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The density-functional approach for charged systems

Marcia C Barbosa

Instituto de Física, Universidade Federal do Rio Grande do Sul, Caixa Postal 15051, 91501-970
Porto Alegre (RS), Brazil

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Abstract

The distribution of an electrolyte solution close to a charge macroion is investigated theoretically. A local density functional form based on one component plasma theory is proposed to incorporate the correlations between the microions into Poisson–Boltzmann theory. Our results are compared with those obtained by the mean-field approximation.

1. Introduction

Macromolecules show several types of instabilities. In solution, the particles agglomerate due to the depletion forces. They also might exhibit a liquid–gas phase transition similar to the phase separation present in molecular liquids. For many biological systems such as proteins, DNA and cholesterol and in industrial applications, such as paints and superabsorbants, these instabilities lead to undesirable effects. The presence of charges is one way of generating the osmotic pressure required to prevent agglomeration. According to traditional Derjaguin–Landau–Verwey–Overbeek (DLVO) [1], theory the competition between screened Coulomb repulsion and van der Waals attraction leads to stabilization of the suspension. However, this conclusion is not obvious. The interaction between charged objects is strongly affected by the electrolytes present in the solution. The macroions attract the counterions and repel the coions which generate large inhomogeneities in the densities of the electrolytes. The main effect of these inhomogeneities is the screening of the Coulomb interaction between the polyions that is characterized by the Debye–Hückel screening length [2] which at the mean-field level would decrease Coulomb repulsion in accordance with DLVO theory. However, for high concentrations of multivalent electrolytes, the fluctuations involved become relevant. In this case, the distribution of microions must be such to withstand the repulsion between the macromolecules and attraction between like-charged particles arises. This is observed both experimentally [3] and in simulations [4].

One of the main theoretical approaches employed to describe the distribution of the microions surrounding a macroion is Poisson–Boltzmann (PB) theory [1, 5]. It treats the microion interactions at mean-field level by neglecting the correlations and the finite size effects. Its linearized form, usually called the Debye–Hückel expression, provides a very simple and intuitive form for screening microions [2]. PB theory has been quite successful in

describing a number of systems with Debye–Hückel low screening lengths as is the case with low ionic strengths or low dielectric constants. The major problems with PB theory is the fact that the ionic correlations are not taken into account and that any effects due to the finite size of microions are neglected. Each ion is assumed to interact with the average electrostatic field as measured by a small test particle. However, if an ion is present at position, r , it tends to push ions away from that point. This effect can be dominant if the ionic strength is high as is the case of systems with low dielectric constants, multivalent counterions or high concentrations of microions.

More sophisticated methods such as integral equations provide a very elegant way of including correlations [6,7]. The problem with these theories is that they can only be solved by lengthy numerical calculations. Therefore, in order to make any progress, approximations at the direct-correlation-function level have to be made. At this point, different theories give different options for this function. Whatever theory is chosen it leads to a series of approximations that instead of clarifying the source of correlations responsible for the physical phenomena tend to obscure it.

To gain some insight into the relevance of the various sources of correlations, we can explore a specific case: high macroion concentration. 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 macroparticle and its counterions are enclosed in a Wigner–Seitz (WS) cell [8–10]. Then the thermodynamic properties of the system are fully determined by the distribution of counterions inside that cell. At the mean-field level, this density profile is given by the PB approximation where correlations are neglected. 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 [11–13] in local fashion. DHHC locally approximates the correlational contributions beyond mean-field theory by the free energy of the one component plasma (OCP) [14, 15]. Applying DHHC to the theoretical description of screening of charged rods and colloids we were able to obtain density profiles in accord with those obtained by the simulations [11–13].

Nevertheless, despite the success of DHHC in describing a wide range of systems where polyions were surrounded solely by counterions, we could not apply its original form to systems where coions were present. Here we extend this approach to include the effects produced by the presence of salt. Our main purpose is to check up to what extent a local theory is able to account for all the correlations, including the ones that ultimately lead to attraction between like-charged macroions.

The remainder of this manuscript goes as follows. The OCP hole cavity theory and the modifications made to include the presence of coions is presented in section 2. We apply the method to a specific geometry, a charged colloid, and give our results and conclusions in section 3.

2. Density-functional approach: Debye–Hückel-hole-cavity

A density-functional theory for inhomogeneous distribution of point-like counterions and coions around a polyion is based on the minimization of free energy

$$F[n_i(\vec{r})] = F_{\text{PB}}[n_i(\vec{r})] + \int d^3r f_{\text{OCPHC}}[n_i(\vec{r})] \quad (1)$$

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

$$\beta F_{\text{PB}}[n_i(\vec{r})] = \int d^3r n_+(\vec{r}) \ln(n_+(\vec{r})a^3) + \int d^3r n_-(\vec{r}) \ln(n_-(\vec{r})a^3) \\ + \beta q v_+ \int d^3r n_+(\vec{r}) \psi[n_i(\vec{r})] - \beta q v_- \int d^3r n_-(\vec{r}) \psi[n_i(\vec{r})] \quad (2)$$

contains in the first part the entropy of the mobile positive and negative ions and in the second part both the electrostatic interaction of the small ions with the macroion and the mean-field electrostatic interaction between the microions. Minimization of (2) gives the Boltzmann distribution that combined with the Poisson equation leads to the mean-field PB density profile. The expression f_{OCPHC} accounts for the correlations between the small ions. The main difficulty is to find an appropriate expression for this correlational energy.

Recently, we derived an expression for f_{OCPHC} when only counterions are present based on the local description of OCP [11]. In order to extend this approach for including correlational effects when positive and negative ions are present, we propose splitting the total correlational energy into two contributions, $f_{\text{OCPHC}} = f_{\text{OCPHC}}^+ + f_{\text{OCPHC}}^-$. The first term accounts for the correlations between the positive ions while the second term takes care of the correlations between the negative ions. Here we will neglect the different-charges correlational effects. The way we derive the expression for f_{OCPHC}^+ goes as follows. Let us assume a number N_+ of identical point particles of valence v_+ and a positive unit charge q inside the volume V . The macroion of charge $-Zq$ and the N_- coions of valence v_- and unit charge $-q$ play the role of a uniform neutralizing background of density $v_+ n_{\text{B}}^+ = Z/V + N_- v_- / V$ and dielectric constant ϵ . The OCP electrostatic free-energy density associated with the correlations between the counterions can be derived from the electrostatic potential $\phi_{\text{OCP}}^+(r)$. To obtain an explicit expression for $\phi_{\text{OCP}}^+(r)$, approximations must be made. We proposed the DHHC strategy that, following the early ideas of the Debye–Hückel-hole theory [16], postulates that around any microion, 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

$$\rho_{\text{OCP}}^+(r) = \begin{cases} q v_+ \delta(\vec{r}) : & 0 \leq r < a_+ \\ -q v_+ n_{\text{B}}^+ : & a_+ \leq r < h_+ \\ -\epsilon \kappa_+^2 \phi_{\text{OCP}}^+(r) : & h_+ \leq r \end{cases} \quad (3)$$

where $\kappa_+ = \sqrt{4\pi \lambda_{\text{B}} v_+^2 n_{\text{B}}^+}$ is the inverse of the screening length, $\lambda_{\text{B}} = q^2 \beta / \epsilon$ is the Bjerrum length. A systematic way of fixing 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_{BT} that gives

$$\kappa_+ h_+ = [(\omega_+ - 1)^3 + (\kappa_+ a_+)^3]^{1/3} \quad (4)$$

with $\omega_+ = (1 + 3v_+^2 \lambda_{\text{B}} \kappa_+)^{1/3}$. Using this prescription together with (3) and the Poisson equation

$$\nabla^2 \phi_{\text{OCP}}^+(r) = -\frac{4\pi}{\epsilon} [\rho_{\text{OCP}}^+(r) - v_+ q n_{\text{B}}^+] \quad (5)$$

an explicit expression for $\phi_{\text{OCP}}^+(r)$ 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 [2].

$$\beta f_{\text{DHHC}}^+(n_{\text{B}}^+) = n_{\text{B}}^+ \frac{(\kappa_+ a_+)^2}{4} - n_{\text{B}}^+ \int_1^{\omega_+} d\bar{\omega}_+ \\ \times \left\{ \frac{\bar{\omega}_+^2}{2(\bar{\omega}_+^3 - 1)} \Omega_+(\bar{\omega}_+)^{2/3} + \frac{\bar{\omega}_+^3}{(1 + \Omega_+(\bar{\omega}_+)^{1/3})(\bar{\omega}_+^2 + \bar{\omega}_+ + 1)} \right\} \quad (6)$$

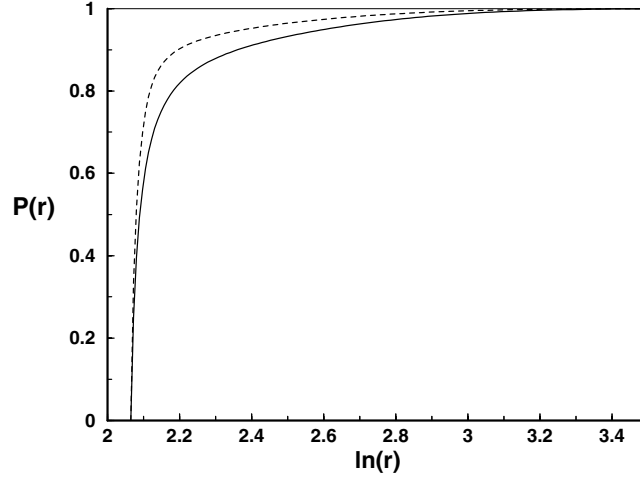


Figure 1. Integrated charge distribution, $P(r)$ versus $\ln r$ for a spherical cell containing a colloid of charge $Z = 180$ and divalent counterions and $2N_s = 180$ divalent salt ions. The cell radius and colloidal radius are $R = 40a$ and $r_0 = 8a$, respectively. The Bjerrum length is $\lambda_B = 2a$. The solid curve is the prediction from PB theory. The increase in the counterion condensation is captured by the DHHC (dashed curve).

where

$$\Omega_+(\bar{\omega}_+) = (\bar{\omega}_+ - 1)^3 + \frac{(\kappa_+ a_+)^3}{3v_+^2 \lambda_B \kappa_+} (\bar{\omega}_+^3 - 1). \quad (7)$$

The derivation of f_{DHHC}^- follows the same lines as described above. The expressions $f_{\text{DHHC}}^+(n_{\text{B}}^+)$ and $f_{\text{DHHC}}^-(n_{\text{B}}^-)$ written in terms of the homogeneous density are used in the local density functional (1) by making the density inhomogeneous $n_{\text{B}}^+ \rightarrow n_+(\vec{r})$ and $n_{\text{B}}^- \rightarrow n_-(\vec{r})$.

Then the equilibrium density profile of the counterions and coions surrounding the macroion are obtained by functional minimization of (1) under the constraint of global charge neutrality. This leads to the distribution for the counterions and coions given by

$$n_{\pm}(r) = n_0^{\pm} \exp(\mp q v_{\pm} \beta \psi(r) - \beta \mu_{\text{OCPHC}}^{\pm} [n_{\pm}(r)]) \quad (8)$$

where

$$\mu_{\text{OCPHC}}^{\pm} = \frac{\partial f_{\text{OCPHC}}^{\pm}}{\partial n_{\pm}(r)} \quad (9)$$

and where n_0^{\pm} is obtained from the required charge neutrality.

3. Results and conclusions

To check our approach, we apply the correlation free-energy density f_{OCPHC} to the problem of the screening of a charged colloid. Colloidal suspensions are present in our everyday life from industrial systems [17, 18] such as clay to biological structures such as cholesterol [19]. Much of the thermodynamic behaviour of solutions of this type is determined by the distribution of counterions around the polyion. Here we explore what effects our correlational free-energy density is able to capture when salt is added to the system. For that purpose, we consider a charged colloid of radius $r_0/a = 8$ with an uniform surface charge $-Zq$ in the centre of a WS cell of radius R/a . The microions are modelled as divalent particles with diameter a . In addition to the counterions, there are N_s positive and negative divalent ions of salt. Inside the

WS cell they are free to move within the annulus $r_0 < |\vec{r}| < R$. We investigate $\lambda_B/a = 2$, the system is thus strongly charged and we expect the ionic correlations to be relevant. To illustrate this, we calculate the integrated charge within a distance r from the centre of the colloid. figure 1 shows the comparison between the PB prediction for this observable and the value obtained from the f_{DHHC} free-energy functional.

It can be seen that the DHHC distribution lies above the PB indicating an increase in condensation. This increase in condensation is also observed in the case where coions are not present. Our results in that case were checked with simulations showing remarkable agreement [11].

In conclusion, in the framework of a density-functional approach we have derived a correlation correction for the case where electrolytes are present. We show that for the case of a strongly charged colloid this contribution is able to capture the increase in condensation. However, since our expression is concave in density, it is unable to show the attraction between like-charged particles or overcharging [20]. For that purpose, one needs to incorporate explicitly hard core effects that we will leave for a future work when our results will be compared with simulations that are currently begin developed.

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