

Size Correlations in Colloidal Suspensions

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Abstract

We study the effect of correlations due to hardcore effects in the distribution of ions around a spherical macroion enclosed in a limited cell. The osmotic pressure is also computed. Both the profile and the pressure are obtained within density functional approaches. Various recipes for the correlations are compared with the Poisson Boltzmann analysis. In the regime of low ionic strength and ionic radius that is not too large, the weighted density functionals based on the Percus-Yevic and the Carnahan-Starling approaches seem to incorporate the size correlations better than the similar local density prescriptions do.

Key words:

PACS:

1 Introduction

Colloidal solutions are ubiquitous in nature and in numerous industrial applications [1]. Precise knowledge of the thermodynamics and phase behavior of these suspensions is of interest in a wide range of disciplines. Large molecules when in solution due to the depletion forces aggregate. This aggregation results in a number of inconveniences in industrial and biological systems. Ionic macromolecules in solution loose ions and become ionized. In principle, the strong electrostatic repulsion between the charged colloidal particles overcome the short range attractive forces and stabilize the solution against coagulation. But the electrostatic interaction between the colloidal particles is not simply the one due to the bare polyions but as that between the overlapping electrical double layers surrounding these aggregates. Then phase behavior and the

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kinetic properties of ionic colloids are determined by the interplay between the short-range attraction and the electrostatic forces that are in principle repulsive but can become attractive under certain circumstances.

Understanding the electrostatic interactions in these systems has been subject of a number studies [1] [2]. In the classical Derjaguin-Landau-Verwey-Overbeek, DLVO, theory[2], the calculation of the double layer rely in the Poisson-Boltzmann, PB, equation. This theory neglects completely the ion-ion correlations and gives only repulsive forces between the electric double layers. The stability of the suspension results from the competition between the van der Waals attraction and the electrostatic repulsion. According the DLVO approach, as the electrolyte concentration is increased, the range of the double layer decreases and the coagulation might occur. This explanation has been accepted until recently when experiments showed that there exists attraction between like charged macroions in the case where the short-range interactions are not relevant [3]-[5] but the high ionic strength play a relevant role. Theory [6][7] and simulation [8]-[10] show attraction for short range distances. However, there is no clear picture for long-range attraction between like ions observed in experiments.

Recent simulations suggest that the attraction between like charges might be related to the mechanism that induces overcharging [11]-[13]. Therefore, understanding the mechanism that leads to overcharging will shed some light in the appearance of attraction between like-charged polyions. Classical intuition suggests that overcharging happens when the correlations between the small ions induce the formation of a cloud of positive ions around a negative macroion that is dominated by the charge of the positive ion. Since the correlations are stronger for multivalent ions, a more dramatic effect is possible in this case. Namely, instead of charge reduction due to the shielding, it is possible to observe a charge reversal due to overscreening. The charge inversion phenomena becomes enhanced with the increasing concentrations of multivalent salt [12][13]. Unfortunately the actual mechanism of this overcharging is not clear. It might be due to electrostatic correlations not included in the original DLVO approach or by exclusion regions, hard core effects, also not considered in the original mean field theories [2][14][15]. This issue needs to be understood so the precise recipe to have overcharging would be clear.

In this paper, we study the effects of ionic size on the double layer around a single colloidal particle in an ionic media. We apply a nonlocal density approximation for the size effects. In section II, we introduce the model and a number of prescriptions for taking into account size correlations. Our results are discussed in section III. Conclusions end this section.

2 The Density Functional Approach

We consider a charged colloid of radius r_0 containing $-Zq$ charged groups uniformly distributed at the macroion surface, which are neutralized by ions of valence v and diameter a . This polyion is embedded in the center of a cell of radius R also containing the counterions of valence v . For simplicity, we will assume that the solvent is modeled as an uniform dielectric continuum characterized by a dielectric constant ϵ .

The thermodynamic behavior of the colloidal system is determined by the distribution of mobile ions around the polyion. A simple type of theory that can give this profile is the density functional theory of electrolytes. The basic notion behind this approach is that the inhomogeneous distributions of counterions, $n(r)$, results from the minimization of a free energy $F[n(r)]$ that depends in the complete function $n(r)$. The simplest equation that can be used to determine the ion distribution around the polyion is derived from minimizing the free energy

$$\beta F_{PB} = \int \{n(r) \ln(n(r)\Lambda^3) - n(r) + \beta f_{el}[n(r)]\} d^3r \quad (1)$$

where Λ is the thermal wavelength. The first term the entropy of the mobile ions. The interaction of the small ions with the macroion potential and the mean-field interaction between the ions is given by

$$f_{el}[n(r)] = \frac{1}{2} qv n(r) \phi_{free}(r) + qv n(r) \phi_p. \quad (2)$$

Here $\phi_{free}(r)$ is the potential due to the free ions and $\phi_p(r)$ is the potential due to the fixed polyion. The extremization of the equation above together with the requirement of charge neutrality leads to the Boltzmann distribution

$$n(r) = n_0 e^{-\beta qv \phi(r)} \quad (3)$$

where

$$n_0 = \frac{Z}{v \int e^{-\beta qv \phi(r)} d^3r} \quad (4)$$

and where $\phi(r) = \phi_{free}(r) + \phi_p(r)$. Eq. (3) together with the Poisson Equation,

$$\nabla^2 \phi(r) = \frac{-4\pi}{\epsilon} \rho_q(r) \quad (5)$$

where ϵ is the dielectric constant and ρ_q is the charge density given by:

$$\rho_q(r) = -Zq\delta(r) + n(r)qv \quad (6)$$

gives the well known Poisson Boltzmann, PB, approximation. The basic approximation of the PB theory is stressed in Eq. (2). Each ion is assumed to interact with the average field as would be measured by an infinitely small test charge. However, if one ion is present at a position \vec{r} , it tends to push away the other ions from that point, which is relevant for high ionic strength. Moreover, this approach does not take into account the ionic size that also becomes important at high concentration. This problem can be circumvented by the addition to the free energy Eq. (1), the inter-particle correlational free energy densities given by

$$F = F_{PB} + F_{corr} \quad (7)$$

where

$$F_{corr} = \int n(r) f_{hc}[n(r)] d^3r \quad (8)$$

that accounts for the excess of free energy due to hard core exclusion. The expression for the functional free energy density per ion, $f_{hc}[n(r)]$, can be taken from the theory for uniform liquids. In this work we adopt the two prescriptions. One is the free volume under the Percus-Yevic approximation, PY, [16] given by

$$\beta f_{hc1}(n) = \frac{3}{2} \left[\frac{1}{(1-\eta)^2} - 1 \right] - \ln(1-\eta) \quad (9)$$

where $\eta = \pi n a^3 / 6$ that works well when the system is not too packed. For higher densities one can employ the Carnahan-Starling, CS, [17] form given by

$$\beta f_{hc2}(n) = \frac{\eta(4-3\eta)}{(1-\eta)^2}. \quad (10)$$

To employ these expressions in the framework of the Local Density Approximation, LDA, the homogeneous density n in Eq. (9) and Eq. (10) has to be replaced by the non-uniform density $n(r)$. The density profile can then be derived by applying the variational principle together with charge neutrality to Eq. (7). For the PY case, the density profile becomes

$$n(r) = n_0 e^{-\beta v q \phi(r) - \beta \mu_{hc1}[n(r)]} \quad (11)$$

where

$$\begin{aligned} \beta \mu_{hc1}[n(r)] = & \frac{3\eta[n(r)]}{(1 - \eta[n(r)])} \left[\frac{1}{(1 - \eta[n(r)])^2} - \frac{1}{6} \right] \\ & + \frac{3}{2} \left[\frac{1}{(1 - \eta[n(r)])^2} - 1 \right] - \ln(1 - \eta[n(r)]) \end{aligned} \quad (12)$$

while for the CS recipe one gets the density profile

$$n(r) = n_0 e^{-\beta v q \phi(r) - \beta \mu_{hc2}[n(r)]} \quad (13)$$

with

$$\beta \mu_{hc2}[n(r)] = \frac{\eta[n(r)](4 - 3\eta[n(r)])}{(1 - \eta[n(r)])^2} + \frac{\eta[n(r)](2 - 4\eta[n(r)])}{(1 - \eta[n(r)])^3} \quad (14)$$

and

$$\eta[n(r)] = \frac{\pi a^3 n(r)}{6}. \quad (15)$$

The local density approximation fails for large values of the exclusion region. Both expressions, Eq. (9) and Eq. (10), diverge when the volume fraction goes beyond a threshold (that is different for each expression). This divergence in the homogeneous system is responsible for not allowing two neighbor particles to overlap. The excess of chemical potential, μ_{hci} pushes particles away from regions close to the polyion until no particle is left there, generating an structural catastrophe that is in fact an artifact of the LDA [18].

Since the LDA fails for high volume fractions, we shall employ another strategy, the Weighted Density Approximation, WDA, that consists in instead of using the local density in the expression for $f_{hc}[n(r)]$, employing an averaged density, \tilde{n} . The coarse-grained density $\tilde{n}(r)$ represents the weighted density average of the local density $n(r)$ given by:

$$\tilde{n}(r) = \int w(\vec{r} - \vec{r}') n(r') d^3 r' \quad (16)$$

Several prescriptions for the weighting function of coarse graining have been suggested. As a test function, we choose the weighted function related to the

Debye-Huckel-Hole-Cavity theory, DHHC, [18]-[20], namely

$$w(\vec{r} - \vec{r}') = \frac{3}{2\pi h^2} \left[\frac{1}{|\vec{r} - \vec{r}'|} - \frac{1}{h} \right] \theta(h - |\vec{r} - \vec{r}'|) \quad (17)$$

where

$$h[n(r)] = \left(\frac{3}{4\pi n(r)} + a^3 \right)^{\frac{1}{3}} \quad (18)$$

is an electrostatic hole where no other particle can be found. The equilibrium density profile of the counterions surrounding the macroion is obtained by functional minimization of Eq. (7) under the constraint of global charge neutrality. This leads to the distribution

$$n(r) = n_0 e^{-qv\beta\phi(r) - \beta\tilde{\mu}_{hci}(r)} \quad (19)$$

where $i=1,2$ represents the PY and the CS, free energy functionals given by Eq. (9) and Eq. (10) respectively. The excess of chemical potential due to the hard core exclusion correlations is given by the weighted density approximation

$$\beta\tilde{\mu}_{hci}(r) = \frac{\delta\beta f_{hci}[n(r), \tilde{n}(r)]}{\delta n(r)}. \quad (20)$$

The resulting density profile defines the screening of the counterions in the presence of size effects.

3 Results and Conclusions

In the following we will concentrate in two observables. The first is the integrated fraction of ions within a radial distance r from the colloid center, which is given by

$$P(r) = \frac{1}{Z} \int_{r_0+a/2}^r n(r') d^3r'. \quad (21)$$

The second observable we look at is the osmotic pressure Π . For PB like free energy functionals with an additional correlational density term it is given by [21]

$$\beta\Pi = \left[n + n \frac{\partial f_{corr}(n)}{\partial n} - f_{corr}(n) \right]_{n=n(R)} \quad (22)$$

where f_{corr} can be any correlational free energy density. In the present work, we use $f_{corr} = f_{hci}$. For the PB case where $f_{corr} = 0$, the pressure reduces to the well known fact that the pressure is given by the boundary density [22]. Since this result actually holds *rigorously* for the full restricted primitive model [23] and since our correlational theory is an approximate way to calculate the boundary density, then we calculate the pressure from $\beta\Pi = n(R)$. The difference between this procedure and using Eq. (22) is small and gives a lower bound for the real pressure value.

Measuring all lengths in the full partition function of the cell model in units of $\lambda = \lambda_B v^2$ where $\lambda_B = q^2/(\epsilon k_B T)$ is the Bjerrum length reveals that the distribution function $P(r)$ is invariant under a rescaling which keeps the number of counterions $N = Z/v$, the coupling length λ , the ionic diameter a/λ and the volume fraction $(r_0/R)^3$ constant [20].

In order to make the comparison between the systems where the counterions have size and the Poisson Boltzmann form where the counterions are point ions, the colloid-counterion closest approach $r_0/\lambda + a/2\lambda = 10$ and the colloid-counterion largest separation $R/\lambda - a/2\lambda = 10$ are kept constant while a/λ is varied. The total integrated charge for the PB case and the two local density approximations are illustrated for two different diameters, $a/\lambda = 1$ and $a/\lambda = 5$, in Fig. (1) and Fig. (2) respectively. The two correlational recipes exhibits similar behavior. The hard core repulsion exclude ions from the vicinity of the polyion. As the ion radius increases, the exclusion zone increases. Beyond $a/\lambda = 8$ no solution is found.

For high ionic size, the LDA fails and therefore we need to employ the WDA. The two prescriptions for WDA and the PB approach are compared for $a/\lambda = 1$ and $a/\lambda = 5$ in Fig. (3) and Fig. (5) respectively. As in the LDA, there is no qualitative difference between the WDA approach using the PY functional or the CS functional. The density profile within the WDA **softens** the size effect when compared with the LDA. No divergence is found when employing the WDA. The osmotic pressure for all these cases is illustrated in table (1). Both the PY and the CS forms are not appropriate for analyzing larger particles and a more sophisticated functional is needed.

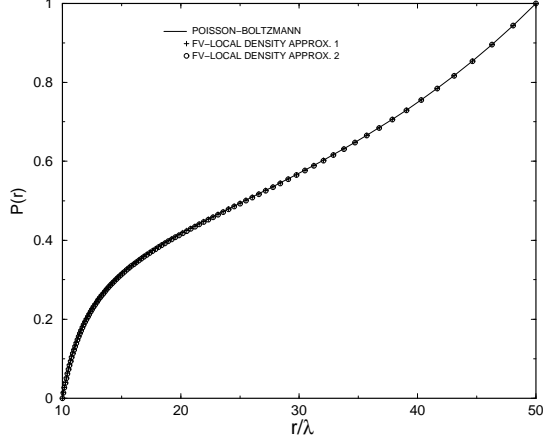


Fig. 1. Integrated charge for PB and LDA cases with $a/\lambda = 1$ and $v^2 = 1$.

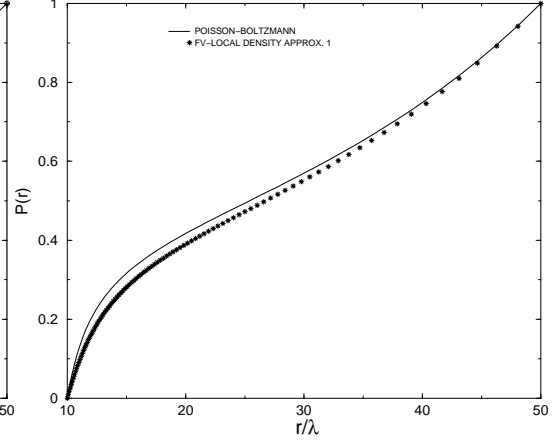


Fig. 2. Integrated charge for PB and PY case with $a/\lambda = 5$ and $v^2 = 1$.

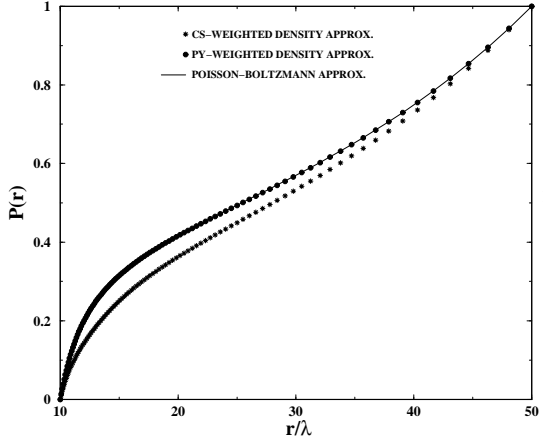


Fig. 3. Integrated charge for PB and WDA cases with $a/\lambda = 1$ and $v = 1$.

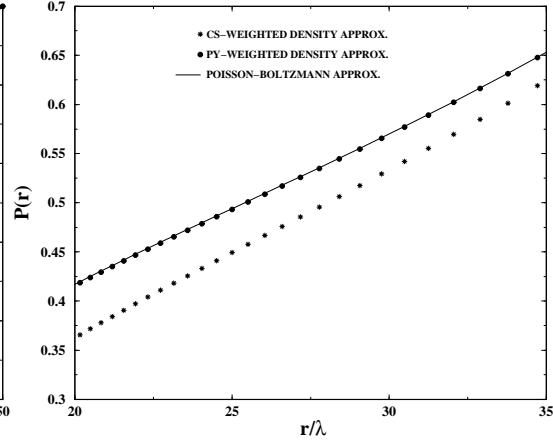


Fig. 4. Enhanced sector of the previous figure.

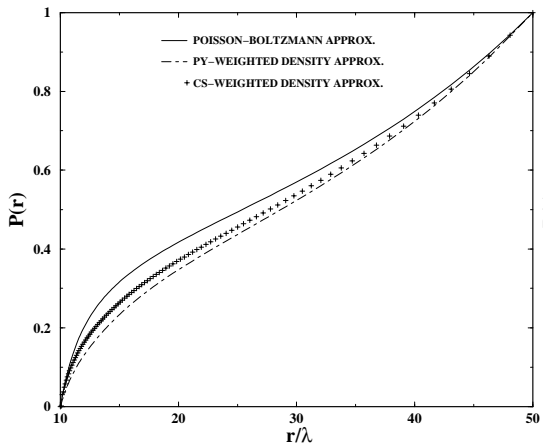


Fig. 5. Integrated charge for PB and WDA cases with $a/\lambda = 5$ and $v^2 = 1$.

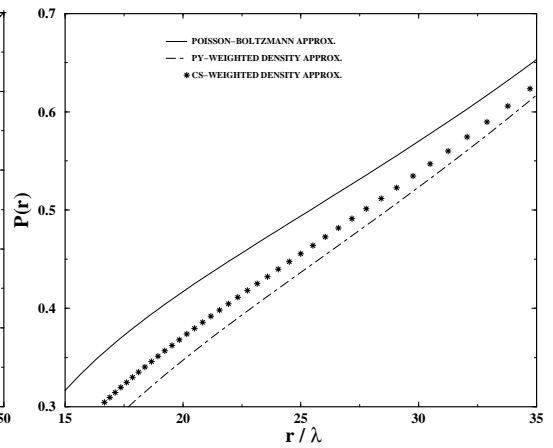


Fig. 6. Enhanced sector of the previous figure.

Table 1

Values of the osmotic pressure in units of λ^3 for $v^2 = 1$

Approximation/ $\Pi[\lambda^3]$	$a/\lambda_B=1$	$a/\lambda_B=5$
P. Boltzmann	$9.62754 \cdot 10^{-5}$	$9.62755 \cdot 10^{-5}$
PY - Local Density Approx.	$9.65298 \cdot 10^{-5}$	$9.65299 \cdot 10^{-5}$
CS - Weighted Density Approx.	$1.05119 \cdot 10^{-4}$	$1.05078 \cdot 10^{-4}$
PY - Weighted Density Approx.	$9.64533 \cdot 10^{-5}$	$1.08582 \cdot 10^{-4}$

In conclusion, in the framework of a density functional approach we have accounted for size effects in the charge distribution around a central colloid. Our approach was tested for two prescriptions of excess of free energy. Both recipes give the expected behavior, pushing the ions away from the colloid as the counterion radius increase. When the counterions are of similar size of the colloid or for high ionic strength, the weight we employ fails and one has to use a combination of a more sophisticated hard core and electrostatic excess of free energies what will be done in a future work.

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