Mean Spherical Model for Hard Ions and Dipoles: Thermodynamics and Correlation Functions

Fernando Vericat[1,2] **and Lesser Blum**[1]

The solution of the mean spherical model of a mixture of equal-size hard ions and dipoles is reinvestigated. Simple expressions for the coefficients of the Laplace transform of the pair correlation function and the other thermodynamic properties are given.

1. INTRODUCTION

In spite of the progress achieved in the theory of ionic solutions, the statistical theory of ion–solvent interactions remains as one of the challenging problems awaiting a simple, yet accurate solution.

The most accurate theory for systems with long-range forces seems to be hypernetted chain equation (HNC),[1,2] but this theory involves the resolution of a highly nonlinear system of equations, and is very difficult. A simplified version of it, the so-called linear hypernetted chain equation (LHNC),[3] which is successful for hard dipoles, was applied to the case of the ion–dipole mixture by Levesque *et al.*[4] for the infinite-dilution case.

We should also mention the work on the solution of the Poisson Boltzmann equation by Outhwaite[5] and the recent mean field theory of Adelman and Chen,[6] which seems to be a promising approach.

The mean spherical approximation (MSA)[7–9] is a theory that yields very simple expressions for the thermodynamic quantities, and which is reasonably

accurate for ionic solutions. The major deficiency of this theory is that it does not describe well the direct correlation function near the repulsive core of particles. This deficiency can be removed by the inclusion of a short-ranged exponential term.[10,11]

The solution of the MSA for the ion–dipole mixture was obtained by Blum[12] and Adelman and Deutch[13] for the equal-size mixture, and by Blum[14] for the unequal-size case.

In the present work, we give further analytic results for the equal-size mixture of ions and dipoles. In Section 2 we review and complete some of the results of previous work.[12] In Section 3 we obtain the pair correlation function on the MSA, while Section 4 is devoted to the thermodynamics of the system.

2. SUMMARY OF PREVIOUS RESULTS

Our model consists of a mixture of equal-size, hard spherical ions of charge $z_i e$ (z_i is the electrovalence, e is the elementary charge) and number density ρ_i, and hard, spherical solvent molecules with dipole moment μ and number density ρ_d. For further simplification we shall assume that there are only two species of ions (positive and negative) and we shall designate their concentrations by ρ_+ and ρ_-. This assumption is not really necessary (equivalent results for an arbitrary mixture of equal-size ions are easily obtained), but will make our notation simpler.

Let us, furthermore, designate the direct pair correlation functions $c_{ij}(r)$ and the indirect pair correlation functions $h_{ij}(r)$ by the generic symbol $f_{ij}(r)$. For the restricted case, we have ion–ion correlations $f_{++}(r), f_{+-}(r) = f_{-+}(r)$, and $f_{--}(r)$, and ion–dipole correlations $f_{+d}(r)$ and $f_{-d}(r)$.

As is the case in the primitive model, the ternary mixture of the positive and negative ions and the dipoles d can be reduced to a binary mixture if we introduce

$$f_{ii}(r) = \tfrac{1}{2}[f_{++}(r) - f_{+-}(r)] = \tfrac{1}{2}[f_{--}(r) - f_{-+}(r)] \tag{2.1}$$

$$f_{id}(1, 2) = \tfrac{1}{2}[f_{+d}(1, 2) - f_{-d}(1, 2)] \tag{2.2}$$

Following the notation of Wertheim,[15] we expand the ion–dipole correlation functions in the invariant combination of spherical harmonics[16]

$$f_{id}(1, 2) = -f_{id}(r)(\hat{r} \cdot \hat{s}_2) \tag{2.3}$$

$$f_{dd}(1, 2) = -\sqrt{3} f_{dd}^{\Delta}(r)(\hat{s}_1 \cdot \hat{s}_2) + (15/2)^{1/2} f_{dd}^{D}(r)[3(\hat{r} \cdot \hat{s}_1)(\hat{r} \cdot \hat{s}_2) - (\hat{s}_1 \cdot \hat{s}_2)] \tag{2.4}$$

where $\mathbf{r}$ is the center-to-center vector. The module of this vector is r, and $\hat{r} = \mathbf{r}/r$ is the unit vector in the center-to-center direction. Here $\hat{s}\alpha$ is the unit vector in the directions of the dipole of molecule α.

The invariant expansion can be transformed into the irreducible representation by choosing a reference frame in which $\hat{r} = z$. This decouples the Ornstein–Zernike equation into matrix sets for correlations of different symmetry around the intermolecular axis, and is an essential step in the solution process.[16]

We define

$$\mathscr{P}_{ii,0}(r) = 2\pi\rho_0 f_{ii}(r), \qquad \rho_0 = \rho_+ + \rho_- \tag{2.5}$$

$$\mathscr{P}_{id,0}(r) = -2\pi(\rho_d\rho_0/3)^{1/2}r \int_r^\infty dr_1\, f_{id}(r_1) \tag{2.6}$$

$$\mathscr{P}_{dd,0}(r) = 2\pi\rho_d\left\{-\frac{1}{\sqrt{3}}\int_r^\infty dr_1\, r_1 f_{dd}^\Delta(r_1)\right.$$
$$\left. + \left(\frac{1}{30}\right)^{1/2}\int_r^\infty dr_1\, r_1\left[3\left(\frac{r}{r_1}\right)^2 - 1\right]f_{dd}^D(r_1)\right\} \tag{2.7}$$

$$\mathscr{P}_{dd,1}(r) = -2\pi\rho_d\left\{\frac{1}{\sqrt{3}}\int_r^\infty dr_1\, r_1 f_{dd}^\Delta(r_1)\right.$$
$$\left. + \frac{1}{2\sqrt{30}}\int_r^\infty dr_1\, r_1\left[3\left(\frac{r}{r_1}\right)^2 - 1\right]f_{dd}^D(r_1)\right\} \tag{2.8}$$

In the above expressions we used

$$\mathscr{P}(r) = \mathbf{J}(r) \quad \text{or} \quad \mathbf{S}(r) \tag{2.9}$$

The matrix $\mathbf{J}(r)$ is a transform of the indirect pair correlation function $\mathbf{h}(r)$, and $\mathbf{h}(r)$ is a transform of the direct pair correlation function $\mathbf{c}(r)$.

In the Baxter factorization method, we introduce another correlation function $\mathbf{Q}(r)$ through the factored Ornstein–Zernike equations (one set for each value of χ)

$$\mathbf{J}(r) = \mathbf{Q}(r) + \int_0^\infty dt\, \mathbf{J}(r - t)\mathbf{Q}(t) \tag{2.10}$$

$$\mathbf{S}(r) = \mathbf{D}(r) + \mathbf{Q}(r) + \int_0^\infty dt\, \mathbf{Q}(t)\mathbf{Q}^T(r - t) \tag{2.11}$$

where, because of the fact that $h(r) = 0$ for $r < 1$ (1 = hard-core diameter), $\mathbf{Q}(r)$ must be a polynomial of the second degree for $r < 1$, and a constant for $r \geqslant 1$: Thus

$$\mathbf{Q}(r) = (r - 1)\mathbf{Q}' + \tfrac{1}{2}(r - 1)^2\mathbf{Q}'' - \mathbf{A}, \qquad r < 1$$
$$= -\mathbf{A}, \qquad\qquad\qquad\qquad\qquad r \geqslant 1 \tag{2.12}$$

For the MSA closure

$$\mathbf{C}(r) = -\beta \mathbf{U}(r)$$

where β is the Boltzmann factor and $\mathbf{U}(r)$ is the potential interaction for $r > 1$. The coefficients for the invariant expansions (2.1)–(2.4) are

$$U_{ii}(r) = e^2/r, \qquad U_{id}(r) = e\mu/r^2, \qquad U_{dd}(r) = -(10/3)^{1/2}\mu^2/r^3 \quad (2.13)$$

From here, and uring the transforms (2.5) and (2.8), we get for the matrix $\mathbf{D}$

$$\mathbf{D} = \lim_{\mu \to 0} \begin{bmatrix} d_0{}^2 e^{-2\mu|r|}/2\mu & d_1 e^{-\mu|r|} \operatorname{sgn}(r) \\ -d_1 e^{-\mu|r|} \operatorname{sgn}(r) & 0 \end{bmatrix} \quad (2.14)$$

where $\operatorname{sgn}(r)$ is the sign function, and

$$d_0{}^2 = 4\pi\beta e^2 \rho_0 \quad (2.15)$$

$$d_2{}^2 = \tfrac{4}{3}\pi\beta\mu^2 \rho_d \quad (2.16)$$

with $\beta = 1/kT$ the Boltzmann factor and

$$d_1 = d_0 d_2 \quad (2.17)$$

(this notation is similar to Ref. 12).

It can be shown that for $r < 1$, $\mathbf{J}(r)$ must be of the form

$$\mathbf{J}(r) = \begin{bmatrix} b_0 & 0 \\ 0 & b_0' \end{bmatrix} + \begin{bmatrix} 0 & b_1 \\ -b_1 & 0 \end{bmatrix} r + \begin{bmatrix} 0 & 0 \\ 0 & b_2 \end{bmatrix} r^2 \quad (2.18)$$

with

$$b_0 = 2\pi\rho_0 \int_1^\infty dr_1 \, r_1 h_{ii}(r_1) \quad (2.19)$$

$$b_1 = 2\pi(\rho_0\rho_d/3)^{1/2} \int_1^\infty dr_1 \, h_{id}(r_1) \quad (2.20)$$

$$b_2 = 3\pi(2/15)^{1/2}\rho_d \int_1^\infty dr_1 \, h_{dd}^D(r_1)/r_1 \quad (2.21)$$

where, as we defined them in (2.1) and (2.2), the function $h_{ii}(r)$ is the ion–ion pair correlation, $h_{id}(r)$ is the ion–dipole pair correlation, and $h_{dd}^D(r)$ is the second coefficient of the dipole–dipole pair correlation. As we will see, b_0, b_1, and b_2 are proportional to the charge–charge, charge–dipole, and dipole–dipole interactions.

The first step in the solution of the MSA for the mixture consists in obtaining the coefficient $\mathbf{Q}$ as functions of the parameters b_0, b_1, b_2 [(2.19)–(2.21)]. Writing

$$\mathbf{Q}' = \begin{bmatrix} Q'_{ii} & Q'_{id} \\ Q'_{di} & Q'_{dd} \end{bmatrix} \tag{2.22}$$

we have, from Ref. 12, after some algebra,

$$Q'_{ii} = -\tfrac{1}{2}[(2 - \beta_6/D_F)^2 + (b_1/2D_F)^2] \tag{2.23}$$

$$Q'_{id} = -Q'_{di} = (b_1/4D_F{}^2)(\beta_6 + \tfrac{1}{2}\Lambda_F) \tag{2.24}$$

$$Q'_{dd} = 6 - 12(1 + b_0)/D_F + (9/2)[(1 + b_0)/D_F]^2 + b_1{}^2/8D_F{}^2 \tag{2.25}$$

Furthermore, the second coefficient in (2.12) is

$$\mathbf{Q}'' = \begin{bmatrix} 0 & 0 \\ Q''_{di} & Q''_{dd} \end{bmatrix} \tag{2.26}$$

with

$$Q''_{di} + 2Q'_{di} + b_1/D_F \tag{2.27}$$

$$2Q''_{dd} = 24 - 30(1 + b_0)/D_F + 9(1 + b_0)^2/D_F{}^2 + b_1{}^2/4D_F{}^2 \tag{2.28}$$

Finally, we recall that

$$\mathbf{A} = \begin{bmatrix} a_1 & a_2 \\ 0 & 0 \end{bmatrix} \tag{2.29}$$

with

$$a_1 = -(1/2D_F{}^2)(2\beta_6 D_F - \Delta) \tag{2.30}$$

$$a_2 = -(b_1/2D_F{}^2\beta_6)(D_F\beta_3 + \Delta/2) \tag{2.31}$$

(the expression for a_2 is slightly different from that of Ref. 12, which is not correct).

In the above formulas we have used the definitions

$$\beta_3 = 1 + \tfrac{1}{3}b_2, \quad \beta_6 = 1 - \tfrac{1}{6}b_2, \quad \beta_{12} = 1 + \tfrac{1}{12}b_2, \quad \beta_{24} = 1 - \tfrac{1}{24}b_2$$

$$\Delta = \beta_6{}^2 + \tfrac{1}{4}b_1{}^2, \quad \Lambda_F = (1 + b_0)b_2 + \tfrac{1}{2}b_1{}^2$$

$$D_F = \tfrac{1}{2}[(1 + b_0)\beta_6 - \tfrac{1}{12}b_1{}^2] = \tfrac{1}{2}(1 + b_0 - \tfrac{1}{6}\Lambda_F) \tag{2.32}$$

For the representations $\chi = \pm$, we get the results of Wertheim[15] for the pure dipole case

$$q' = -b_2\beta_{24}/\beta_{12}^2 \tag{2.33}$$

$$q'' = -b_2 y_1 \tag{2.34}$$

where we have used

$$y_1 = \beta_6/\beta_{12}^2 \tag{2.35}$$

An interesting set of relations can be deduced from (2.11) and the analyticity of $\mathbf{C}(r)$ at $r = 0$:

$$Q'_{ii} = -\tfrac{1}{2}[(Q'_{ii} + a_1)^2 + (Q'_{id} + a_2)^2] \tag{2.36}$$

$$Q''_{di} = -[(Q'_{ii} + a_1)(\tfrac{1}{2}Q''_{di} - Q'_{di}) + (Q'_{id} + a_2)(\tfrac{1}{2}Q''_{dd} - Q'_{dd})] \tag{2.37}$$

$$Q''_{dd} - Q'_{dd} = \tfrac{1}{2}[(\tfrac{1}{2}Q''_{dd} - Q'_{dd})^2 + (\tfrac{1}{2}Q''_{di} - Q'_{di})^2] \tag{2.38}$$

From (2.23)–(2.31) we see that the combinations of coefficients appearing in the above set are particularly simple:

$$Q'_{ii} + a_1 = -2 + \beta_6/D_F \tag{2.39}$$

$$Q'_{id} + a_2 = -\tfrac{1}{2}Q'_{di} + Q'_{di} = -b_1/2D_F \tag{2.40}$$

$$\tfrac{1}{2}Q''_{dd} - Q'_{dd} = 6 - 3(1 + b_0)/D_F = -\Lambda_F/2D_F \tag{2.41}$$

where we have used the definitions (2.32).

To obtain the actual values of the three parameters b_0, b_1, and b_2, we have to consider the particular boundary condition of the MSA

$$\mathbf{C}(r) = -\beta\mathbf{U}(r), \qquad r < 1 \tag{2.42}$$

From (2.11), using the transforms (2.5)–(2.7), we get (see Ref. 12)

$$a_1^2 + a_2^2 = d_0^2 \tag{2.43}$$

$$-a_1 K_{di} + a_2(1 - K_{dd}) = -d_0 d_2 \tag{2.44}$$

$$K_{di}^2 + (1 - K_{dd})^2 = y_1^2 + d_2^2 \tag{2.45}$$

where d_0 and d_2 are defined by (2.15) and

$$K_{\alpha\beta} = \int_0^1 dr\, Q_{\alpha\beta}(r) \tag{2.46}$$

$$= -\tfrac{1}{2}Q'_{\alpha\beta} + \tfrac{1}{6}Q''_{\alpha\beta} \tag{2.47}$$

From (2.43) and (2.44), and (2.25) and (2.26) of Ref. 12, we get the following simple relation:

$$a_1\beta_3 + a_2 b_1/2 = d_0 y_1 \Delta \tag{2.48}$$

which can be rewritten as

$$\beta_3 + (b_1/2)A = y_1\Delta(1 + A^2)^{1/2} \tag{2.49}$$

with

$$A = a_2/a_1 = +(b_1/2\beta_6)[(\Delta + 2D_F\beta_3)/(\Delta - 2D_F\beta_6)] \tag{2.50}$$

We found that a very simple way of solving this problem is by assuming values of b_0 and b_2 and solving (2.49) numerically for b_1. It is clear that $0 > b_0 > 1$ and $0 < b_2 < 3$.

Once the values of b_0, b_1, and b_2 are known, we can compute the corresponding values of d_0 and d_2.

Finally, if we combine (2.43) and (2.48) with the results of (2.22), etc., we obtain alternative expressions for the coefficients of the Baxter functions:

$$Q'_{ii} = -\tfrac{1}{2}[d_0(1 + b_0) - b_1 d_2]^2 - \tfrac{1}{2}b_1{}^2 y_1{}^2 \tag{2.51}$$

$$Q'_{id} = \beta_6 b_1 y_1{}^2 + (\beta_6 d_2 - \tfrac{1}{12}b_1 d_0)b_1 d_2 + (1 + b_0)d_0 \tag{2.52}$$

$$Q'_{dd} = 2[-1 + \beta_6{}^2 y_1{}^2 + (\beta_6 d_2 - \tfrac{1}{12}b_1 d_0)^2] \tag{2.53}$$

3. PAIR CORRELATION FUNCTIONS

Consider again Eq. (2.10), and let us define

$$\mathbf{H}(r) = -(\tfrac{1}{2}\pi) \,\partial \mathbf{J}(r)/\partial r, \qquad r \geqslant 1 \tag{3.1}$$

$$\mathbf{F}(r) = -(\tfrac{1}{2}\pi) \,\partial \mathbf{J}(r)/\partial r, \qquad r < 1 \tag{3.2}$$

Since, for $r < 1$, $\mathbf{J}(r)$ is of the form[12]

$$\mathbf{J}(r) = \begin{bmatrix} b_0 & 0 \\ 0 & b_0' \end{bmatrix} + r\begin{bmatrix} 0 & b_1 \\ -b_1 & 0 \end{bmatrix} + r^2\begin{bmatrix} 0 & 0 \\ 0 & b_2 \end{bmatrix} \tag{3.3}$$

Then

$$\mathbf{F}(r) = \frac{1}{2\pi} \begin{bmatrix} 0 & -b_1 \\ b_1 & -2b_2 r \end{bmatrix} \tag{3.4}$$

We now extend $\mathbf{F}(r)$ to the entire range of $0 < r < \infty$. Then, following a procedure similar to that of Høye and Blum[17] [Section 2, Eq. (17)], we get, from the derivative of (2.10),

$$\mathbf{G}(r) = \mathbf{Q}'(r)/2\pi + \int_1^r dt\, \mathbf{G}(r - t)\mathbf{Q}(t) \tag{3.5}$$

where we have also extended $\mathbf{Q}'(r)$ to values of $r > 1$, and we used

$$\mathbf{G}(r) = \mathbf{H}(r) - \mathbf{F}(r) \tag{3.6}$$

Equation (3.5) is a convolution-type equation, which can be easily solved by Laplace transformation

$$\tilde{\mathbf{G}}(s) = \frac{e^{-s}}{2\pi s^2} (s\mathbf{Q}' + \mathbf{Q}'')[\mathbf{I} - \tilde{\mathbf{Q}}(s)]^{-1} \tag{3.7}$$

where $\mathbf{Q}'$ and $\mathbf{Q}''$ have been given by (2.22) and (2.26), while the Laplace transform of the Baxter function (2.12)

$$\tilde{\mathbf{X}}(s) = \int_0^\infty dr\, e^{-sr}\mathbf{X}(r) \qquad (\mathbf{X} \equiv Q) \tag{3.8}$$

has matrix elements

$$\tilde{Q}_{ii} = (1/s)\varphi_0(s)Q'_{ii} - (1/s)(Q'_{ii} + a_1) \tag{3.9}$$

$$\tilde{Q}_{id}(s) = (1/s)\varphi_0(s)Q'_{id} - (1/s)(Q'_{id} + a_2) \tag{3.10}$$

$$\tilde{Q}_{di}(s) = (1/s)\varphi_0(s)(Q'_{di} + Q''_{di}/s) + (1/s)(-Q'_{di} + \tfrac{1}{2}Q''_{di}) - (1/s^2)Q''_{di} \tag{3.11}$$

$$\tilde{Q}_{dd}(s) = (1/s)\varphi_0(s)(Q'_{dd} + Q''_{dd}/s) + (1/s)(-Q'_{dd} + \tfrac{1}{2}Q''_{dd}) - (1/s^2)Q''_{dd} \tag{3.12}$$

$$\varphi_0 = (1/s)(1 - e^{-s}) \tag{3.13}$$

The algebra involved in carrying out the calculations indicated by (3.7) is considerable. However, using the new expressions for the coefficients of **Q** obtained in the last section, a surprising number of simplifications occur, and the result has the relatively simple form

$$\tilde{\mathbf{G}}(s) = \begin{bmatrix} \tilde{\mathbf{G}}_{ii}(s) & \tilde{\mathbf{G}}_{id}(s) \\ \tilde{\mathbf{G}}_{di}(s) & \tilde{\mathbf{G}}_{dd}\tilde{Q}(s) \end{bmatrix} \tag{3.14}$$

$$\tilde{\mathbf{G}}_{ii}(s) = \{e^{-s}/[2\pi s^2 \tilde{D}(s)]\}\tilde{\Gamma}_{ii}(s) \tag{3.15}$$

$$\tilde{\mathbf{G}}_{id}(s) = -\tilde{\mathbf{G}}_{di}(s) = \{e^{-s}/[2\pi s^2 \tilde{D}(s)]\}\tilde{\Gamma}_{id}(s) \tag{3.16}$$

$$\tilde{\mathbf{G}}_{dd}^0(s) = \{e^{-s}/[2\pi s^2 \tilde{D}(s)]\}\tilde{\Gamma}_{dd}(s) \tag{3.17}$$

$$\tilde{\Gamma}_{ii}(s) = sQ'_{ii} - \varphi_0(s)(C_1 + C_0/s) - C_3 + C_0/s \tag{3.18}$$

$$\tilde{\Gamma}_{id}(s) = sQ'_{id} + C_2 \tag{3.19}$$

$$\tilde{\Gamma}_{dd}(s) = sQ'_{dd} - \varphi_0(s)(C_1 + C_0/s) + C_4 + C_5/s \tag{3.20}$$

$$\begin{aligned}
\tilde{D}(s) = {} & 1 - (2D_F/sb_1)Q''_{di} + (C_4 - \tfrac{1}{2}C_5)/s^2 + C_5/s^3 \\
& + [\varphi_0(s)/s][-Q''_{ii} - Q''_{dd} + (C_3 - C_4)/s - (C_0 + C_5)/s^2] \\
& + [\varphi_0^2(s)/s^2](C_0 + C_1/s)]
\end{aligned} \tag{3.21}$$

where the constants C are defined by

$$\begin{aligned}
C_0 &= Q'_{ii}Q''_{dd} - Q'_{id}Q''_{di} \\
C_1 &= Q'_{ii}Q''_{dd} - Q'_{id}Q'_{di} \\
C_2 &= Q'_{id}a_1 - Q'_{ii}a_2 \\
C_3 &= Q'_{ii}(\tfrac{1}{2}Q''_{dd} - Q'_{dd}) - Q'_{id}(\tfrac{1}{2}Q''_{di} - Q'_{di}) \\
C_4 &= Q''_{dd} - (Q'_{id} + a_2)Q''_{di} + (Q'_{ii} + a_1)Q''_{dd} \\
C_5 &= -(Q'_{id} + a_2)Q''_{di} + (Q'_{ii} + a_1)Q''_{dd}
\end{aligned} \tag{3.22}$$

After use of (2.23), etc., and considerable algebra, we find the surprisingly simple results

$$C_0 = d_0 y_1 (2b_0 b_2 + b_1{}^2) \qquad (3.23)$$

$$C_1 = y_1{}^2 (b_1{}^2 - 4d_0{}^2 D_F{}^2) - [b_1 d_2 + (1 + b_0) d_0]^2 \qquad (3.24)$$

$$C_2 = d_0 y_1 b_1 \qquad (3.25)$$

$$C_3 = \tfrac{1}{2} C_0 - C_1 \qquad (3.26)$$

$$C_4 = -3 d_0 y_1 - \tfrac{1}{4} C_0 + 6 Q'_{di} (1 + b_0 - \beta_3)/b_1 \qquad (3.27)$$

$$C_5 = 2 b_2 d_0 y_1 + C_0 \qquad (3.28)$$

where we have used the definitions (2.15) and (2.35). Extensive use of the relation

$$b_0 \beta_3 + b_1{}^2/6 = 2 d_0 y_1 D_F{}^2 \qquad (3.29)$$

was also made.

The problem now is to obtain the coefficients of the pair correlation functions h_{ii}, h_{id}, h_{dd}^{Δ}, h_{dd}^{D} defined by Eq. (2.1), etc. A method which we believe is convenient computationally derives from the general inversion formula[18]

$$2\pi^2 i^l (\rho_\alpha \rho_\beta)^{1/2} h^l_{\alpha\beta}(r) = \int_0^\infty dk \, k^2 j_l(kR)[\tilde{J}_{\alpha\beta}(ik) + (-)^l \tilde{J}_{\alpha\beta}(-ik)] \qquad (3.30)$$

where α, $\beta = i, d$. For the ion–ion correlations, $l = 0$; for ion–dipole, $l = 1$; and for dipole–dipole, $l = 0 (\Delta)$ and $l = 2 (D)$. Here $j_l(x)$ is the usual notation for the spherical Bessel functions, and the functions $\tilde{J}_{\alpha\beta}(s)$ are the Laplace transforms of the functions $J_{\alpha\beta}(r)$ defined by (2.8), (3.8).

Clearly, from the definitions (3.1), (3.2), and (3.6), and also using (3.3),

$$\tilde{J}_{ii}(s) = b_0/s - (2\pi/s)\tilde{H}_{ii}(s) \qquad (3.31)$$

$$= b_0/s - (2\pi/s)\tilde{G}_{ii}(s) \qquad (3.32)$$

$$\tilde{J}_{id}(s) = -b_1/s^2 - (2\pi/s)\tilde{G}_{id}(s) \qquad (3.33)$$

$$\tilde{J}_{dd}^0(s) = b_0'/s + 2b_2/s^3 - (2\pi/s)\tilde{G}_{dd}(s) \qquad (3.34)$$

We need also the transform of the irreducible representation $\chi = 1$: This is the same as in the pure dipole case,[15] and can be obtained from our expressions simply by setting b_0, $b_1 = 0$ and $b_2 \to -b_2/2$:

$$\tilde{J}'_{dd}(s) = b_0''/s - b_2/s^3 - (2\pi/s)\tilde{G}'_{dd}(s) \qquad (3.35)$$

with

$$\tilde{G}'_{dd}(s) = (e^{-s}/2\pi s^2)(sq' + q'')/[1 - \varphi_1(s)q' - \varphi_2(s)q''] \qquad (3.36)$$

where q' and q'' are defined by (2.33) and (2.34) with

$$\varphi_1 = (1/s^2)(1 - s - e^{-s}), \qquad \varphi_2 = (1/s^3)(1 - s + s^2/2 - e^{-s}) \qquad (3.37)$$

Summarizing, our expressions are

$$h_{ii}(R) = (-1/\pi\rho_0) \int_0^\infty dk \, kj_0(kR)[\text{Im } \tilde{J}_{ii}(ik)] \tag{3.38}$$

$$h_{id}(R) = (3/\rho_0\rho_D)^{1/2}(2/\pi) \int_0^\infty dk \, kj_1(kR)[\text{Re } \tilde{J}_{id}(ik)] \tag{3.39}$$

$$h_{dd}^\Lambda(R) = (2/\pi\rho_d)(1/\sqrt{3}) \int_0^\infty dk \, kj_0(kR) \, \text{Im}[2\tilde{J}_{dd}^1(ik) + \tilde{J}_{dd}^0(ik)] \tag{3.40}$$

$$h_{dd}^D(R) = -(2/\pi\rho_d)(10/3)^{1/2} \int_0^\infty dk \, kj_2(kR) \, \text{Im}[\tilde{J}_{dd}^1(ik) - \tilde{J}_{dd}^0(ik)] \tag{3.41}$$

To avoid numerical problems stemming from the discontinuity at $r = 1$, it is convenient to add and subtract a function with a known transform that eliminates this problem. Fortunately, the discontinuities can be evaluated from Eq. (2.10),

$$h_{ii}(1) = Q'_{ii}/2\pi\rho_0 \tag{3.42}$$

$$h_{id}(1) = -(3/\rho_0\rho_d)^{1/2}(Q'_{id}/2\pi) \tag{3.43}$$

$$h_{dd}^\Lambda(1) = [1/(2\pi\rho_d\sqrt{3})](2q' + Q'_{dd}) \tag{3.44}$$

$$h_{dd}^D(1) = (1/2\pi\rho_d)(10/3)^{1/2}(q' - Q'_{dd}) \tag{3.45}$$

A convenient function for this purpose is

$$\begin{aligned} \varphi(x) &= 0, \quad r < 1 \\ \varphi_l(x) &= h_{\alpha\beta}(1)e^{-\lambda x}x^{l-1} \quad (l = 0, 1, 2) \end{aligned} \tag{3.46}$$

since

$$(2/\pi) \int_0^\infty dk \, 2^l l! \, j_l(kR)[k/(\lambda^2 + k^2)]^{l+1} = e^{-\alpha x}x^{l-1} \tag{3.47}$$

Let us now evaluate the direct correlation function. We introduce the functions

$$\mathscr{E}_{\alpha\beta}(r) = -(\tfrac{1}{2}\pi r) \, dS_{\alpha\beta}(r)/dr \tag{3.48}$$

where $S_{\alpha\beta}(r)$ is given by (2.11). We get

$$\mathscr{E}_{ii}(r) = (1/2\pi)\{a_1 Q'_{ii} + a_2 Q'_{id} + \tfrac{1}{2}[(Q)'_{ii})^2 + (Q_{id})^2]r\} \tag{3.49}$$

$$\mathscr{E}_{id}(r) = (1/2\pi)[\tfrac{1}{2}(Q'_{ii}Q'_{di} + Q'_{di}Q'_{dd})r - \tfrac{1}{6}(Q'_{ii}Q''_{di} + Q'_{id}Q''_{dd})r^2] \tag{3.50}$$

$$\begin{aligned} \mathscr{E}_{dd}(r) = (1/2\pi)\{Q''_{dd} - \tfrac{1}{6}[(Q''_{dd})^2 + (Q''_{di})^2] + \tfrac{1}{2}(Q''_{dd}Q'_{dd} + Q''_{di}Q'_{di}) \\ + \tfrac{1}{2}[(Q'_{dd})^2 + (Q'_{di})^2]r - \tfrac{1}{24}[(Q''_{dd})^2 + (Q''_{di})^2]r^3\} \end{aligned} \tag{3.51}$$

After considerable algebra, it can be shown that[13]

$$\ell_{ii}(r) = (1/2\pi)\{d_0^2 b_0 - d_0 d_2 b_1 + \tfrac{1}{2}[(d_0 b_0 - d_2 b_1)^2 + b_1^2 y_1^2]r\} \qquad (3.52)$$

$$\begin{aligned}\mathscr{C}_{id}(r) = (1/2\pi)\{[b_0 d_1 - b_1(d_2^2 + y_1^2)](1/r) + \tfrac{1}{4}[b_1 d_0^2 + 2b_2 d_1]r \\ + \tfrac{1}{6}[b_0 b_1 d_0^2 - b_1^2 d_1 + 2b_0 b_2 d_1 - 2b_1 b_2(d_2^2 + y_1^2)r^2\}\end{aligned} \qquad (3.53)$$

4. THERMODYNAMIC PROPERTIES

As is known, the best values of the thermodynamic properties in the MSA are obtained from the energy. Høye and Stell[19] have given a very elegant, closed formulation for the thermodynamic properties calculated from the internal energy:

$$\beta E/V = (1/4\pi)(d_0^2 b_0 - d_0 d_2 b_1 - 2d_2^2 b_2) \qquad (4.1)$$

which can be checked to be identical with

$$- \beta E/V = \tfrac{1}{2}[\mathscr{H}_{ii}(0) - \ell_{ii}(0)] + \tfrac{1}{2}[\mathscr{H}_{dd}(0) - \ell_{dd}(0)] - (b_2/2\pi)(y_1^2 - 1) \qquad (4.2)$$

since

$$\ell_{ii}(0) = (1/2\pi)d_0(d_0 b_0 - d_2 b_1) \qquad (4.3)$$

$$\ell_{dd}(0) = -(d_2/2\pi)(d_0 b_1 + 2b_2 d_2) - b_2 y_1^2/2\pi \qquad (4.4)$$

$$\mathscr{H}_{dd}(0) = -b_2/\pi \qquad (4.5)$$

For most chemical applications, the relevant thermodynamic quantities are the excesses with respect to the pure solvent. For the pure solvent

$$\beta E_0/V = -d_2^2 b_2^{(0)}/2\pi \qquad (4.6)$$

where $b_2^{(0)}$ is the value of (2.21) for $\rho_0 = 0$. Thus, for infinite dilution, we recover Høye and Stell's[20]

$$\frac{\beta \Delta E}{V} = \frac{\beta(E - E_0)}{V} \simeq \frac{-1}{8\pi}\left(\frac{d_0}{\sqrt{\epsilon_w^0}}\right)^3 - \frac{\epsilon_w^0 - 1}{8\pi\epsilon_w^0}\frac{\beta_3^0}{\beta_{12}^0}d_0^2 \qquad (4.7)$$

Here, the superscript 0 means that $\rho_0 = 0$, or that the quantity is taken for the pure solvent. Wertheim's dielectric constant is defined by

$$\epsilon_w = \beta_3^2 \beta_{12}^4/\beta_{12}^6, \qquad \epsilon_w^0 = (\beta_3^0)^2(\beta_{12}^0)^4/(\beta_{12}^0)^6 \qquad (4.8)$$

and the β_n^0 are defined by (2.32) but with $b_2^{(0)}$ instead of b_2.

To compute the excess Helmholtz free energy, we follow again Ref. 14 (see also Ref. 21), to get

$$\begin{aligned}\beta A/V = -(1/12\pi)[-2d_0^2 b_0 + 2d_0 d_2 b_1 + (Q_{ii}')^2 \\ + 2(Q_{id}')^2 + (Q_{dd}')^2 + 2(q')^2]\end{aligned} \qquad (4.9)$$

For the limiting case with no dipoles this formula is obviously correct. In the limit of a pure, we recover the result of Rushbrooke et al.[22]

$$
\begin{aligned}
-\beta A^0/V &= (1/12\pi)[(Q'_{dd})^2 + 2(q')^2] \\
&= [(b_2{}^0)^2/3\pi][(\beta_{12}^0)^2/(\beta_6{}^0)^4 + \tfrac{1}{2}(\beta_{24}^0)^2/(\beta_{12}^0)^4] \quad (4.10)
\end{aligned}
$$

The excess chemical potential can be evaluated from (4.9). For the ions, we get

$$
\beta\mu_i = \partial(\beta A/V)/\partial\rho_0 = (d_0/4\pi\rho_0)(d_0 b_0 - d_2 b_1) \quad (4.11)
$$

while for the dipoles

$$
\beta\mu_d = \partial(\beta A/V)/\partial\rho_d = -(d_2/4\pi\rho_d)(2d_2 b_2 + d_0 b_1) \quad (4.12)
$$

The total excess Gibbs free energy yields

$$
\beta G/V = \rho_0\mu_i + \rho_d\mu_d = \Delta E/V \quad (4.13)
$$

which agrees with the standard MSA result that the excess Gibbs free energy is equal to the excess internal energy.

Finally, the osmotic coefficient can be obtained from the excess pressure and (4.12),

$$
\beta P = \beta(E - A)/V \quad (4.14)
$$

$$
\begin{aligned}
\Delta\phi = \beta P/\Sigma\rho = (1/12\pi)[&d_0{}^2 b_0 - 4d_0 d_2 b_1 - 6d_2{}^2 b_2 + (Q'_{ii})^2 \\
&+ 2(Q'_{id})^2 + (Q'_{dd})^2 + 2(q')^2] \quad (4.15)
\end{aligned}
$$

REFERENCES

1. J. C. Rasaiah and H. L. Friedman, *J. Chem. Phys.* **48**:2742 (1968).
2. J. C. Rasaiah and H. L. Friedman, *J. Chem. Phys.* **50**:3965 (1969).
3. M. S. Wertheim, *Mol. Phys.* **26**:1425 (1973).
4. D. Levesque, J. L. Weis, and G. N. Patey, *Phys. Lett.* **66A**:115 (1978).
5. C. W. Outhwaite, *Mol. Phys.* **31**:1345 (1976).
6. S. A. Adelman and J. H. Chen, *J. Chem. Phys.* **70**:4291 (1979).
7. J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **144**:251 (1966).
8. E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **52**:4307 (1970); **56**:3086, 3093 (1972).
9. L. Blum, *Mol. Phys.* **30**:1529 (1975).
10. J. S. Høye, J. L. Lebowitz, and G. Stell, *J. Chem. Phys.* **61**:3252 (1974).
11. B. Larsen, G. Stell, and K. C. Wu, *J. Chem. Phys.* **67**:530 (1977).
12. L. Blum, *Chem. Phys. Lett.* **26**:200 (1974); *J. Chem. Phys.* **61**:2129 (1974).
13. S. A. Adelman and J. M. Deutch, *J. Chem. Phys.* **60**:3935 (1974).
14. L. Blum, *J. Stat. Phys.* **18**:451 (1978).
15. M. S. Wertheim, *J. Chem. Phys.* **55**:4291 (1971).
16. L. Blum, *J. Chem. Phys.* **56**:303 (1972); **57**:1862 (1973); **58**:3295 (1973).
17. J. S. Høye and L. Blum, *J. Stat. Phys.* **16**:399 (1977).
18. L. Blum, *J. Chem. Phys.* **58**:3295 (1973).
19. J. S. Høye and G. Stell, *J. Chem. Phys.* **67**:439 (1977).
20. J. S. Høye and G. Stell, *J. Chem. Phys.* **68**:4145 (1978).
21. L. Blum and J. S. Høye, *J. Phys. Chem.* **81**:1311 (1977).
22. G. S. Rushbrooke, G. Stell, and J. S. Høye, *Mol. Phys.* **26**:1199 (1973).