Ion–ion correlations in charged colloidal suspensions

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Abstract

We investigate the role played by the correlations between the screening counterions in the thermodynamic behavior as a colloidal suspension. A local density functional based on the one component plasma theory is employed to incorporate this effect into the Poisson–Boltzmann theory for this problem. The Helmholtz free energy for this system is derived, showing no indication of phase separation. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, colloidal particles have received a lot of attention not only for their practical applications but also because they are model systems for testing new theories. Large particles are present in our everyday life, from biological to industrial systems and, in general, they show several types of instabilities. In solution, the interaction between the macromolecules are dominated by van der Waals forces resulting from quantum fluctuations of the electron charge density on the surface of the colloidal particle. As a result of this attractive depletion forces, the macromolecules agglomerate. Related to this phenomena, colloids can be unstable against sedimentation in an external gravitation field. This irreversible process is very common and can lead to a number of undesirable medical and industrial problems. The necessary condition for stabilizing the

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suspension is by introducing a repulsive interaction between the colloids. Charging the particles is one way to generate the required forces that will withstand the destabilizing interactions in the system.

As a result of the presence of charges in the system, another type of instability might arise: a reversible liquid–gas phase separation similar to the one present in molecular liquids. Therefore, it becomes necessary to explore the possibility of this phase separation in detail. The very existence of a phase separation in a charged colloidal solution is a long-standing problem which has prompted many attempts for a theoretical definitive answer. While experimental results are quite controversial [1–3], simulations show that this transition exists for multivalent counterions [4]. Due to computational limitations, this result was verified only for moderately charged particles.

At the theoretical level, the situation is also unclear. While modern theories of liquids show the existence of two coexisting phase even for monovalent ions [5,6], a mean-field extended Debye–Hückel–Bjerrum analysis indicates that charge renormalization simply washes the transition out [7]. The simplicity of these analytic approaches is valuable, however the lack of correlations is their major flaw. Therefore, their conclusions are limited to the analysis of monovalent counterions in water where the correlations play a less important role. Other more sophisticated methods such as integral equations provide a very elegant way to include correlations [8,9]. The problem with these theories is that they can only be solved by lengthy numerical calculations. Therefore, in order to make progress, approximations at the level of a direct correlation function have to be made. At this point, different theories will make different choices for this function. Whatever theory is chosen it leads to a series of approximations such that instead of clarifying the source of correlations responsible for the physical phenomena they tend to obscure it.

Hence, to gain some insight into the relevance of the various sources of correlations to the phase behavior of the colloidal mixture, in this paper we explore a specific case: a high density colloidal suspension. The description of this mixture is much simpler because, when the volume fraction of polyions is not low, the macroions arrange themselves in a regular structure. Thus, one can take advantage of the translational invariance of the lattice and assume that each colloid and its counterions are enclosed in a Wigner–Seitz (*WS*) cell [10–12]. Then the thermodynamic properties of the system are fully determined by the distribution of counterion inside that cell. At the mean-field level, this density profile is given by the Poisson–Boltzmann (*PB*) approximation. In this case, the Helmholtz free energy is a convex function of the cell radius R. However, the *PB* approach is unable to give a complete description of the system because the ionic correlations are not taken into account. To circumvent this problem without losing the simplicity of the density functional approximation, we recently derived the Debye–Hückel–Hole–Cavity (*DHHC*) theory that takes into account the ion correlations [13] in a local fashion. The *DHHC* locally approximates the correlational contributions beyond the mean-field theory by the free energy, the one component plasma (*OCP*) [14,15]. Applying the *DHHC* to the theoretical description of screening of charged rods and colloids, we were able to obtain density profiles in correspondence with the ones obtained by simulations [13,16].

Here, we employ our method to derive the Helmholtz free energy $F_{cell}(R)$ for a cell containing one charged colloid and its counterions as a function of the cell radius R. We then relate the physical behavior of the suspension to that of one cell by defining a functional that contains the cell Helmholtz free energy of one cell, F_{cell}, and the interactions between this cell and the others through the osmotic pressure, P_o. Minimization of this functional for a fixed P_o gives the optimum cell radius that is ultimately related to that density of the suspension at P_o. In order to check if the correlations between the counterions induce phase separation, we study the convexity of $F_{cell}(R)$ as a function of R. The remainder of this manuscript goes as follows. The one component plasma hole cavity theory is introduced in Section 2, its Helmholtz free energy is derived and the theory is checked for instabilities in Section 3 followed by Results and conclusions.

2. Debye–Hückel–Hole–Cavity theory for charged colloid

We consider a solution made of N spherical polyions inside a homogeneous medium. The solvent is assumed to be uniform and represented by a dielectric constant ε. In the solution, each polyion loses Z/v positive counterions of valence v and gets negatively ionized. If the density of macroions is not low, the colloids arrange themselves in a periodic structure. In this case, it is sufficient to consider just one isolated polyion in an appropriate Wigner–Seitz cell. To simplify the problem, a further approximation is to replace the polyhedral cell by a sphere with the same volume. Thus, exploiting the underlying periodicity of the colloidal suspension, our model system consists of one polyion of radius r_0 with a uniform surface charge $-Zq$ in the center of a WS cell of radius R. The microions are modeled as particles with diameter a and charge vq. Inside the WS they are free to move within the annulus $r_0 < |\vec{r}| < R$.

The distribution of counterions is strongly determined by the electrostatic potential, $\psi[n(\vec{r})]$, induced by the polyion and by the interaction between the microions. 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 distribution of counterions, $n(\vec{r})$, results from the minimization of a free energy $F(n(\vec{r}))$ that depends on the complete function $n(\vec{r})$. In the particular case we are analyzing, one has to minimize the expression [13]:

$$F[n(\vec{r})] = F_{PB}[n(\vec{r})] + \int d^3r \, f_{OCPHC}[n(\vec{r})], \tag{1}$$

under the constraint of charge neutrality. The first term in Eq. (1),

$$\beta F_{PB}[n(\vec{r})] = \int d^3r \{ n(\vec{r}) \ln(n(\vec{r})a^3) + \beta qvn(\vec{r})\psi[n(\vec{r})] \}, \tag{2}$$

contains in the first parcel the entropy of the mobile ions and in the second both the electrostatic interaction of the small ions with the macroion and the mean-field electrostatic interaction between the counterions. Minimization of Eq. (2) gives the Boltzmann distribution that combined with the Poisson–Equation leads to the mean-field Poisson–Boltzmann density profile. In PB theory, 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. This effect, which becomes relevant at high ionic strength, can be taken into account by the addition of a correlational free energy density, f_{OCPHC}, in Eq. (1). The main difficulty with this approach is to find an appropriate expression for f_{OCPHC}.

Recently, we did circumvent this difficulty by introducing a theory that locally approximates the correlational contributions beyond the mean-field theory by the correlational free energy of the *OCP* [15]. The way we derive this free energy goes as follows. The *OCP* consists of Z/v identical point-particles of valence v and positive unit charge q inside a volume $V = 4\pi(R^3 - r_0^3)/3$. The macroion plays the role of a uniform neutralizing background of density $vn_B = Z/V$ and dielectric constant ε. The *OCP* electrostatic free energy density associated with the correlations between the counterions can be derived from the electrostatic potential $\phi_{OCP}(r)$. For obtaining an explicit expression for $\phi_{OCP}(r)$, approximations must be made. We propose the *DHHC* strategy which, following the early ideas of the Debye–Hückel–Hole theory [17], postulates that around any central ion, there is a correlation hole of radius h where no other ion can be found and also a cavity $a < h$ where no background is present. In this case, the charge density is given by

$$
\rho_{OCP}(r) = \begin{cases} qv\delta(\vec{r}): & 0 \leqslant r < a\,, \\ -qvn_B: & a \leqslant r < h\,, \\ -\varepsilon\kappa^2\phi_{OCP}(r): & h \leqslant r\,, \end{cases} \tag{3}
$$

where $\kappa = \sqrt{4\pi\lambda_B v^2 n_B}$ is the inverse of the screening length, $\lambda_B = q^2\beta/\varepsilon$ is the Bjerrum length. A systematic way to fix h results from excluding particles from a region where their Coulomb energy is larger than some threshold. A natural choice for the latter is the thermal energy $k_B T$ which gives

$$
\kappa h = [(\omega - 1)^3 + (\kappa a)^3]^{1/3}\,, \tag{4}
$$

with $\omega = (1 + 3v^2\lambda_B\kappa)^{1/3}$. Using this prescription together with Eq. (3) and the Poisson equation

$$
\nabla^2\phi_{OCP}(r) = -\frac{4\pi}{\varepsilon}[\rho_{OCP}(r) - vqn_B]\,, \tag{5}
$$

an explicit expression for $\phi_{OCP}(r)$ is found. Once the potential at the position of the central ion is known, the electrostatic contribution to the free energy density, f_{DHHC} is obtained by the Debye charging process [18].

$$
\beta f_{DHHC}(n_B) = n_B\frac{(\kappa a)^2}{4} - n_B\int_1^\omega \mathrm{d}\bar{\omega}\left\{\frac{\bar{\omega}^2}{2(\bar{\omega}^3 - 1)}\,\Omega(\bar{\omega})^{2/3}\right.
$$
$$
\left. + \frac{\bar{\omega}^3}{(1 + \Omega(\bar{\omega})^{1/3})(\bar{\omega}^2 + \bar{\omega} + 1)}\right\}\,, \tag{6}
$$

where

$$\Omega(\bar{\omega}) = (\bar{\omega} - 1)^3 + \frac{(\kappa a)^3}{3v^2 \lambda_B \kappa} (\bar{\omega}^3 - 1).$$ (7)

The correlational free energy density for the homogeneous system, $f_{DHHC}(n_B)$, can then be used at the local density functional theory by simply making the density inhomogeneous, $n_B \rightarrow n(\vec{r})$. The equilibrium density profile of the counterions surrounding the macroion is obtained by the functional minimization of Eq. (1) under the constraint of global charge neutrality. This leads to the distribution

$$n_{cell}(r) = n_0\, \mathrm{e}^{-qv\beta\psi(r) - \beta\mu_{OCPHC}[n(r)]},$$ (8)

where

$$\mu_{OCPHC} = \frac{\partial f_{OCPHC}}{\partial n(r)},$$ (9)

and where

$$n_0 = \frac{Z}{v \int \mathrm{d}^3 r\, \mathrm{e}^{-qv\beta\psi(r) - \beta\mu_{OCPHC}[n(r)]}}.$$ (10)

These expressions define the screening of the counterions in the presence of correlational effects.

3. Helmholtz free energy

Once the distribution of free ions is obtained, the Helmholtz free energy for the cell is computed by introducing the optimum profile into Eq. (1) which gives

$$\beta F_{cell}[R] = -\frac{Z}{v}[1 + \ln(n_0(R))] - \frac{\beta\varepsilon}{8\pi} \int \mathrm{d}^3 r (\nabla\psi)^2 - \int \mathrm{d}^3 r \beta\, p_{OCPHC}[n(\vec{r})],$$ (11)

where

$$p_{OCPHC}[n(\vec{r})] = -f_{OCPHC}[n(\vec{r})] + n(\vec{r})\mu_{OCPHC}[n(\vec{r})].$$ (12)

From Eq. (11), all the properties of the cell can be carried out. In principle, the thermodynamic information about the suspension would require the knowledge of the total Helmholtz free energy, F_{tot}. For instance, if F_{tot} would be a convex function of the density, the suspension would be homogeneous. If instead, F_{tot} would be a concave function, instabilities that result in inhomogeneities in the density would be present. In that case, the system would separate into two phases: a low and a high density liquid.

However, due to translational invariance of the system, the instabilities the total solution reflects in non-convexities in F_{cell}. Moreover, for a fixed osmotic pressure of the total system, P_o, we can define a cell functional

$$F_{func}[R] = F_{cell}[R] - P_o V$$ (13)

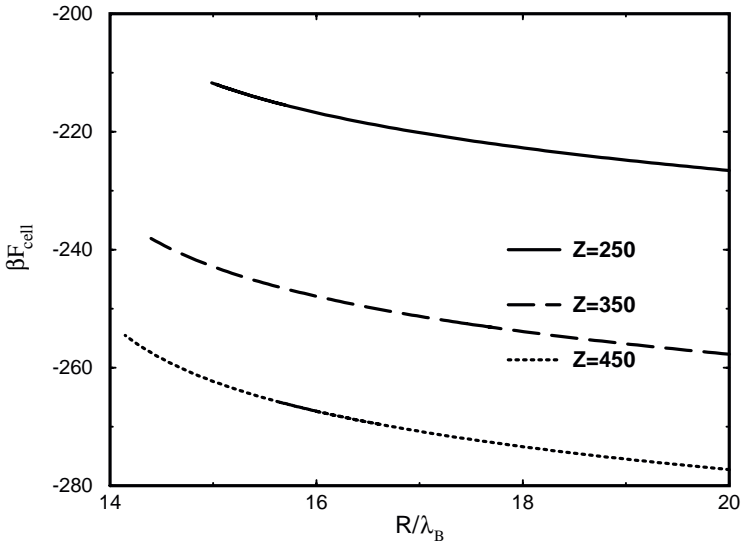Fig. 1. Helmholtz free energy βF_{cell} vs. cell radius R/λ_B for colloidal radius $r_0/\lambda_B = 13$, $Z = 250, 350, 450$ and trivalent counterions.

that relates the behavior of the total system with the one at an isolated cell. Thus, minimization of Eq. (13) for a fixed value of P_o gives the optimum cell radius. If this value is unique, the cell has just one possible optimum radius and the overall suspension is homogeneous. If, instead, F_{func} has two minima, the cell has two possible radii and the solution phase separates into two liquid phases.

Thus, to check if the correlation between the counterions leads to fluid–fluid phase transition, we analyze the behavior of $F_{cell}(R)$ for a wide range of colloidal radius and ionic strengths. The cases illustrated in Fig. 1 clearly show that $F_{cell}[R]$ is a convex function of R. Furthermore, assuming that P_o is the osmotic pressure of the system, we find that the functional $F_{func}[R]$ has always just one minimum at R_0 which indicates the absence of instabilities.

The thermodynamic properties of colloidal solutions at high densities or ionic strength are closely related to the presence of mutual macroions, ion–ion and particle-ion correlations. Taking them into account properly is a difficult task, so one needs to employ approximations that mix the different sources of correlations at different levels. Thus, in order to identify which one of them is responsible for instabilities in the system, one needs to study them exclusively. In this paper, we analyzed the role played by correlations between the screening ions for a model system in which the particle–particle and particle non-screening ions correlations were not taken into account. Within our approach no instabilities were found, indicating that the correlations between the screening ions do not induce phase transition. Since phase separation is observed in simulations, one has to look for other correlational effects that might lead to that phenomena. Therefore, in the future we shall explore the role played by interactions between counterions in neighboring cells in the phase separation of a colloidal suspension.

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