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The Laplace Transform of the MSA Pair Distribution Functions between Macroions in an Ion–Dipole Fluid

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The Laplace transform is obtained for the pair distribution function between a pair of ions, an ion and a macroion, and a pair of macroions in an ion–dipole fluid. This fluid is a simplified model of an electrolyte with a discrete model of solvent (hard spheres with embedded point dipoles). From these results, an expression for the solvation force between macroions is obtained. This result consists of the classical DLVO result plus a series of corrections.

KEY WORDS: Colloids; solvation force; ion–dipole fluid; mean spherical approximation; macroions; electrolyte; solvent; correlation functions.

1. INTRODUCTION

The study of the interaction force between macroions is an important problem in colloidal chemistry. The theory of Derajaguin, Landau, Verwey, and Overbeek (DLVO)[1] is widely accepted and used in diverse applications. In the DLVO theory, the force between macroions (or colloidal particles) immersed in an electrolyte is the sum of a repulsive long-range electrostatic interaction, described by the Poisson–Boltzmann equation, and an attractive short-range van der Waals attraction.

In recent years, the improvement of the DLVO theory has been the object of several publications. This work was stimulated by the recent experiments of Israelachvili and collaborators,[2] who have measured the

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force between macroions with great precision. They find the DLVO theory to be accurate at large separations, but that at a small separations (less than 20–30 Å) the force between the colloidal particles has an oscillatory character not seen in the DLVO theory.

In the DLVO theory, the ions are treated as point charges and, more seriously because the number of solvent molecules is greater, the solvent is treated as a dielectric continuum whose presence is manifest only through its dielectric constant. Thus, an improvement of this DLVO theory requires the transition from point to nonpoint ions and, more significantly, to a molecular solvent. Recently, Henderson and Lozada-Cassou(3) have obtained new contributions to the force between colloidal particles by assuming the solvent to be a hard-sphere fluid whose polar character is manifest by a dielectric constant. This model gives an extra oscillatory contribution to the force between macrospheres resulting from the hard-core exclusion forces between the solvent molecules. This oscillatory force was obtained from the formulas for the correlation functions of hard-sphere mixtures in the Percus–Yevick approximation, given approximation, given by Lebowitz.(4) The resulting force between the macrospheres in this model electrolyte is in qualitative agreement with experiment. To obtain quantitative agreement, Henderson and Lozada-Cassou argued that there was an additional monotonic repulsive contribution due to dielectric saturation in the vicinity of the macrospheres. They obtained a simple approximation to this contribution. In a later publication, Henderson(5) obtained an approximation to this term using qualitative arguments about the correlation function between the macrospheres.

Our goal in this paper is to attempt to put the qualitative arguments of Henderson and Lozada on a firmer basis. The model of a colloidal suspension used here is similar to that of Henderson and Lozada-Cassou. The suspension is treated as a highly asymmetric electrolyte with a molecular solvent. The colloidal particles are large, charged hard spheres and the ions are small, charged hard spheres. The solvents can be general, although, for reasons that will be apparent shortly, in this paper we treat the solvent as a fluid of hard spheres with imbedded point dipoles. For simplicity, we assume that there are only a very small number of large spheres. The study of the interactions between colloidal particles, whose concentration is not small, is an interesting problem, but is deferred for future work.

The advantage of this ion–dipole model is that the correlation functions and thermodynamic properties of this model electrolyte can be obtained analytically using the mean spherical approximation (MSA). The solution of the MSA for the ion–dipole mixture for particles of arbitrary diameter has been given recently.(6–10) The results are a generalization of the work of Blum,(11) who solved the MSA for a mixture of ions of arbitrary diameter. The purpose of this paper is to obtain an expression for the force between the large spheres in this model using the MSA.

2. SOME GENERAL CONSIDERATIONS

We consider an M-component ion–dipole mixture consisting of dipolar hard spheres with density ρ_s, diameter d_s, and dipole moment μ_s, large spheres with density ρ_s, charge $z_c e$ (e is the magnitude of the electronic charge), and diameter $d_c = 2R$, and $M-2$ species of charged hard spheres with density ρ_i, charge $z_i e$, and diameter d_i. For simplicity, we will consider $M = 4(+, -, c$ and $s)$ and we will take the cation and anion diameters to be equal $(d_+ = d_- = d_0)$. The densities are defined as the number of particles of that species divided by the volume.

For this model, the pair interactions are

$$u_{ij}(r) = \begin{cases} \infty, & r < d_{ij} \\ \dfrac{z_i z_j e^2}{\varepsilon r}, & r > d_{ij} \end{cases} \tag{1}$$

where i and $j = (+, -, c)$, for an ion–ion, ion–large sphere, or large sphere–large sphere pair,

$$u_{is}(r) = \begin{cases} \infty, & r < d_{ij} \\ \dfrac{z_i e \mu_s}{r^2} (\hat{\mathbf{r}} \cdot \hat{\boldsymbol{\mu}}_s), & r > d_{ij} \end{cases} \tag{2}$$

where $\hat{\boldsymbol{\mu}}_s$ and $\hat{\mathbf{r}}$ are unit vectors and $i = (+, -, c)$, for an ion–dipole or a large ion–dipole pair, and

$$u_{ij}(r) = \begin{cases} \infty, & r < d_{ij} \\ \dfrac{\mu_s^2}{r^3} D(i, j), & r > d_{ij} \end{cases} \tag{3}$$

where i and j are both solvent molecules. In Eqs. (1)–(3)

$$d_{ij} = (d_i + d_j)/2 \tag{4}$$

and

$$D(i, j) = 3(\hat{\boldsymbol{\mu}}_i \cdot \hat{\mathbf{r}})(\hat{\boldsymbol{\mu}}_j \cdot \hat{\mathbf{r}}) - \hat{\boldsymbol{\mu}}_i \cdot \hat{\boldsymbol{\mu}}_j \tag{5}$$

The mean spherical approximation (MSA) is obtained by combining the exact core condition

$$h_{ij}(r) = g_{ij}(r) - 1 = -1, \qquad r < d_{ij} \tag{6}$$

where $g_{ij}(r)$ is the radial distribution function (RDF), and the approximation

$$c_{ij}(r) = -\beta\mu_{ij}(r), \qquad r > d_{ij} \tag{7}$$

where $\beta = 1/kT$ (k is Boltzmann's constant and T is the temperature) with the Ornstein–Zernike relation. In Eqs. (6) and (7), i and $j = (+, -, c, s)$.

We are interested ultimately in the large ion–large ion RDF, since the derivative of this function gives the force between these large colloidal spheres. Thus, we confine our attention to the charged hard sphere–charged hard sphere RDFs. Following refs. 9 and 10, the Laplace transform of these RDFs can be written

$$G_{ij}(s) = \mathscr{L}[rg_{ij}(r)] = G_{ij}^{\mathrm{HS}}(s) + G_{ij}^{\mathrm{EL}}(s) \tag{8}$$

where i and $j = (+, -, c)$; $G_{ij}^{\mathrm{HS}}(s)$ is the Laplace transform of the RDFs for a mixture of hard spheres of diameters d_s, d_0, and d_c. Expressions for $G_{ij}^{\mathrm{HS}}(s)$ have been given by Lebowitz.(4)

The functions of $G_{ij}^{\mathrm{HS}}(s)$ are mainly responsible for the oscillations in the colloidal force, although $G_{ij}^{\mathrm{EL}}(s)$ can sometimes exhibit oscillations. The other correction to the DLVO theory seen in experiment (the extra monotonic repulsion) must come from $G_{ij}^{\mathrm{EL}}(s)$. General expressions for these functions are given in refs. 9 and 10 and have been repeated recently.(12) The expressions are implicit and quite complex, involving 11 parameters, and are not repeated here.

The solution to the colloidal problem requires the consideration of three limits:

1. $\rho_c \to 0$, corresponding to the case of an ionic impurity in an ion–dipole fluid.
2. $D_c \gg d_0$, corresponding to the case of macroions in an ion–dipole fluid.
3. $\rho_0 \to 0$, corresponding to low ionic concentration, where

$$\rho_0 = \sum_{k=1}^{M-2} \rho_k z_k \tag{2}$$

In general, only step 2 is required for a colloidal suspension. We use step 1 because in this paper we are interested only in the interaction between a pair of colloidal particles. The more general problem where ρ_c is finite is also of interest, but is considerably more complex. We use step 3 because without it the results are implicit. Using step 3, we obtain explicit results. Fortunately, most experiments are done at low ionic concentration.

In the general case ($d_+ \neq d_-$), the ion–dipole fluid is described by nine parameters. However, in our special case ($d_+ = d_- = d_0$) only the three parameters b_0, b_1, and b_2 remain. These parameters are related to the interaction parameter,

$$\alpha_0^2 = 4\pi\beta e^2 \tag{10}$$

$$\alpha_2^2 = \frac{4\pi}{3}\beta\mu_s^2 \tag{11}$$

and

$$\alpha_1^2 = \alpha_0\alpha_2 \tag{12}$$

Details may be found in refs. 7–10 and 12.

3. RESULTS

We have, to order x,

$$\begin{aligned} G_{ij}^{\mathrm{EL}}(s) = {} & -\frac{\beta z_i z_j e^2}{\varepsilon} e^{-s_0}\left[\frac{d_0}{s_0 + x_\varepsilon} + \frac{(\varepsilon - 1)\,\beta_6^2 d_s^3}{(d_s + d_0\,y_0)^2}\,\frac{s_s^2 - 2s_s + 2 - 2e^{-s_s}}{S(s) + 2b_2 L(s)e^{-s_s}}\right. \\ & \left. - \frac{S_1(s) + L_1(s)e^{-s_s}}{(s_0 + x_\varepsilon)[S(s) + 2b_2 L(s)e^{-s_s}]}\,\frac{2x_\varepsilon(\varepsilon - 1)\,\beta_6 d_s^2}{d_s + d_0\,y_0}\right] \end{aligned} \tag{13}$$

$$\begin{aligned} G_{ic}^{\mathrm{EL}}(s) = {} & -\frac{4\beta z_i z_c e^2 d_0 e^{-s_0/2}}{\varepsilon d_c^2 x_\varepsilon}\left[\frac{d_0}{s_0 + x_\varepsilon} + \frac{x_\varepsilon(\varepsilon - 1)\,\beta_6 d_s^2 d_0}{2\beta_3 d_0(d_s + d_0\,y_0)(s_0 + x_\varepsilon)}\right] \\ & \times\left[1 - 2\beta_3\,\frac{S_1(s) + L_1(s)e^{-s_s}}{S(s) + 2b_2 L(s)e^{-s_s}}\right] \end{aligned} \tag{14}$$

and

$$G_{cc}^{\mathrm{EL}}(s) = -\frac{4\beta z_c^2 e^2 d_0(1 + x_\varepsilon)}{\varepsilon d_c^3 x_\varepsilon^2(s_0 + x_\varepsilon)} \tag{15}$$

where $i, j = (+, -)$, $x = \kappa d_0$, $x_\varepsilon = x/\sqrt{\varepsilon}$,

$$\kappa^2 = 4\pi\beta e^2\rho_0 \tag{16}$$

is the Debye parameter, and $s_0 = sd_0$ and $s_s = sd_s$. The functions $L(s)$, etc., are

$$L(s) = \beta_{12}s_s + \beta_3 \tag{17}$$

$$S(s) = \beta_6^2 s_s^3 + b_2\beta_6 s_s^2 + \tfrac{1}{2}b_2^2 s_s - 2\beta_3 b_2 \tag{18}$$

$$L_1(s) = \beta_3 s_s + b_2 \tag{19}$$

and

$$S_1(s) = \beta_6 s_s^2 - (\beta_3 - b_2) s_s - b_2 \tag{20}$$

The parameters b_2, μ, and ε, the solvent dielectric constant, are related by$^{(13)}$

$$\varepsilon = \frac{\beta_3^2 \beta_{12}^4}{\beta_6^6} \tag{21}$$

and

$$\frac{4\pi}{3} \beta \mu^2 \rho_s = \frac{\varepsilon - 1}{\varepsilon} \frac{\beta_3^2}{\beta_6^4} \tag{22}$$

where

$$\beta_{3 \times 2^m} = 1 + b_2 \frac{(-1)^m}{3 \times 2^m} \tag{23}$$

Considerable algebra is required to obtain Eqs. (13)–(15). We do not give this here. Full details can be found in ref. 12.

Thus, for $g_{ij}^{\mathrm{EL}}(r)$, we have three terms. The first corresponds to the classical result

$$-\frac{\beta z_i z_j e^2}{\varepsilon r} \exp\left(-x_\varepsilon \frac{r - d_0}{d_0}\right) \tag{24}$$

The other two terms describe the contributions of the dipole–dipole and ion–dipole interactions and lead to the oscillations about the asymptotic form (24).$^{(14, 15)}$

For ion–colloidal distribution functions, we have two terms. The first also corresponds to the classical result

$$-\frac{\beta z_i e E d_0}{\varepsilon x_\varepsilon} \exp\left(-x_\varepsilon \frac{z - d_0/2}{d_0}\right), \qquad z = r - R \tag{25}$$

where $E = z_c e/(d_0/2)^2 = 4\pi\sigma$ is the electric field at the surface of the large sphere and σ is the uniform charge density on the surface of the large sphere. The second term describes the contribution from ion–dipole interactions and in the case of $d_s = d_0$ corresponds to the result obtained by Henderson$^{(16)}$ with the change $d_0/(x_e + s_0) \rightarrow s_0^2/(x_\varepsilon + s_0)^2$. The difference between these two expression (also see Blum and Henderson$^{(17)}$) is of higher order. This change does not lead to differences in the asymptotic behavior of $G_{ic}^{\mathrm{EL}}(s)$ in the limits $s \rightarrow 0$ and $s \rightarrow \infty$.

As $s \to 0$,

$$S_1(s) + L_1(s)e^{-s_s} \to \frac{1}{2} s_s^3$$

$$S(s) + 2b_2 L(s)e^{-s_s} \to \beta_3 s_s^3 \tag{26}$$

$$1 - 2\beta_3 \frac{S_1(s) + L_1(s)e^{-s_s}}{S(s) + 2b_2 L(s)e^{-s_s}} = O(s_s) \tag{27}$$

and

$$G_{ic}^{\mathrm{EL}}(s) = -\frac{\beta z_i eEd_0^2}{x^2} + O(s)$$

As $s \to \infty$,

$$\frac{s_s[S_1(s) + L_1(s)e^{-s_s}]}{S(s) + 2b_2 L(s)e^{-s_s}} \to \frac{1}{\beta_6} \tag{28}$$

and

$$sG_{ic}^{\mathrm{EL}}(s) \to g_{ic}^{\mathrm{EL}}(d_{ic}^+) = -\frac{\beta z_i eEd_0}{\varepsilon x_\varepsilon}\left[1 + \frac{1}{2} x_\varepsilon \frac{(\varepsilon - 1)\,\beta_6 d_s^2}{\beta_3 d_0(d_s + d_0 y_0)}\right] \tag{29}$$

where $y_0 = \beta_3 \beta_6$. This result is the contact value of $g_{ic}^{\mathrm{EL}}(d_0^+)$.

For the colloid–colloid distribution function, $g_{cc}^{\mathrm{EL}}(r)$, we have one term corresponding to the classical result$^{(5)}$

$$-\frac{\beta E^2 d_c d_0^2}{x^2} \exp\left(-x_\varepsilon \frac{r - d_c}{d_0}\right) \tag{30}$$

The correction term for $g_{cc}^{\mathrm{EL}}(r)$ also corresponds to the classical result,

$$\Delta g_{cc}^{\mathrm{EL}}(r) = -\frac{\beta E^2 d_c x_\varepsilon}{x^2} \exp\left(-x_\varepsilon \frac{r - d_c}{d_0}\right) \tag{31}$$

where the dipole contribution leads only to the appearance of ε. Thus, taking into account terms $O(\rho_0)$ leads to a modified form for the classical result for $g_{cc}^{\mathrm{EL}}(r)$.

These results for $g_{ic}^{\mathrm{EL}}(r)$ and $g_{cc}^{\mathrm{EL}}(r)$ have an infinity in the case $\rho_0 = 0$. However, we can still make progress. After some algebra, we obtain

$$\begin{aligned} G_{ic}^{\mathrm{EL}}(s) = {} & \beta z_i eEd_s^2 \left(\frac{\varepsilon - 1}{2\varepsilon}\right) \frac{\beta_6^2}{\beta_3} e^{-s_0/2} \\ & \times \left[\frac{d_s \beta_6}{d_s + d_0 y_0} \frac{s_s^2 - 2s_s + 2 - 2e^{-s_s}}{S(s) + 2b_2 L(s)e^{-s_s}}\right. \\ & \left. + x_\varepsilon \frac{S_1(s) + L_1(s)e^{-s_s}}{(s_0 + x_\varepsilon)[S(s) + 2b_2 L(s)e^{-s_s}]}\right] \end{aligned} \tag{32}$$

$$G_{cc}^{\mathrm{EL}}(s)=-\frac{\beta E^2 d_c}{16}\left(\frac{\varepsilon-1}{\varepsilon}\right)\left(\frac{\beta_6^4 d_s^3}{\beta_3^2}\right)\frac{s_s^2-2s_s+2-2e^{-s_s}}{S(s)+2b_2L(s)e^{-s_s}} \tag{33}$$

and for the contact values we have

$$G_{ic}^{\mathrm{EL}}(d_{cc}^+)=-\frac{\beta z_i eE}{2}\left(\frac{\varepsilon-1}{\varepsilon}\right)\frac{\beta_6 d_s^2}{\beta_3(d_s+d_0\,y_0)} \tag{34}$$

$$G_{ic}^{\mathrm{EL}}(d_c^+)=-\frac{\beta E^2 d_c d_s^2}{16}\left(\frac{\varepsilon-1}{\varepsilon}\right)\frac{\beta_6^2}{\beta_3^2} \tag{35}$$

Details are given in ref. 12. Using

$$1-2\beta_3\frac{S_1(s)+L_1(s)e^{-s_s}}{S(s)+2b_2L(s)e^{-s_s}}=\frac{\beta_6^2 s_s[s_s^2-2s_s+2-2e^{-s_s}]}{S(s)+2b_2L(s)e^{-s_s}} \tag{36}$$

we obtain that the first term in the expression (32), which exactly corresponds in the limit $x\to 0$ to the second term (14). Using an analogous correspondence between (34) and (29), we have also obtained the contact value $g_{ic}^{\mathrm{EL}}(d_{cc}^+)$. Thus, for $g_{ic}^{\mathrm{EL}}(r)$ we have two terms; one corresponds to (25) and is proportional x^{-1}, the second corresponds to (32) and is not dependent on x in the limit $x\to 0$. As for $g_{cc}^{\mathrm{EL}}(r)$, we expect that it will have three terms: one corresponds to (30) and is proportional to x^{-2}, the second is proportional to x^{-1}, and the third does not depend on x in the limit $x\to 0$. As yet we do not know about the connection of the last term with (33). For the answer to these questions, we need to analyze our general results, taking into account terms $O(\rho_0)$. We will consider this problem in a second article. As for $g_{cc}^{\mathrm{EL}}(d_c^+)$, we have

$$\begin{aligned} g_{cc}^{\mathrm{EL}}(d_c^+)=\frac{\beta E^2 d_c}{4}\Bigg[\left(\frac{d_0}{x}\right)^2+\frac{d_0}{\sqrt{\varepsilon}\,x}+\frac{1}{4}\left(\frac{\varepsilon-1}{\varepsilon}\right)\frac{\beta_6^2}{\beta_3^2}d_s^2 \\ -\frac{1}{4\varepsilon}\left(d_0^2+(\varepsilon-1)\frac{\beta_6^2 d_s^4}{\beta_3^2(d_s+d_0\,y_0)^2}\right)\Bigg] \end{aligned} \tag{37}$$

where for terms independent of x, we do not have exact correspondence with (35). The last term

$$\frac{\beta E^2 d_c}{16_\varepsilon}\left(d_0^2+(\varepsilon-1)\frac{\beta_6^2 d_s^4}{\beta_3^2(d_s+d_0\,y_0)^2}\right) \tag{38}$$

characterizes this difference.

4. CONCLUSION

We have obtained, using the MSA, a general expression of the Laplace transform of the pair distribution functions between two ions, an ion and macroion, and two macroions in ion–dipole liquids. This result is a special case of Holovko and Protsykevich,(10, 11) who solved the MSA for the ion–dipole mixture with arbitrary sizes of particles. We give explicit first corrections for the classical Debye-like result for this function in the limit of small ionic concentrations. Our result for the pair distribution function of an ion–macroion pair is a generalization of the result of Blum and Henderson,(18) where the first correction corresponds to including a Stern-like layer term. We have shown that including the second-order correction terms $O(x^2)$ in the classical result corresponds to taking into account Stern-like layer terms for the hydration force between two macroions.

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