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

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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 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 a 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 development of experimental and theoretical techniques and accumulation of new data incompatible with classical theories [1, 2, 3]. Considerable theoretical efforts have been invested into an upgrade of existing mean-field approaches with an inclusion of additional correlation effects such as 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 [4, 5]. The role of counterion correlations has been extensively studied by various means, including integral equation theories and molecular simulations starting from eighties [6, 7, 8, 9, 10, 11] and is currently well understood [2, 4, 6, 7]. In contrast, macroion correlation effects are usually not included in the mean-field approaches and therefore not 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 an hierarchy of interactions from a quite general viewpoint. If we look at a system of macroions and small ions (including counterions and salt ions) we can divide 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 are operating. Macroions repel each other, so that their interaction 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 $\beta u_{II} \approx \lambda_I Z_I^2 \exp(-\kappa d)/d_I$. Here, $\lambda_B = e^2/(4\pi\varepsilon\varepsilon_0 k_B T)$ is the Bjerrum length, $\beta^{-1} = k_B T$ the inverse of the thermal energy, $k_B$ the Boltzmann constant, $T$ the temperature, $Z_M$, $Z_I$ macroion and ion valence respectively, $a$ the macroion radius, $\kappa = 4\pi \lambda_B (Z_M^2 c_s + n Z_M)$ the screening parameter, $d = n^{-1/3}$ and $d_I = c_s^{-1/3}$ the mean macroion-macroion and ion-ion distance respectively, $c_s$ the salt content and $n$ the macroion number density. Setting $Z_M = 1000$, $Z_I = \pm 1$, $c_{salt} = 1$ 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 naive estimate, one can conclude that at $\kappa a \gg 1$ the two last 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 strong screening, the thermodynamic properties of such dispersion do not differ much from a simple electrolyte, except for small

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layer of thickness $\kappa^{-1}$ around the macroion surface. One observes a much different picture in the regime of thick double layers $\kappa a \ll 1$. A similar estimate for $c_{\text{salt}} = 1\mu M$ gives $\beta_{\text{MM}} \approx 80$, $\beta_{\text{MI}} \approx 5$ and $\beta_{\text{II}} \approx 4 \times 10^{-3}$. 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.\textsuperscript{[3]} 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 common method of dealing with this situation involves: (i) solving the Poisson-Boltzmann (PB) equation for 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 with an effective interaction potential $u_{\text{eff}}$.\textsuperscript{[2, 12, 13]} This procedure respects the leading role of the MI interaction, while the effect of MM correlations in this approach enters only on the level of the one-component (OCM) description. The latter approach can be modified in different ways to account for more pronounced role of macroion correlations and the resulting charge inhomogeneities using the Wigner-Seitz cell model.\textsuperscript{[13]} 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 charged colloidal dispersions.\textsuperscript{[3, 12, 13]}

An alternative route to include macroionic contribution into electrostatic screening is based on the jellium approximation for macroions\textsuperscript{[13, 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\textsuperscript{[17]} or asymmetric electrolytes and, particularly, its equation of state takes a simple analytical form (see equation (2) below).

In this work, we follow the jellium description, which we improve using a simple construction that introduces spatial macroion correlations. The main goal of the present work is therefore to study the effect of macroion correlations on the parameters of the OCM and the corresponding dispersion thermodynamics. Another issue we would like to address is the calculation of the equation of state of the dispersion. It is well known that recovering the accurate equation of state basing on the OCM representation is problematic, as the ionic degrees of freedom are omitted from the description and wall effects are not included on the macroion virial contribution\textsuperscript{[18]}. At the same time, the thermodynamic properties can be easily extracted from the same two-component (or multi-component) description that is used for calculation of the OCM effective charge and screening length, i.e. directly from the WS cell or jellium model.\textsuperscript{[12, 14, 15, 16, 19, 20]} These models are usually solved using the non-linear PB equation including only one colloidal particle, or MC simulation.\textsuperscript{[2, 12, 21, 22]} In this work we will use non-linear PB equation with the jellium boundary conditions.

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 $g_{\text{MM}}(r)$ 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 $g_{\text{MM}}(r) = 1$ 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 $g_{\text{MM}}(r)$ 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 $g_{\text{MM}}(r)$ with a characteristic lengthscale described by the mean interparticle distance $d = n^{-1/3}$.\textsuperscript{[23]} In particular for $r < d$, $g_{\text{MM}}(r)$ 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

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

where $g_{\text{MM}}(r) = 0$ for $r < d$, and $g_{\text{MM}}(r) = 1$ for $r \geq d$; $\rho_+(r)$ are the concentrations of salt cations and anions and $e$ is the elementary charge. We should stress that the "correlation hole" approximation for $g_{\text{MM}}(r)$ can be justified only for low-salt systems where the main peak position of $g_{\text{MM}}(r)$ scales with $n^{-1/3}$. In a more general case, one should consider a "correlation hole" of size $d^*$ such that the main peak position scales with $d^*$ and which should be valid for higher salt concentrations or weakly charged macroions. This point will be addressed elsewhere\textsuperscript{[24]}. Our model includes now the major part of macroion correlations by placing a macroion at the center of its correlation hole with 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.\textsuperscript{[15]} We enforce the smeared-out background charge, $Z_{\text{eff}}$, representing the other macroions around the tagged macroion to coincide with the effective charge, $Z_{\text{eff}}$, as in the original work of Trizac and Levin.\textsuperscript{[10]} The $Z_{\text{eff}}$ is determined by the electroneutrality condition for the total charge density in the
bulk, $2c_s \sinh [e\phi(\infty)/k_BT] = nZ_{\text{back}}$, where $\phi(\infty)$ represents the electrostatic potential in the bulk. The electroneutrality condition also allows us to determine the effective screening parameter, $\kappa_{\text{eff}}^{-2} = 4\pi\lambda_B \sqrt{Z_{\text{eff}}^2 n^2 + 4c_s^2}$ [10]. We therefore call our model a modified jellium model (m-jellium).

The effect of the introduced modification is illustrated in Fig. 1. 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 ($Z_M \lambda_B/a = 1000$) and moderately charged systems ($Z_M \lambda_B/a = 10$), 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 pressure in the salt-free case is proportional to the effective charge, equation (2), so the effective charge variation in both models is also described by the same equation. 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.

For comparing different systems it is convenient to present the effective charge in the form $Z_{\text{eff}} \lambda_B/a$. In Fig. 2b we compare the effective macroion charge 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 ($Z_{\text{bare}} \rightarrow \infty$). However, for small bare charges all of them recover the correct limiting behavior $Z_{\text{eff}} = Z_{\text{bare}}$. It is interesting to note that for the salt-free case at saturation the system properties are determined by only one parameter: the macroion volume fraction, $\varphi = 4\pi a^3 n/3$. In Fig. 2b we compare the saturated effective charges obtained from each model. The behavior of $Z_{\text{eff}}$ in the range $\varphi \lesssim 10^{-2}$ can be understood by a compression of the ionic double layers. As $\varphi$ increases, counterions are pushed towards the macroion surfaces thus reflecting the win of the entropy over the energy and therefore leading to a gradual decrease of $Z_{\text{eff}}$ until a well-defined minimum appears around $\varphi \approx 10^{-2}$ and we observe the growth in the effective charge at $\varphi > 10^{-2}$. This reduction in the effective charge in the m-jellium as compared to the orig-
Within the jellium model, the equation of state reads

\[ \beta P = n + \sqrt{Z_{\text{eff}}^2 a^2 + 4 c_s^2}. \tag{2} \]

After exclusion of the condensed counterions by the charge renormalization procedure only the free ions contribute to the pressure. In the salt-free case, \( c_s = 0 \), the equation of state given by Eq. \( \text{(2)} \) simply reduces to

\[ \beta P = n(1 + Z_{\text{eff}}). \]

In the low electrostatic coupling regime (where \( Z_{\text{eff}} \) coincides with \( Z_{\text{bare}} \)), equation \( \text{(2)} \) recovers (see also Fig. \( \text{(2)} \) the ideal gas pressure \( \beta P \approx \rho \varepsilon (1 + Z_{\text{bare}}) \)) \( \beta \). In Fig. \( \text{(3a)} \) we compare predictions from the renormalized and the m-jellium models for the osmotic pressure data from Reus et al. \( \text{[25]} \), 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. \( \text{(3b)} \) we compare the results from both jellium-like models with data from primitive model simulations for salt-free asymmetric electrolyte with an asymmetry in charge \( 60:1 \) (we use the same cluster MC simulation protocol and settings as in Ref. \( \text{[5]} \) with 80 macroions). Here we observe that both models reproduce the pressure behaviour qualitatively, while the m-jellium gives 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. \( \text{(3b)} \), where both models are compared to the osmotic coefficients for the same simulated system. From this representation, it is clear that the m-jellium describes the results of numerical simulations better. Thus, our model improves the osmotic pressure for suspensions in the counterion-dominated screening regime.

IV. STRUCTURE

The effective charge and the screening parameter computed from our m-jellium can be used to calculate the effective pair potential and the structure of the suspension. We assume the effective pair interaction between macroions to have the Yukawa form \( \text{[13]} \)

\[ \beta u_{\text{eff}}(r) = Z_{\text{eff}}^2 \lambda_B \left\{ \frac{\exp(-\kappa_{\text{eff}} a)}{1 + \kappa_{\text{eff}} a} \right\}^2 \frac{\exp(-\kappa_{\text{eff}} r)}{r}. \tag{3} \]

The pair distribution of the macroions interacting through the effective pair potential \( \text{[3]} \) can be computed using the Ornstein-Zernike (OZ) equation \( \text{[26]} \),

\[ h_{\text{MM}}(r) = c_{\text{eff}}(r) + n \int d^3 r' c_{\text{eff}}(r') h_{\text{MM}}(|r - r'|), \tag{4} \]

where \( h_{\text{MM}}(r) = g_{\text{MM}}(r) - 1 \) and \( c_{\text{eff}}(r) \) is the so-called effective direct correlation function \( \text{[13, 27]} \). An additional closure relation is needed to solve the OZ equation. In particular, the Rogers-Young (RY) closure relation \( \text{[28]} \) can be used to solve the OZ equation self-consistently. The RY closure enforces both thermodynamic and density fluctuations to be the same in order to calculate both the structure and thermodynamics of

FIG. 3: 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 the Reus’ experiments \( \text{[25]} \). No adjustable parameters have been used and effective charges at saturation correspond to the Reus’ experiments \( \text{[25]} \). 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 \( Z_{\text{bare}} \lambda_B / a = 19.47 \) and \( \Lambda_B / a = 0.3245 \). Symbols correspond to primitive model simulations.
a colloidal suspension and it is known to accurately describe Yukawa systems [23]. Technically, this is done by computing the isothermal compressibility using the virial route for the OCM, $\chi_c^{-1} = (\beta \partial P_{MM}/\partial n)_T$, where $P_{MM}$ is the macro-ion–macro-ion virial contribution and can be written as

$$\beta P_{MM} = \rho_c - \frac{\rho_c^2}{6} \int_{r=2a}^{\infty} g(r) \frac{d\chi_{\text{eff}}(r)}{dr} r^3 dr. \quad (5)$$

The isothermal compressibility can be also computed through the relation $\chi_c^{-1} = 1 - m \chi_{\text{eff}}(q = 0)$ [13], 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 [23].

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 dominance of microion contribution to the pressure. In fact, the total pressure can be well approximated by the partial pressure of the small ions measured using the contact value theorem at the WS cell boundary or at infinity [3]. Moreover, as we have seen in the last section, equation (2) provides an excellent equation of state for highly charged colloids. It is now clear that equation (4) is not able to reproduce the isothermal compressibility of the suspension and thus it cannot be used to reproduce the structure of the suspension. Nevertheless, if the total pressure (or compressibility) of the system is known from the original system (or a solution of the multicomponent m-jellium model), then it can be combined with the OCM to get the thermodynamically consistent description. Thus, the OCM pressure should be replaced with the pressure in the full system, which is given by Eq. (2) within our mean-field approach. We stress that the pressure in our procedure is evaluated from the same mean-field parameters that guarantee, at least partially, the thermodynamic consistency [23].

We would like to note also that these simple ideas can be applied for interpretation of experimental data. The effective macroion charge is usually extracted from the structure factors measured in scattering experiments through fitting the curve with a OZ-RY scheme with an effective Yukawa potential. A reverse version of our approach can be used to predict accurately the equation of state of colloidal suspensions at low salt via the relation between the effective charge and the osmotic pressure.

In figure (4a) we compare the radial distribution functions (RDF) from our primitive model simulations (symbols) and from our OZ-RY scheme (solid lines) with effective m-jellium parameters (dashed lines). a) From the standard OZ-RY scheme (solid lines) with the OCM equation of state and PB-cell parameters (dashed lines), and b) from our OZ-RY scheme with effective jellium parameters (dotted lines). From left to right, the packing fractions are a) $\varphi = 0.08, 0.01, 0.0025, 0.00125$, and b) $\varphi = 0.089, 0.022, 0.0055, 0.0027, 0.00069$.

![Fig 4](image-url)
ences 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 [30]. However, our results show a visibly better agreement with simulations than those obtained with other mean-field approaches (dashed lines). In figure (4a) we compare the RDF from the primitive model simulations described in section [11] with numerical results obtained using our OZ-RY scheme with both m-jellium and jellium parameters. We observe that the jellium model always overestimates the structure of the suspension while m-jellium shows a better agreement. It is remarkable that the behavior of $g_{MM}(r)$ in figure (4) is accurately reproduced by our scheme in the whole range of distances, whereas other mean-field schemes overestimate the short-range behaviour of $g_{MM}(r)$. Also, we note that at high densities the mean peak of the pair correlation is predicted less accurately.

V. CONCLUSIONS

We have introduced a procedure of including 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 the 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 a modification of the renormalized jellium approach by Trizac and Levin. The obtained results suggest that these correlations are important in systems with thick double layers such as deionized colloidal suspensions, i.e. in the counterion-dominated screening regime.

Our model describes well experimental results of thermodynamic quantities in colloidal dispersions, such as the osmotic pressure. The static structure of colloidal suspensions is also accurately reproduced by an OCM scheme that uses the screening parameters of the m-jellium model. Moreover, from the experimental point of view, the effective parameters of the RY integral equation scheme can be used to predict accurately the equation of state via the relation between the effective charge and the osmotic pressure in our model.

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