

Solvation energy of ions in dipolar solvents^{a)}

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The solvation energy of hard spherical ions immersed in dipolar hard sphere solvents is investigated as a function of ion diameter. We apply both the mean spherical and linearized hypernetted-chain approximations and show that for ions of physically realistic size both theories give qualitatively similar results. The ion solvation energy is obtained as the sum of two competing terms: U_{ID} , the direct ion-solvent interaction energy, which is negative, and U_{DD} , the change in the solvent-solvent interaction energy per ion at infinite dilution. U_{DD} is found to be positive and to make an important contribution to the solvation energy for all ion diameters.

I. INTRODUCTION

The primitive model of electrolyte solutions assumes that the ions are immersed in a dielectric continuum, thus ignoring the molecular nature of the solvent. Recently, the study of electrolyte solutions has progressed well beyond this simple model. In particular, integral equation theories have been successfully used to determine the structural, thermodynamic, and dielectric properties of mixtures consisting of charged hard spheres in dipolar hard sphere solvents.¹⁻⁷ The ion behavior, both in solution and near charged surfaces⁸⁻¹⁰ has been investigated using these dipolar solvent models. More complex solvent models, which can mimic the dielectric constant of water from 25 to 300 °C, have also been studied.¹¹ These models will hopefully improve our understanding of aqueous electrolyte solutions.

Despite this recent interest in nonprimitive models of electrolyte solutions, not much attention has been given to the calculation of ion solvation (hydration) energies, i.e., the energy released in transferring an ion from the (ideal) gas phase to the solution phase. The ion solvation energy is not simply the direct ion-solvent interaction energy at infinite dilution. The ions in solution influence the structure of the solvent and hence the solvent-solvent interaction energy. This change in solvent-solvent interaction energy (with respect to the pure solvent) *per ion*, at infinite dilution, must be added to the direct ion-solvent interaction energy to determine the total ion solvation energy.

The classical Born model of ionic solvation^{12,13} assumes that the solvent is a dielectric continuum and that the ion (a hard sphere with embedded point charge) does not affect the bulk solvent properties even near the surface of the ion. This implies that dielectric saturation effects are not incorporated into the Born model. However, in the nonprimitive solvent models, the saturation of the dielectric constant is indirectly reflected³ in the structure of the solvent around an ion and hence is implicitly included in the calculation of the ion solvation energy.

In this paper we consider a model electrolyte solution consisting of a mixture of ions (hard spheres with embedded point charges) in a dipolar solvent (hard spheres with embedded point dipoles). The ions and solvent particles may have different diameters. The Ornstein-Zernike (OZ) equations for this model are well known¹⁻⁷ and are used to calculate the ion solvation energy. Both the linearized hypernetted-chain (LHNC)^{6,14} and mean spherical approximation (MSA)¹⁻⁷ closures have been used to solve the OZ equations. The MSA and LHNC results for the total ion solvation energy agree surprisingly well considering the failure^{15,16} of the MSA to predict the energy of the pure dipolar solvent. The solvent-solvent energy contribution to the total solvation energy was found to be positive and important for all ion diameters.

II. ION-SOLVENT MODEL

We consider a mixture of hard spheres each of which may carry a point charge and a permanent dipole moment. It is convenient to write the equations for this general case, and later, to obtain results for specific ionic solutions by setting appropriate charges and dipole moments to zero. Species α is characterized by a diameter d_α , a charge q_α , a dipole moment μ_α , and a number density ρ_α . The system is taken to be electrically neutral so that

$$\sum_{\alpha} q_{\alpha} \rho_{\alpha} = 0. \quad (2.1)$$

The pair potential between two particles of species α and β , separated by a distance r , can be written as

$$u_{\alpha\beta}(12) = u_{\alpha\beta}^{000}(r)\Phi^{000}(12) + u_{\alpha\beta}^{101}(r)\Phi^{101}(12) + u_{\alpha\beta}^{011}(r)\Phi^{011}(12) + u_{\alpha\beta}^{112}(r)\Phi^{112}(12), \quad (2.2)$$

where

$$u_{\alpha\beta}^{000}(r) = u_{\alpha\beta}^{\text{HS}}(r) + q_{\alpha}q_{\beta}/r, \quad (2.3a)$$

$$u_{\alpha\beta}^{101}(r) = \mu_{\alpha}q_{\beta}/r^2, \quad (2.3b)$$

$$u_{\alpha\beta}^{011}(r) = -q_{\alpha}\mu_{\beta}/r^2, \quad (2.3c)$$

and

$$u_{\alpha\beta}^{112}(r) = -\mu_{\alpha}\mu_{\beta}/r^3. \quad (2.3d)$$

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The hard sphere interaction, $u_{\alpha\beta}^{\text{HS}}(r)$, is defined by

$$u_{\alpha\beta}^{\text{HS}}(r) = \begin{cases} \infty, & r < d_{\alpha\beta}, \\ 0, & r > d_{\alpha\beta}, \end{cases} \quad (2.3e)$$

where $d_{\alpha\beta} = (d_{\alpha} + d_{\beta})/2$. The rotational invariants,¹⁷ $\Phi^{mnl}(12)$, depend upon the dipolar orientations. These functions are not explicitly used in this paper and their definition can be found in the paper of Levesque, Weis, and Patey (LWP).⁶

III. THEORY

A. The LHNC and MSA approximations

The development of the theory begins with the OZ integral equations for a mixture,

$$h_{\alpha\beta}(12) - c_{\alpha\beta}(12) = \frac{1}{4\pi} \sum_{\gamma} \rho_{\gamma} \int h_{\alpha\gamma}(13)c_{\gamma\beta}(32)d(3), \quad (3.1)$$

where $c_{\alpha\beta}(12)$ and $h_{\alpha\beta}(12)$ are the direct and pair correlation functions, respectively, and $d(3)$ indicates that the integration is to be taken over the position and angular coordinates of particle 3. (We use the notation of LWP in this section.) The OZ equation must be supplemented with approximate expressions relating $c_{\alpha\beta}$ and $h_{\alpha\beta}$. In the present work we shall use the LHNC or MSA closures which are defined below.

In Fourier space, the OZ equation can be reduced to a set of algebraic equations. This is achieved, following Blum,¹⁷ by expanding the correlation functions $h_{\alpha\beta}(12)$ and $c_{\alpha\beta}(12)$ in a set of rotational invariants, for example,

$$h_{\alpha\beta}(12) = \sum_{mnl} h_{\alpha\beta}^{mnl}(r)\Phi^{mnl}(12) \quad (3.2)$$

and using the orthogonality properties of the rotational invariants to obtain a set of integral equations for the functions $h_{\alpha\beta}^{mnl}(r)$ and $c_{\alpha\beta}^{mnl}(r)$. These equations are then Fourier transformed to obtain a set of algebraic equations.^{6,17} Only a finite number of terms are usually included in the expansion (3.2). For the ion-solvent model described in Sec. II, only the terms with $0 \leq m, n \leq 1$, and $0 \leq l \leq 2$ are retained. These terms are sufficient to determine the thermodynamic and dielectric properties of the system.^{6,7}

The complete set of algebraic equations derived using the procedure described above are given in LWP. Only the equations for h^{011} , h^{112} , and h^{110} are required to calculate the ion solvation energy and these will, for convenience, be summarized below. These equations which describe a three component (positive ions, negative ions, and solvent molecules) electrolyte solution are obtained by setting $q_1 = q_+$, $q_2 = q_-$, $q_3 = 0$, $\mu_1 = \mu_2 = 0$, $\mu_3 = \mu$, $d_1 = d_+$, $d_2 = d_-$, and $d_3 = d_{\mu}$, where we have labeled the positive and negative ions and the dipolar solvent with the subscripts $+$, $-$, and μ . One finds

$$\tilde{h}_{i\mu}^{011} - \tilde{c}_{i\mu}^{011} = \sum_n \rho_n \tilde{h}_{in}^{000} \tilde{c}_{n\mu}^{011} + \frac{1}{3} \rho_{\mu} \tilde{h}_{i\mu}^{011} (\tilde{c}_{\mu\mu}^{110} + 2\tilde{c}_{\mu\mu}^{112}), \quad (3.3a)$$

$$\tilde{h}_{\mu\mu}^{110} - \tilde{c}_{\mu\mu}^{110} = -\frac{1}{3} \sum_n \rho_n \tilde{h}_{n\mu}^{011} \tilde{c}_{n\mu}^{011} + \frac{1}{3} \rho_{\mu} (\tilde{h}_{\mu\mu}^{110} \tilde{c}_{\mu\mu}^{110} + 2\tilde{h}_{\mu\mu}^{112} \tilde{c}_{\mu\mu}^{112}), \quad (3.3b)$$

$$\tilde{h}_{\mu\mu}^{112} - \tilde{c}_{\mu\mu}^{112} = -\frac{1}{3} \sum_n \rho_n \tilde{h}_{n\mu}^{011} \tilde{c}_{n\mu}^{011} + \frac{1}{3} \rho_{\mu} \times (\tilde{h}_{\mu\mu}^{110} \tilde{c}_{\mu\mu}^{112} + \tilde{h}_{\mu\mu}^{112} \tilde{c}_{\mu\mu}^{110} + \tilde{h}_{\mu\mu}^{112} \tilde{c}_{\mu\mu}^{112}), \quad (3.3c)$$

where i can represent either $+$ or $-$ and the sum on n is over the subscripts $+$ and $-$. The tilde denotes the Hankel transform

$$\tilde{h}_{\alpha\beta}^{mnl}(k) = 4\pi i^l \int_0^{\infty} r^2 j_l(kr) h_{\alpha\beta}^{mnl}(r) dr, \quad (3.4)$$

where $j_l(kr)$ is the spherical Bessel function, and $\tilde{h}^{mnl}(k)$ and $\tilde{c}^{mnl}(k)$ have been written as \tilde{h}^{mnl} and \tilde{c}^{mnl} , respectively, in Eqs. (3.3).

As previously mentioned, the OZ equation will be solved in conjunction with the LHNC or MSA closure relations. The LHNC equations, as the name implies, are obtained by a linearization¹⁴ of the usual hypernetted-chain approximation. The details can be found in LWP. The LHNC closure relations are

$$c_{i\mu}^{011}(r) = \begin{cases} g_{i\mu}^{\text{HS}}(r) [-\beta u_{i\mu}^{011}(r) + \eta_{i\mu}^{011}(r)] - \eta_{i\mu}^{011}(r), & r > d_{i\mu}, \\ -\eta_{i\mu}^{011}(r), & r < d_{i\mu}, \end{cases} \quad (3.5a)$$

$$c_{\mu\mu}^{110}(r) = \begin{cases} g_{\mu\mu}^{\text{HS}}(r) \eta_{\mu\mu}^{110}(r) - \eta_{\mu\mu}^{110}(r), & r > d_{\mu}, \\ -\eta_{\mu\mu}^{110}(r), & r < d_{\mu}, \end{cases} \quad (3.5b)$$

and

$$c_{\mu\mu}^{112}(r) = \begin{cases} g_{\mu\mu}^{\text{HS}}(r) [-\beta u_{\mu\mu}^{112}(r) + \eta_{\mu\mu}^{112}(r)] - \eta_{\mu\mu}^{112}(r), & r > d_{\mu}, \\ -\eta_{\mu\mu}^{112}(r), & r < d_{\mu}, \end{cases} \quad (3.5c)$$

where $\beta = 1/kT$ (k being the Boltzmann constant and T the absolute temperature),

$$g_{\alpha\beta}^{\text{HS}}(r) = h_{\alpha\beta}^{\text{HS}}(r) + 1$$

and

$$\eta_{\alpha\beta}^{mnl}(r) = h_{\alpha\beta}^{mnl}(r) - c_{\alpha\beta}^{mnl}(r).$$

In Eqs. (3.5) the "exact" pair correlation functions for hard sphere mixtures, $g_{\alpha\beta}^{\text{HS}}(r)$, have been used in order to reduce the error resulting from the LHNC treatment of the hard sphere potential. The MSA closure equations are obtained by setting $g_{\alpha\beta}^{\text{HS}}(r) = 1$ in Eqs. (3.5).

B. Ion solvation energy

The total internal energy U of the ion-dipole mixture is the sum of ion-ion, ion-dipole, and dipole-dipole contributions. U does not include the kinetic energy of the particles. The various contributions to U are given by the formulas⁶

$$U(\text{ion-ion}) = \frac{2\pi N}{\rho} \sum_{i,j} \rho_i \rho_j q_i q_j \int_0^{\infty} h_{ij}^{000}(r) r dr, \quad (3.6a)$$

$$U(\text{ion-dipole}) = -\left(\frac{4\pi N}{3\rho}\right) \rho_{\mu} \mu \sum_i \rho_i q_i \int_0^{\infty} h_{i\mu}^{011}(r) dr, \quad (3.6b)$$

$$U(\text{dipole-dipole}) = -\frac{4\pi N}{3\rho} (\rho_{\mu})^2 \mu^2 \int_0^{\infty} \frac{h_{\mu\mu}^{112}(r)}{r} dr, \quad (3.6c)$$

where the indices i and j refer to the ionic species only, $\rho = \sum_{\alpha} \rho_{\alpha}$ and N is the total number of particles in the mixture ($N = N_+ + N_- + N_{\mu}$).

The ion solvation energy, $U_{\text{Sol}}^{(i)}$, of the i th ion is the excess internal energy of the ion-dipole mixture, at infinite dilution, due to the presence of the ion. $U_{\text{Sol}}^{(+)}$, for example, can be calculated from the expression

$$U_{\text{Sol}}^{(+)} = \lim_{\rho_+ \rightarrow 0} \lim_{\rho_- \rightarrow 0} \left(\frac{U - U^{[0]}}{N_+} \right), \quad (3.7)$$

where the limits are taken in the indicated order and the superscript [0] is used to indicate the infinite dilution or pure solvent results, e.g., $U^{[0]}$ is the internal energy of the dipolar solvent in the absence of ions. In writing Eq. (3.7), the internal energy of a gas phase ion (apart from kinetic energy) was taken as zero. Since, for the dipolar solvents of interest in this paper, the ion solvation energy is independent of the sign (but not the magnitude) of the ion charge, we henceforth drop the superscript (+) on U_{Sol} .

Equations (3.6) can be used to divide U_{Sol} into its constituent parts. The ion-ion interaction energy does not contribute to U_{Sol} in the infinite dilution limit; therefore

$$U_{\text{Sol}} = U_{ID} + U_{DD}, \quad (3.8)$$

where U_{ID} is the contribution from the direct ion-dipole interaction energy (3.6b) and U_{DD} is the contribution due to the change in the dipole-dipole interaction energy (3.6c) induced by the presence of the ion. Explicit expressions for U_{ID} and U_{DD} can be derived using Eqs. (3.6) and (3.7). At

infinite dilution, we obtain

$$U_{ID} = -\frac{4\pi}{3} \rho_{\mu} \mu q_i \int_0^{\infty} h_{i\mu}^{011[0]}(r) dr \quad (3.9)$$

and

$$U_{DD} = -\frac{4\pi}{3} (\rho_{\mu})^2 \mu^2 \int_0^{\infty} \frac{\delta_i h_{\mu\mu}^{112}(r)}{r} dr, \quad (3.10)$$

where $i = +$ or $-$ and we have written $h_{\mu\mu}^{112}(r)$ in the form

$$h_{\mu\mu}^{112}(r) = h_{\mu\mu}^{112[0]}(r) + \sum_i \rho_i \delta_i h_{\mu\mu}^{112}(r) + \dots \quad (3.11)$$

The ρ_i^z dependence, with $z = 1$, shown in Eq. (3.11) is essential for obtaining a finite nonzero value for U_{DD} . If $z < 1$ or $z > 1$ then U_{DD} would be infinite or zero, respectively [see Eq. (3.7)]. The expansion in Eq. (3.11) is also consistent with the exact results of Høye and Stell^{5,7} for low ionic concentrations.

Equations (3.3) and (3.5) must be solved in the infinite dilution limit in order to calculate U_{ID} and U_{DD} . $h_{i\mu}^{011[0]}$ is obtained by solving Eqs. (3.3a) and (3.5a) with $\rho_+ = \rho_- = 0$. The set of coupled equations, which can be solved for $\delta_i h_{\mu\mu}^{112}(r)$, are derived by expanding the functions $h_{\mu\mu}^{112}$, $h_{\mu\mu}^{110}$, $c_{\mu\mu}^{112}$, $c_{\mu\mu}^{110}$, and $g_{\mu\mu}^{\text{HS}}$ in the form shown in Eq. (3.11) for $h_{\mu\mu}^{112}$ and collecting terms of equal order in the ion concentration ρ_i . The resulting equations are

$$\delta_i \tilde{h}_{\mu\mu}^{110} - \delta_i \tilde{c}_{\mu\mu}^{110} = -\frac{1}{3} \tilde{h}_{i\mu}^{011[0]} \tilde{c}_{i\mu}^{011[0]} + \frac{1}{3} \rho_{\mu} (\tilde{h}_{\mu\mu}^{110[0]} \delta_i \tilde{c}_{\mu\mu}^{110} + \delta_i \tilde{h}_{\mu\mu}^{110} \tilde{c}_{\mu\mu}^{110[0]}) + 2\tilde{h}_{\mu\mu}^{112[0]} \delta_i \tilde{c}_{\mu\mu}^{112} + 2\delta_i \tilde{h}_{\mu\mu}^{112} \tilde{c}_{\mu\mu}^{112[0]} \quad (3.12a)$$

and

$$\begin{aligned} \delta_i \tilde{h}_{\mu\mu}^{112} - \delta_i \tilde{c}_{\mu\mu}^{112} = & -\frac{1}{3} \tilde{h}_{i\mu}^{011[0]} \tilde{c}_{i\mu}^{011[0]} + \frac{1}{3} \rho_{\mu} (\tilde{h}_{\mu\mu}^{110[0]} \delta_i \tilde{c}_{\mu\mu}^{112} + \delta_i \tilde{h}_{\mu\mu}^{110} \tilde{c}_{\mu\mu}^{112[0]}) + \tilde{h}_{\mu\mu}^{112[0]} \delta_i \tilde{c}_{\mu\mu}^{110} \\ & + \delta_i \tilde{h}_{\mu\mu}^{112} \tilde{c}_{\mu\mu}^{110[0]} + \tilde{h}_{\mu\mu}^{112[0]} \delta_i \tilde{c}_{\mu\mu}^{112} + \delta_i \tilde{h}_{\mu\mu}^{112} \tilde{c}_{\mu\mu}^{112[0]}. \end{aligned} \quad (3.12b)$$

The LHNC closure relations become

$$\delta_i c_{\mu\mu}^{110}(r) = \begin{cases} \delta_i h_{\mu\mu}^{\text{HS}}(r) \eta_{\mu\mu}^{110[0]}(r) + h_{\mu\mu}^{\text{HS}[0]}(r) \delta_i \eta_{\mu\mu}^{110}(r), & r > d_{\mu}, \\ -\delta_i \eta_{\mu\mu}^{110}(r), & r < d_{\mu}, \end{cases} \quad (3.13a)$$

$$\delta_i c_{\mu\mu}^{112}(r) = \begin{cases} \delta_i h_{\mu\mu}^{\text{HS}}(r) [-\beta u_{\mu\mu}^{112}(r) + \eta_{\mu\mu}^{112[0]}(r)] + h_{\mu\mu}^{\text{HS}[0]}(r) \delta_i \eta_{\mu\mu}^{112}(r), & r > d_{\mu}, \\ -\delta_i \eta_{\mu\mu}^{112}(r), & r < d_{\mu}, \end{cases} \quad (3.13b)$$

where

$$\delta_i \eta_{\mu\mu}^{mnl}(r) = \delta_i h_{\mu\mu}^{mnl}(r) - \delta_i c_{\mu\mu}^{mnl}(r).$$

The MSA closure relations are obtained by setting $\delta_i h_{\mu\mu}^{\text{HS}} = 0$ and $h_{\mu\mu}^{\text{HS}[0]} = 0$ in Eqs. (3.13). $\tilde{h}_{\alpha\beta}^{mnl[0]}$ and $\tilde{c}_{\alpha\beta}^{mnl[0]}$ are infinite dilution or pure solvent correlation functions. These functions satisfy Eqs. (3.3) and (3.5) with $\rho_+ = \rho_- = 0$.

The function $\delta_i h_{\mu\mu}^{\text{HS}}(r)$, which appears in the LHNC closure relations (3.13), accounts for the change in the spherically symmetric part of the dipole-dipole pair correlation function caused by the addition of the ions, at constant volume, to the solvent. The constant volume solvation of the ion, in essence, increases the effective solvent density. Therefore, this effect will not be strongly dependent on the ion charge and should be more important for larger ions (i.e., $d_i > d_{\mu}$) and/or at higher solvent densities.

C. Asymptotic behavior of $h_{i\mu}^{011[0]}(r)$ and $\delta_i h_{\mu\mu}^{112}(r)$

The asymptotic (large r) behavior of the functions $h_{i\mu}^{011[0]}(r)$ and $\delta_i h_{\mu\mu}^{112}(r)$, which appear in the expressions for U_{ID} and U_{DD} , respectively, can be easily determined. First, Eqs. (3.3), with $\rho_+ = \rho_- = 0$, and (3.12) are solved for $\tilde{h}_{i\mu}^{011[0]}(k)$ and $\delta_i \tilde{h}_{\mu\mu}^{112}(k)$, respectively, in the limit $k \rightarrow 0$, and then the Hankel transforms are inverted to obtain the asymptotic r dependences of $h_{i\mu}^{011[0]}(r)$ and $\delta_i h_{\mu\mu}^{112}(r)$. These asymptotic r dependences are exact for any solvent with a permanent dipole moment. Therefore, knowledge of the asymptotic r behavior of $h_{i\mu}^{011[0]}$ and $\delta_i h_{\mu\mu}^{112}$ should provide some general insights into the solvation of ions in polar solvents.

It can be shown,^{5,7} using Eq. (3.3a), with $\rho_+ = \rho_- = 0$, and Eqs. (17)–(20) of LWP, that in the limit $k \rightarrow 0$,

$$\tilde{h}_{i\mu}^{011[0]}(k) \rightarrow 4\pi\beta q_i \mu \left(\frac{\epsilon_0 - 1}{3y\epsilon_0} \right) \frac{i}{k}, \quad (3.14)$$

where ϵ_0 is the pure solvent dielectric constant and $y = (4\pi/9)\rho_\mu\beta\mu^2$. Inversion of the Hankel transform yields, for $r \rightarrow \infty$,

$$h_{i\mu}^{011(0)}(r) \rightarrow \left(\frac{\epsilon_0 - 1}{3y\epsilon_0}\right) \frac{\beta q_i \mu}{r^2}. \quad (3.15)$$

This result is not unexpected since the ion-dipole interaction potential (2.3b) is also proportional to r^{-2} .

The functions $\delta_i c_{\mu\mu}^{112}$ and $\delta_i c_{\mu\mu}^{110}$, which appear in Eqs. (3.12), are short ranged compared to $\delta_i h_{\mu\mu}^{112}$ and $\delta_i h_{\mu\mu}^{110}$. Therefore, they do not contribute in the limit $k \rightarrow 0$ and using Eq. (3.14), we obtain

$$\delta_i \bar{h}_{\mu\mu}^{112}(k) \rightarrow 3 \left(\frac{\epsilon_0 - 1}{\epsilon_0}\right)^2 \frac{q_i^2}{(\rho_\mu \mu)^2 k^2}, \quad (3.16)$$

or in r space,

$$\delta_i h_{\mu\mu}^{112}(r) \rightarrow -\frac{3}{8\pi} \left(\frac{\epsilon_0 - 1}{\epsilon_0}\right)^2 \frac{q_i^2}{(\rho_\mu \mu)^2 r} \quad (3.17)$$

as $r \rightarrow \infty$. The long range nature of this function is surprising, since the pure solvent dipole-dipole correlation function falls off as r^{-3} for large r . The ion-dipole interactions [the first term on the right-hand side of Eq. (3.12b)] at infinite dilution, i.e., in the absence of screening, lead to this long range behavior of the dipole-dipole correlation function. The sign of $\delta_i h_{\mu\mu}^{112}(r)$ implies that dipoles have an enhanced tendency to align in opposite directions in the ion-dipole mixture as compared to the pure dipolar fluid (i.e., U_{DD} is positive).

If Eqs. (3.15) and (3.17) are used in Eqs. (3.9) and (3.10), respectively, *very crude* approximations, which neglect short range correlations, can be obtained for U_{ID} and U_{DD} . These approximations, which will be denoted by $U_{ID}^{(\infty)}$ and $U_{DD}^{(\infty)}$, are given by

$$U_{ID}^{(\infty)} = -\left(\frac{\epsilon_0 - 1}{\epsilon_0}\right) \frac{q_i^2}{d_{i\mu}} \quad (3.18)$$

and

$$U_{DD}^{(\infty)} = \frac{1}{2} \left(\frac{\epsilon_0 - 1}{\epsilon_0}\right)^2 \frac{q_i^2}{d_\mu}. \quad (3.19)$$

Great importance should not be placed on the exact form of these expressions. In particular, Eq. (3.19) suggests that U_{DD} should be independent of the ion diameter. This, as we shall see, is not correct. However, it should be pointed out that both $U_{ID}^{(\infty)}$ and $U_{DD}^{(\infty)}$ depend on q_i^2 only. More importantly, if $d_i \simeq d_\mu$ and ϵ_0 is large, $U_{DD}^{(\infty)}$ contributes significantly to the total ion solvation energy. These general observations are consistent with the more exact calculations presented in Sec. IV.

IV. RESULTS AND DISCUSSION

The solvation of ions in dipolar hard sphere solvents was investigated as a function of the ion radius. The set of equations given in Sec. III B were solved numerically, for both the MSA and LHNC approximations, using iteration techniques described elsewhere.¹⁴ The functions $h_{\mu\mu}^{HS(0)}(r)$ and $\delta_i h_{\mu\mu}^{HS}(r)$ in Eqs. (3.13) were obtained using the semiempirical expressions of Lee and Levesque.¹⁸ At infinite dilu-

tion, the ion-dipole system is totally characterized by the dimensionless parameters, $\rho_\mu^* = \rho_\mu d_\mu^3$, $\mu^* = (\beta\mu^2/d_\mu^3)^{1/2}$, $q_i^* = (\beta q_i^2/d_\mu)^{1/2}$, and the ratio d_μ/d_i . It is also convenient to define dimensionless energies, for example, $U_{ID}^* = U_{ID} d_\mu/q_i^2$.

The MSA has been extensively used to study primitive electrolyte models,^{19,20} dipolar fluids,^{16,17} and ion-dipole mixtures¹⁻⁷ even though it often gives poor results for the thermodynamic, structural, or dielectric properties of these systems. However, interest in the MSA persists since the MSA integral equations can usually be solved analytically. In fact, it is possible to derive an analytical expression for the energy U of an ion-dipole mixture^{1,3} (for low ion concentrations) without explicitly determining the correlation functions $h_{\alpha\beta}^{nl}(r)$ appearing in Eq. (3.6). Once U is known for low but finite ion concentrations, U_{Sol} can be calculated using Eq. (3.7).

The MSA energy, $U_{ID}(\text{MSA})$, for an ion-dipole mixture with $d_+ = d_- = d$, and $d_\mu \neq d_i$, has been derived³ by Chan *et al.* Moreover, for $d_\mu = d_i$, $U_{DD}(\text{MSA})$ can be extracted from the work of Adelman and Deutch² (essentially z_2 in Eq. IV.35 of their paper). Although Blum has solved the MSA for an arbitrary mixture of ions and dipoles¹ (with $d_\mu \neq d_i$), it is difficult to extract $U_{DD}(\text{MSA})$ from the expressions given in his paper. Therefore, we have rederived, using the Baxter factorization method,^{1,17,21} the set of seven nonlinear algebraic equations that is required to determine $U_{ID}(\text{MSA})$ and $U_{DD}(\text{MSA})$ for $d_i \neq d_\mu$. These equations, for convenience, are summarized in the Appendix.

The expression obtained for $U_{ID}^*(\text{MSA})$ agrees with the result of Chan *et al.*³:

$$U_{ID}^*(\text{MSA}) = -\left(\frac{\epsilon_0 - 1}{\epsilon_0}\right) \left[\frac{d_{i\mu}}{d_\mu} - \frac{3\xi_0}{1 + 4\xi_0} \right]^{-1}, \quad (4.1)$$

where ξ_0 is the real solution of the equation

$$\frac{4\pi}{3} (\mu^*)^2 \rho_\mu^* = \frac{(1 + 4\xi_0)^2}{(1 - 2\xi_0)^4} - \frac{(1 - 2\xi_0)^2}{(1 + \xi_0)^4} \quad (4.2)$$

in the range $0 \leq \xi_0 < 1/2$ and the pure solvent dielectric constant ϵ_0 is given by

$$\epsilon_0 = \frac{(1 + 4\xi_0)^2(1 + \xi_0)^4}{(1 - 2\xi_0)^6}. \quad (4.3)$$

$U_{DD}^*(\text{MSA})$ is more complex. We obtain

$$U_{DD}^*(\text{MSA}) = \left(\frac{\epsilon_0 - 1}{\epsilon_0}\right)^2 \frac{(1 + \xi_0)\epsilon_0 D}{16(1 - \xi_0/2)(1 + 4\xi_0)^2} \left[\frac{d_{i\mu}}{d_\mu} - \frac{3\xi_0}{1 + 4\xi_0} \right]^{-2} \times \left[\frac{16d_{i\mu}}{d_\mu} (1 + \xi_0)(1 + 4\xi_0) - 3(1 + 14\xi_0 + 16\xi_0^2) \right] \quad (4.4)$$

with

$$D = \left[1 + \frac{2\epsilon_0(1 + \xi_0)^2}{(1 + 4\xi_0)(1 - \xi_0/2)} \right]^{-1}. \quad (4.5)$$

This expression for $U_{DD}^*(\text{MSA})$ has not previously appeared in the literature.

At infinite dilution, the Helmholtz free energy for charging a hard sphere in a dipolar solvent (at constant volume) can be obtained from U_{ID} .

$$[A_{\text{sol}}(q_i) - A_{\text{sol}}(0)] = \int_0^{q_i} \frac{U_{ID}(q)}{q} dq = \frac{1}{2} U_{ID}(q_i), \quad (4.6)$$

where the second equality applies in the MSA to the ion-solvent models considered in this paper. $A_{\text{sol}}(x)$ is the Helmholtz free energy for transferring a hard sphere of charge x from the gas phase to the dipolar solvent and the q_i dependence of U_{ID} has been explicitly indicated in Eq. (4.6). In the limit of a large ion ($d_\mu/d_i \rightarrow 0$) Eq. (4.6) reduces to the classical expression for the Born free energy of solvation.^{12,13} More interestingly, $U_{\text{sol}}(q_i) - U_{\text{sol}}(0)$ can be obtained from Eq. (4.6) using the thermodynamic relation $U = (\partial \beta A / \partial \beta)_V$. In the MSA, $U_{\text{sol}}(0) = 0$ and an explicit determination of this derivative shows that the expression (4.4) for $U_{DD}(\text{MSA})$ is recovered exactly. Therefore, the MSA results for U_{ID} and U_{DD} are self-consistent in the sense that U_{DD} can be derived from U_{ID} . It is not known if this property of the MSA applies to other ion-solvent models.

The expression for $U_{ID}(\text{MSA})$ can be rewritten in the form

$$U_{ID}(\text{MSA}) = - \left(1 - \frac{1}{\epsilon_0} \right) q_i^2 (R_i + \Delta)^{-1}, \quad (4.7)$$

where

$$\Delta = \left[\frac{1}{2} - \frac{3\xi_0}{1 + 4\xi_0} \right] d_\mu \quad (4.8)$$

and R_i is the ion radius. Therefore, in the MSA, the expression for $\Delta A_{\text{sol}}(q_i) = [A_{\text{sol}}(q_i) - A_{\text{sol}}(0)]$, as has been noted,³ resembles the empirical formula that is often used to fit experimental data.¹² The renormalized ion radius $(R_i + \Delta)$ depends on the solvent properties and temperature. This temperature dependence of Δ is important, since ΔA_{sol} can be used to calculate all the thermodynamic properties of ion solvation, e.g., entropy and constant volume heat capacity. It is interesting to note that $\Delta = 0$ in the limit $\xi_0 \rightarrow 1/2$ (or $\epsilon_0 \rightarrow \infty$), i.e., the classical Born expression for ΔA_{sol} is recovered exactly (for all ion sizes) in this limit.

$U_{ID}^*(\text{MSA})$, $U_{DD}^*(\text{MSA})$, and hence $U_{\text{sol}}^*(\text{MSA})$ are, for a given value of ξ_0 , only dependent on the parameter d_μ/d_i . These functions are plotted in Fig. 1 for $\xi_0 = 0.1313$ or, equivalently, for the dipolar solvent described by the parameters $\mu^* = 1.5$ and $\rho_\mu^* = 0.8$. The dielectric constant ϵ_0 , for this particular solvent, is calculated to be 23.7 or 78.5 using the MSA or LHNC approximation, respectively. The importance of U_{DD}^* is shown clearly in Fig. 1. The absolute value of the ratio U_{DD}^*/U_{ID}^* is approximately 0.30 for small ions ($d_\mu/d_i \approx 0.2$) and 0.50 for large ions ($d_\mu/d_i \approx 0$).

$U_{\text{sol}}^*(\text{MSA})$ is plotted in Fig. 2 for various values of ξ_0 [$\epsilon_0(\text{MSA}) = 2.05, 4.18, 10.95,$ and 64.0 for $\xi_0 = 0.03, 0.06, 0.10$ and 0.17 , respectively]. The ion solvation energy is more negative for smaller ions (at fixed ξ_0) and for larger values of ξ_0 , i.e., larger values of μ^* and ϵ_0 (at a given value of d_μ/d_i). This is, in general, consistent with experimental observations and with the classical Born theory of ion solvation.^{12,13} In the limit $d_\mu/d_i \rightarrow 0$, $U_{\text{sol}}^*(\text{MSA})$ is equal to the Born solvation energy calculated using $\epsilon_0(\text{MSA})$. However, in contrast to the MSA, the U_{sol}^* vs d_μ/d_i plots are linear in the classical Born theory.

The LHNC approximation was used to study the solva-

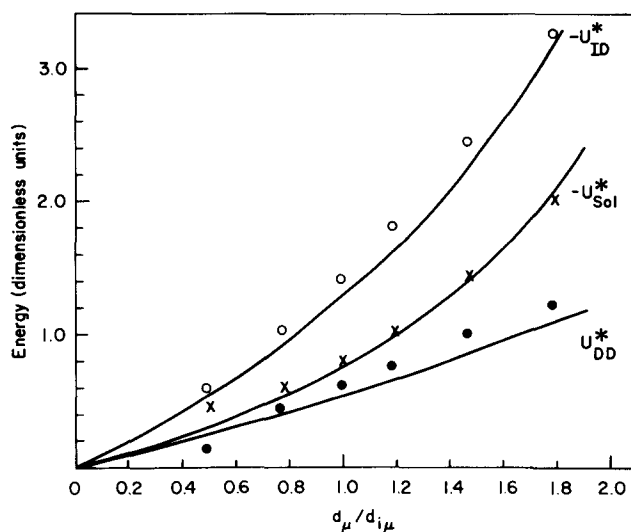


FIG. 1. Comparison of different approximations for U_{ID}^* , U_{DD}^* , and U_{sol}^* for a dipolar hard sphere solvent at $\mu^* = 1.5$, $\rho_\mu^* = 0.8$, and $\xi_0 = 0.1313$: solid curves, MSA; points, LHNC results for $d_\mu = 0.28$ nm and $q_i^* = 14.152$.

tion of ions in the dipolar solvent described by the parameters $\mu^* = 1.5$, $\rho_\mu^* = 0.8$, and $d_\mu = 0.28$ nm. For an ion of unit electron charge ($q_i^* = 14.152$), the LHNC values for U_{ID}^* , U_{DD}^* , and U_{sol}^* are shown in Fig. 1. The MSA and LHNC values for U_{sol}^* agree surprisingly well (within 5%) for $d_\mu/d_i \gtrsim 0.9$. Since the MSA and LHNC values for U_{ID}^* and U_{DD}^* agree only to within 8% and 15%, respectively, the good agreement for U_{sol}^* is partially due to cancellation of errors.

The much larger deviations between the MSA and LHNC approximations, for $d_\mu/d_i \approx 0.5$, are due to the solvation of the ion at constant volume, i.e., the function $\delta_i h_{\mu\mu}^{\text{HS}}$ in Eqs. (3.13) ($\delta_i h_{\mu\mu}^{\text{HS}} = 0$ in the MSA). In fact, setting $\delta_i h_{\mu\mu}^{\text{HS}} = 0$ in the LHNC calculations makes the MSA and LHNC values for U_{sol}^* agree to within 5% over the whole range of ion diameters.

The effects of $\delta_i h_{\mu\mu}^{\text{HS}}$ are easily understood. The con-

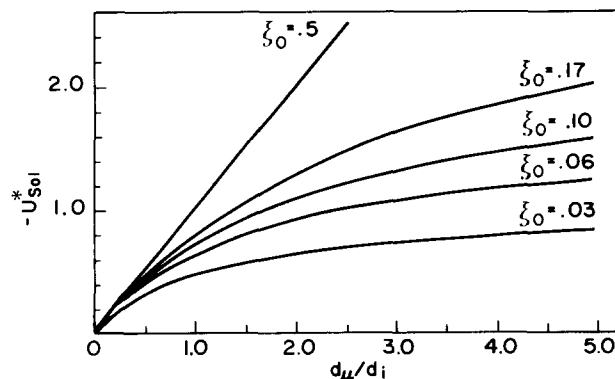


FIG. 2. MSA values of U_{sol}^* for various values of ξ_0 .

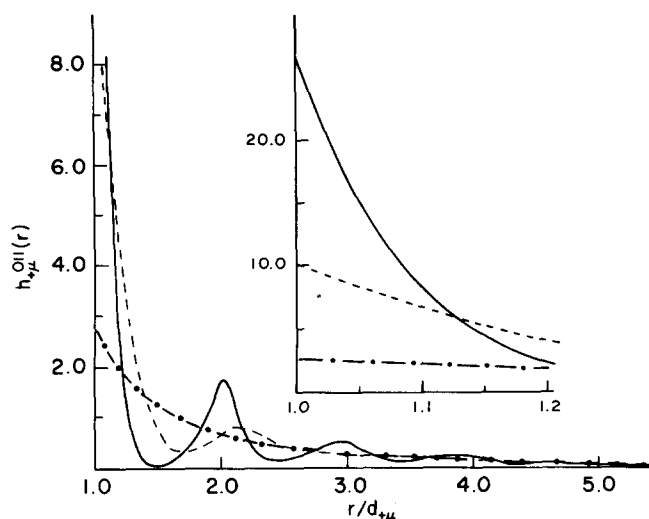


FIG. 3. Comparison of different approximations for $h_{+\mu}^{011[0]}(r)$ for a dipolar hard sphere solvent at $\mu^* = 1.5$, $\rho_\mu^* = 0.8$, $d_i = d_\mu = 0.28$ nm, and $q_i^* = 14.152$: dashed curves, MSA; solid curves, LHNC; dots and dashes, asymptotic limit from Eq. (3.15).

stant volume solvation of the ions increases the effective solvent density (i.e., the excluded volume increases) and, therefore, the dipole-dipole interaction energy becomes more negative. (This effect is absent in the MSA since $\delta_i h_{\mu\mu}^{112}$, which determines U_{DD} , is not coupled to changes in the hard sphere pair correlation function, $\delta_i h_{\mu\mu}^{HS}$.) Since the ion charge tends to make the dipole-dipole interaction energy more positive [$U_{DD}^*(\text{MSA}) > 0$], the net effect is a decrease in the value of U_{DD}^* compared to the MSA result. U_{ID}^* , however, is not affected by $\delta_i h_{\mu\mu}^{HS}$.

In Figs. 3 and 4 we have presented the correlation functions $h_{+\mu}^{011[0]}(r)$ and $\delta_i h_{\mu\mu}^{112}(r)$, for $d_i = d_\mu$, determined using the MSA and LHNC calculations. These functions appear in the expressions for U_{ID} and U_{DD} , respectively. The figures

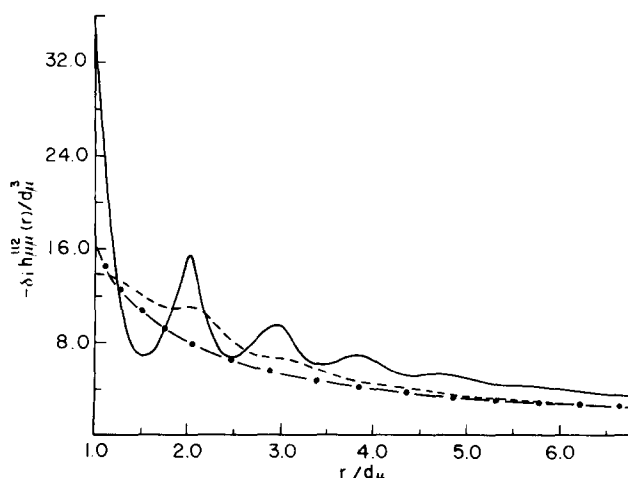


FIG. 4. Comparison of different approximations for $\delta_i h_{\mu\mu}^{112}(r)$ for a dipolar hard sphere solvent at $\mu^* = 1.5$, $\rho_\mu^* = 0.8$, $d_i = d_\mu = 0.28$ nm, and $q_i^* = 14.152$: dashed curves, MSA; solid curves, LHNC; dots and dashes, asymptotic limit from Eq. (3.17).

show that the MSA probably does not accurately describe the structural properties of the ion-dipole mixture at infinite dilution. Obviously, the energies U_{ID} and U_{DD} are not sensitive to the exact structure of the correlation functions $h_{i\mu}^{011[0]}$ and $\delta_i h_{\mu\mu}^{112}$. The functions obtained by extending the asymptotic r dependences of $h_{i\mu}^{011[0]}(r)$ and $\delta_i h_{\mu\mu}^{112}(r)$ up to $r = d_\mu$ have also been plotted in Figs. 3 and 4, respectively.

V. CONCLUSIONS

In this article the solvation of ions in dipolar solvents has been investigated using both the MSA and LHNC approximation. In particular, we have calculated ion solvation energies U_{Sol} at infinite dilution. U_{Sol} is the energy released in transferring an ion from the gas phase to a dipolar solvent. The ion solvation energy is the sum of two competing terms: U_{ID} , the direct ion-solvent interaction energy (negative) and U_{DD} , the change in solvent energy (per ion) due to the solvation of the ions. U_{DD} can be considered as a measure of the change in solvent structure produced by the ions. For dipolar solvents, U_{DD} is large and positive. Therefore, the effect of ion solvation on the solvent structure is important. This is evident from the long range nature [Eq. (3.17)] of the non-spherical part of the dipole-dipole pair correlation function (at infinite dilution), which implies that many solvent molecules are influenced by ions in solution and hence contribute to U_{DD} .

The LHNC and MSA results for U_{ID} and U_{DD} agree reasonably well. However, for larger ions ($d_i > d_\mu$), differences between the LHNC and MSA become more important. This can be explained in terms of excluded volume effects which are not taken into account by the MSA. These excluded volume effects make $U_{\text{Sol}}(0)$ (the solvation energy of an uncharged hard sphere) nonzero in the LHNC approximation.

The ion solvation energies, for the dipolar solvents studied in this paper, are not dependent on the sign of the ion charge. This is clearly not in agreement with experiment.^{12,13} Solvent models that can distinguish between solvation of anions and cations are not difficult to devise. For example, dipolar solvents consisting of hard spheres with off-centered point dipoles²² can be used to study the differences between the solvation of anions and cations. We are currently pursuing the study of ion solvation using solvent models that give a good description of the dielectric properties of water.¹¹ This model will also be modified to give different solvation energies for anions and cations of the same size.

APPENDIX

The equations used to derive the expressions for $U_{ID}^*(\text{MSA})$ and $U_{DD}^*(\text{MSA})$ given in Eqs. (4.1) and (4.4), respectively, are summarized below. These equations were derived from the OZ equations for an ion-dipole mixture ($d_+ = d_- = d_i \neq d_\mu$) using the Baxter factorization method.^{1,21} The derivation is straightforward, although care must be taken in handling the ion-ion and ion-dipole potentials,^{1,20} and draws heavily on previous work.^{1,3,10,17} These equations, with enough effort, could also have been extracted from the work of Blum^{1(b)} or Carnie and Chan.¹⁰

The various contributions to the energy of an ion-dipole mixture are given by the formulas:

$$U(\text{ion-ion}) = \lambda^3 V H_0, \quad (\text{A1a})$$

$$U(\text{ion-dipole}) = -(2/3)\lambda^2 \rho_\mu \mu V H_1, \quad (\text{A1b})$$

and

$$U(\text{dipole-dipole}) = -\frac{8\rho_\mu \mu^2 V}{d_\mu^3} \xi, \quad (\text{A1c})$$

where V is the volume of the mixture, $\lambda^2 = \sum_\alpha \rho_\alpha q_\alpha^2$ and the parameters H_0 , H_1 , and ξ are obtained by solving the following set of equations:

$$4\pi\beta = A_1^2 + \rho_\mu A_2^2/3, \quad (\text{A2})$$

$$4\pi\beta\mu = \lambda A_1 Q_1 - Q_2 A_2, \quad (\text{A3})$$

$$\frac{4\pi\beta\mu^2\rho_\mu}{3} = Q_2^2 + \frac{\lambda^2\rho_\mu Q_1^2}{3} - Q_- \equiv Q_+ - Q_-, \quad (\text{A4})$$

$$[(1-2\xi)^2 + B]Q_1 = \frac{H_1 d_\mu^2}{12} \times \{2\lambda A_1 [3d_{i\mu} - d_\mu(1+\xi)] + 3\lambda^2 d_i^2 A_1 H_0 - 6\}, \quad (\text{A5})$$

$$[(1-2\xi)^2 + B]Q_2 = 1 + 4\xi - \frac{\lambda^2\rho_\mu d_\mu^2 H_1 A_2}{36} \times [3\lambda d_i^2 H_0 + 6d_{i\mu} - 2d_\mu(1+\xi)] \quad (\text{A6})$$

$$X A_1 = \frac{\lambda\rho_\mu d_\mu^2 H_1^2}{9} [3d_{i\mu} - d_\mu(1+\xi)] - 2H_0(1-2\xi)^2, \quad (\text{A7})$$

and

$$X A_2 = \lambda d_i^2 H_0 H_1 (1+4\xi) + d_i H_1 (1+4\xi) + d_\mu H_1 (1-2\xi + \frac{2}{3}B), \quad (\text{A8})$$

where

$$Q_- = (1-2\xi)^2/(1+\xi)^4, \quad (\text{A9})$$

$$B = \frac{1}{12} \lambda^2 d_i^2 d_\mu^2 \rho_\mu H_1^2, \quad (\text{A10})$$

and

$$X = \frac{2}{3} \lambda d_\mu B H_0 (1-2\xi) + \frac{\lambda^2 \rho_\mu d_\mu^2 H_1^2}{18} \times \left(d_i d_\mu (1-2\xi) - \frac{d_\mu^2 B}{6} \right) - (1 + \lambda d_i H_0)^2 (1-2\xi)^2. \quad (\text{A11})$$

The set of seven equations, (A2) to (A8), cannot be solved in closed form. For low ion concentrations each variable appearing in these equations (i.e., $A_1, A_2, Q_1, Q_2, H_0, H_1, \xi$) can be expanded in a power series in λ , for example,

$$\xi = \xi^{(0)} + \lambda \xi^{(1)} + \lambda^2 \xi^{(2)} + \dots \quad (\text{A12})$$

U_{ID} and U_{DD} can be calculated if $H_1^{(0)}$, $\xi^{(0)} \equiv \xi_0$, and $\xi^{(2)}$ ($\xi^{(1)} = 0$) are known. An explicit calculation gives

$$H_0^{(0)} = \frac{1}{2} A_1^{(0)} = -\frac{1}{2} \left(\frac{4\pi\beta}{\epsilon_0} \right)^{1/2}, \quad (\text{A13})$$

$$A_2^{(0)} = -4\pi\beta\mu(Q_+^{(0)})^{-1/2}, \quad (\text{A14})$$

$$Q_+^{(0)} = (1 + 4\xi_0)^2 / (1 - 2\xi_0)^4, \quad (\text{A15})$$

$$\epsilon_0 = \frac{Q_+^{(0)}}{Q_-^{(0)}}, \quad (\text{A16})$$

$$H_1^{(0)} = \frac{2\pi\beta\mu}{d_\mu Q_+^{(0)}} \left[\frac{d_{i\mu}}{d_\mu} - \frac{3\xi_0}{1 + 4\xi_0} \right]^{-1}, \quad (\text{A17})$$

and

$$\xi^{(2)} = -\frac{\pi\beta d_\mu^3}{96Q_-^{(0)}} \left(\frac{\epsilon_0 - 1}{\epsilon_0} \right) \frac{(1 + \xi_0)}{(1 - \xi_0/2)} \times D [d_{i\mu}(1 + 4\xi_0) - 3d_\mu \xi_0]^{-2} \times [16d_{i\mu}(1 + \xi_0)(1 + 4\xi_0) - 3d_\mu(1 + 14\xi_0 + 16\xi_0^2)], \quad (\text{A18})$$

where ξ_0 and D are given by Eqs. (4.2) and (4.5), respectively.

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