibility can be also computed through the relation $\chi_c^{-1} = 1 - n\tilde{c}^{\text{eff}}(q=0)$ [14], where $\tilde{c}^{\text{eff}}(q)$ is the Fourier transform of the effective direct correlation function. Then, the RY closure relation enforces both routes to give the same isothermal compressibility ($\chi_v = \chi_c$) in order to guarantee, at least partially, the thermodynamic consistency [27].

It is important to note that the OCM pressure is usually very different from the pressure measured in the full multicomponent electrolyte. This discrepancy follows from the

prevalence of the microion contribution to the pressure. In fact, in many cases the macroion contribution is negligible and the total pressure can be well approximated by the partial pressure of the small ions [18]. Moreover, as we have seen in the last section, Eq. (3) provides an excellent virial equation of state for highly charged colloids at low salt. It therefore can be combined with the OCM to get the thermodynamically consistent description. The effective OCM parameters can be used, on one hand, to get the osmotic pressure via Eq. (3) and, on the other hand, to predict the accurate macroion structure. One expects to meet less problems on the compressibility route [14]. The osmotic compressibility χ_c is related to the infinite wavelength limit of the macroion structure factor. Knowing the macroion structure is therefore enough to compute the correct osmotic compressibility of the multicomponent system. The consistency between both routes then can be controlled by comparing the result obtained from the structure factor to $\chi_v^{-1}=(\partial\beta P/\partial n)_T$, where P is given by Eq. (3), which obviously gives the same result in our case.

We would like to note that these simple ideas can be applied to interpret experimental data. The effective macroion charge is usually extracted from the structure factors measured in scattering experiments by fitting the scattering curves by means of an OZ-RY scheme with an effective Yukawa potential. Our approach can be applied inversely to predict the equation of state of colloidal suspensions at low salt via the relation between the effective charge and the osmotic pressure.

In Fig. 4(a) we compare the radial distribution functions (RDF) from our primitive model Monte Carlo simulations (symbols) with numerical results obtained using our OZ-RY scheme with the m-jellium model parameters (solid lines). Also, results from the standard RY route [27] and screening parameters from the PB-cell model are shown (dashed lines). For the sake of clarity, the results with parameters from the renormalized jellium through the standard RY route are not shown, however, it has been found that they underestimate the structure (for a more detailed analysis see [28]). The highest macroion charge taken in the simulations ($Z_M=60$) does not bring the system into the fully saturated effective charge regime. The value for λ_B/a considered (among others) was 0.324. In Fig. 4(a) we clearly observe a good agreement between simulations and m-jellium model results, although still small differences around the main peak of the RDF for the higher volume fractions ($\varphi>0.04$) can be observed. These small differences might result from the macroion shielding effect, which usually rises the macroion distribution peak in dense suspensions [29], and from counterion correlations, which are strong in this system [5]. However, our results show a visibly better agreement with simulations than those obtained with other mean-field approaches (dashed lines). In Fig. 4(b) we compare the RDF from the primitive model simulations (symbols) described in Sec. III with numerical results obtained using our OZ-RY scheme with both m-jellium (solid lines) and jellium (dotted lines) parameters. We observe that the jellium model always overestimates the structure of the suspension while m-jellium shows a better agreement. Also, we note that at high densities the main peak of the pair correlation is predicted less
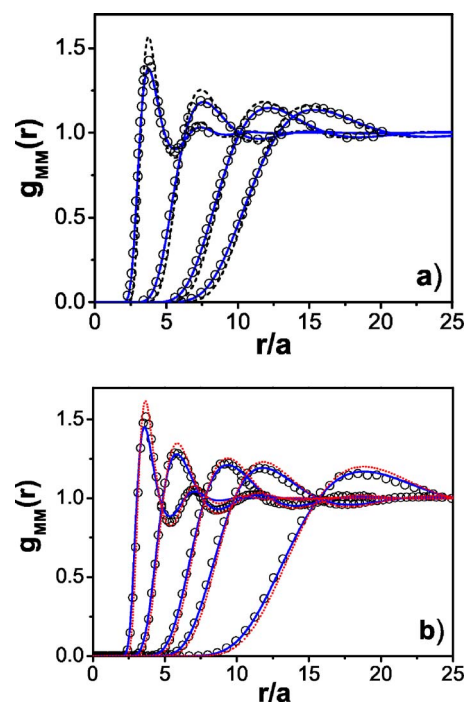

FIG. 4. (Color online) Macroion-macroion pair-correlation functions from primitive model Monte Carlo simulation (symbols) and from our OZ-RY scheme (see text) with effective m-jellium parameters (solid lines). (a) From the "standard" OZ-RY scheme (see text) with the OCM equation of state and PB-cell parameters (dashed lines) and (b) from our OZ-RY scheme with effective renormalized jellium model parameters (dotted lines). From left to right, the packing fractions are (a) $\varphi=0.08$, 0.01, 0.0025, and 0.00125 and (b) $\varphi=0.089$, 0.022, 0.0055, 0.0027, and 0.00069.

accurately. It is remarkable that the behavior of $g_{MM}(r)$ in Fig. 4 is accurately reproduced by our scheme in the whole range of distances, whereas other mean-field schemes overestimate the short-range behavior of $g_{MM}(r)$.

V. CONCLUSIONS

We have introduced a procedure to include macroion correlations into a mean-field theory of screening in charged colloidal dispersions, which leads to modification of the effective parameters of the OCM: the macroion effective charge and screening length. The evaluation of colloidal effective charges in suspensions with weak screening is based on the solution to the nonlinear PB equation for the electric double layer in the presence of other macroions. Our model represents an extension of the renormalized jellium approach by Trizac and Levin. It predicts somewhat lower macroion effective charges, as compared to the renormalized jellium approach, which suggests that macroion correlations are important in describing systems with thick double layers such as deionized colloidal suspensions, i.e., in the counterion-dominated screening regime.

The proposed model describes well experimental as well as MC simulation results of thermodynamic quantities in highly charged colloidal dispersions at low salt. The static

structure of model colloidal suspensions is also accurately reproduced by an OCM scheme that uses the screening parameters of the m-jellium model. Moreover, we show that these effective parameters could be used to predict accurately the equation of state via the relation between the effective charge and the osmotic pressure in our model, which can be used for interpreting experimental results.

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