

## Analytical solution of the mean spherical approximation for an arbitrary mixture of ions in a dipolar solvent

L. Blum and D. Q. Wei

Citation: *J. Chem. Phys.* **87**, 555 (1987); doi: 10.1063/1.453604

View online: <http://dx.doi.org/10.1063/1.453604>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v87/i1>

Published by the [American Institute of Physics](#).

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



**Goodfellow**  
metals • ceramics • polymers • composites  
70,000 products  
450 different materials  
**small quantities fast**  
[www.goodfellowusa.com](http://www.goodfellowusa.com)

# Analytical solution of the mean spherical approximation for an arbitrary mixture of ions in a dipolar solvent

L. Blum and D. Q. Wei<sup>a)</sup>

Department of Physics, University of Puerto Rico, Rio Piedras, Puerto Rico 00931

(Received 19 December 1986; accepted 3 February 1987)

We show that in the mean spherical approximation for a mixture of arbitrary size and charge hard ions in a dipolar solvent all the properties are expressible in terms of three parameters; a screening parameter  $\Gamma$ , a ion-dipole interaction parameter  $B^{10}$ , and a dipole-dipole interaction parameter  $b_2$ , which are given by the solution of a set of algebraic equations. In the case of equal ionic size, the solution is quite simple and very similar to previous results which the size of ion are equal to the size of dipole ( $\sigma = \sigma_n = 1$ ). In the low density and high coupling limits, explicit results are given for the three parameters and for the thermodynamics. The calculations show that the model becomes the primitive model for infinite dilution and vanishingly small solvent molecules.

## INTRODUCTION

In many technological and scientific applications, it is important to be able to represent the thermodynamic properties of real ionic solution by simple analytical expressions. It is desirable that the analytical expression should correspond to some well defined physical model, from which, by means of a statistical mechanical theory, simple representations of the thermodynamic properties can be extracted.

Such is the combination of the primitive model of electrolyte, in which ions, represented by charged hard sphere are dissolved in a continuum dielectric, representing the solvent is solved in the mean spherical approximation (MSA)<sup>1,2</sup> which yields, for general mixture, analytical expression for thermodynamic properties in terms of one single parameter  $\Gamma$ <sup>3,4</sup> which plays the role the Debye-Hückel inverse length  $\kappa$ . The usefulness of this approach lies in the fact that it is very simple, and that its accuracy can be improved by some rather simple device such as the redefinition of the size and the charge.<sup>5-8</sup> The redefined model parameters can be considered as a variational solution to the more accurate hypernetted chain approximation (HNC).<sup>9,10</sup> Furthermore it yields rigorous bounds to the internal energy of the system.

The next logical step is to incorporate the solvent into the picture. The simplest such model is the ion-dipole mixture<sup>11,12</sup> which has been solved analytically in the MSA for the restricted case of equal sizes of the ions and dipoles. The model has also been solved in more accurate approximations such as the HNC<sup>13-20</sup> and is, in general, useful in discussing solvent effects, for example, in inhomogeneous systems.<sup>21</sup>

However, for the realistic situation in which the ions are of arbitrary size and charge, no such simple solution for the MSA exists. A partial solution was discussed by one of us previously,<sup>22</sup> but the conclusions about the scaling are not correct in that work. The correct answer, which is given here, is that, just as in the case of the primitive model, only one ionic scaling parameter  $\Gamma$  is needed for the full solution

of the problems. The algebraic equations for the three parameters are, however, much more complicated than in the restricted case of all equal sizes. We discuss the solution formally and give explicit results for the cases in which all ions are of equal diameter which, however, is not the same as the solvent one. We also discuss approximations for dilute ionic systems.

## I. METHOD OF SOLUTION

For the sake of clarity, we will summarize the procedure used in our previous work. The notation is similar to that of reference.<sup>22</sup>

The system consists of a mixture of  $n - 1$  hard spheres of diameter  $\sigma_i$ , number density  $\rho_i$ , and with a charge  $Z_i e$ , where  $e$  is the elementary charge. The solvent has a hard core diameter  $\sigma_n$ , density  $\rho_n$ , and a point dipole  $\mu$ .

The pair correlation function  $g_{ij}(X_i, X_j)$  can be expanded as<sup>23,24</sup>

$$g_{ij}(X_i, X_j) = \sum_{m, n, l} \hat{g}_{ij}^{mnl}(r_{ij}) \Phi^{mnl}(\Omega_i, \Omega_j, \hat{R}_{ij}), \quad (1.1)$$

where  $X_i = \Omega_i, R_i$  and  $\Omega_i = \alpha_i, \beta_i, \gamma_i$  are the three Euler angles that give the orientation of the molecule  $i$ . The orientation of the intermolecular, center-to-center vector  $\hat{R}_{ij}$  is given by  $\hat{R}_{ij} = \theta_{ij}, \phi_{ij}$ . The coefficient  $\hat{g}_{ij}^{mnl}$  depend only on center-to-center distance  $r_{ij}$ , while the angular dependence of the correlations is given by the invariant products

$$\Phi^{mnl} = [(2m+1)(2n+1)]^{1/2} \sum_{\mu, \nu, \lambda} \begin{pmatrix} m & n & l \\ \mu & \nu & \lambda \end{pmatrix} \times D_{0\mu}^m(\Omega_i) D_{0\nu}^n(\Omega_j) D_{0\lambda}^l(\hat{R}_{ij}), \quad (1.2)$$

where we have used the customary notation for the Wigner 3- $j$  symbols, and generalized spherical harmonics  $D_{\mu\mu}^m(\Omega_i)$  (we will use the notation and conventions of Edmonds<sup>25</sup> throughout). Using the reference frame in which the  $z$  axis points along the  $\hat{r}_{ij}$  vector, we get the irreducible representation<sup>23,24</sup>

$$g_{ij}(X_i, X_j) = \sum_{m, n, x} g_{ij, x}^{mn}(\mathbf{R}_{ij}) \Phi_x^{mn}(\Omega_i, \Omega_j), \quad (1.3)$$

with

<sup>a)</sup> On leave of Normal University of Henan, XinXiang, Henan, P.R. China.

$$g_{ij,\chi}^{mn} = \sum_l \begin{pmatrix} n & m & l \\ \chi & -\chi & 0 \end{pmatrix} g_{ij}^{mnl} \quad (1.4)$$

and

$$\Phi_{\chi}^{mn} = [(2m+1)(2n+1)]^{1/2} D_{0\chi}^m(\Omega_i) D_{0-\chi}^n(\Omega_j). \quad (1.5)$$

With this expansion, the Ornstein-Zernike equation becomes a set of  $\chi + 1$  matrix equations. If the order of the highest multipole in a particular expansion is  $n$ , there will be  $n + 1$  matrix equations for  $\chi < n$ . A similar expansion is valid for the direct correlation function  $C_{ij}(X_1, X_2)$ . Consider now the pair of transforms

$$J_{ij,\chi}^{mn}(r) = (-1)^{\chi} 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \times \int_r^{\infty} dr_1 r_1 P_l(r/r_1) \hat{h}_{ij}^{mnl}(r_1) \quad (1.6)$$

and

$$S_{ij,\chi}^{mn}(r) = (-1)^{\chi} 2\pi \sum_l \begin{pmatrix} m & n & l \\ \chi & -\chi & 0 \end{pmatrix} \times \int_r^{\infty} dr_1 r_1 P_l(r/r_1) \hat{c}_{ij}^{mnl}(r_1). \quad (1.7)$$

The matrix  $J_{\chi}(r)$  and  $S_{\chi}(r)$  are formed by the elements of Eqs. (1.4) and (1.5). The Fourier transforms of these functions are, in matrix form

$$\mathcal{H}_{\chi}(k) = \int_{-\infty}^{\infty} dr \exp(ikr) J_{\chi}(r), \quad (1.8)$$

$$\mathcal{C}_{\chi}(k) = \int_{-\infty}^{\infty} dr \exp(ikr) S_{\chi}(r). \quad (1.9)$$

Using these functions, we write the Ornstein-Zernike (OZ) equation in matrix form

$$[I + \rho^{1/2} \mathcal{H}_{\chi}(k) \rho^{1/2}] [I - \rho^{1/2} \mathcal{C}_{\chi}(k) \rho^{1/2}] = I. \quad (1.10)$$

Now write the direct correlation in factored form using Baxter-Wertheim's procedure

$$I - \rho^{1/2} \mathcal{C}_{\chi} \rho^{1/2} = Q(k) Q^T(-k). \quad (1.11)$$

Because of the long range of the ion-ion, ion-dipole, and dipole-dipole interactions the direct correlation function is also long ranged. In fact, we may write

$$C_{ij}^{mnl}(r) = C_{ij}^{(0)mnl}(r) - \beta U_{ij}^{mnl}(r), \quad (1.12)$$

where  $U_{ij}^{mnl}(r)$  is the radial part of the electrostatic interaction, and  $C_{ij}^{(0)mnl}(r)$  is the short ranged function. Clearly

$$U_{ij}^{000} = Z_i Z_j e^2 / r, \quad (1.13)$$

$$U_{in}^{011} = Z_i e \mu / r^2, \quad (1.14)$$

$$U_{nn}^{112} = -\sqrt{10/3} \mu^2 / r^3. \quad (1.15)$$

Performing the transformation (1.6) to (1.9), we get

$$\mathcal{C}(k) = \mathcal{C}^{(0)}(k) - D, \quad (1.16)$$

where  $D$  is a matrix with components

$$D = \begin{pmatrix} Z_i Z_j \alpha_0^2 & Z_i \alpha_0 \alpha_2 \\ -Z_i \alpha_0 \alpha_2 & 0 \end{pmatrix}, \quad (1.17)$$

where

$$\alpha_0^2 = 4\pi\beta e^2, \quad (1.18)$$

$$\alpha_2^2 = (4\pi/3)\beta\mu^2. \quad (1.19)$$

The factor function  $Q(k)$  of the direct correlation function must then be of the form

$$Q_{ij}^{mn}(k) = \delta_{ij} \delta_{mn} - (\rho_i \rho_j)^{1/2} \times \left\{ \int_{\lambda_{ji}}^{\sigma_{ij}} dr \exp(ikr) Q_{ij}^{mn}(r) - A_{ij}^{mn} \times \int_{\lambda_{ji}}^{\infty} dr \exp[r(ik - \mu)] \right\}, \quad (1.20)$$

where  $m, n = 0, 1$ ;  $1 < i, j < n$ , and

$$\lambda_{ji} = (\sigma_j - \sigma_i)/2. \quad (1.21)$$

The functional form of  $Q(r)$  is obtained from the Fourier inverse of

$$[I + \rho^{1/2} \mathcal{H}_0(k) \rho^{1/2}] Q(k) = [Q^T(-k)]^{-1}, \quad (1.22)$$

which is

$$J_{ij}^{mn}(r) = Q_{ij}^{mn}(r) - A_{ij}^{mn} + \sum_{k \neq i} \rho_k \int_{\lambda_{jk}}^{\infty} dr_1 J_{ik}^{mn}(r - r_1) \times [Q_{kj}^{n,n}(r_1) - A_{kj}^{n,n}], \quad (1.23)$$

where we have included in  $Q_{ij}^{mn}(r)$  the Heaviside function that makes this function zero for  $r > \sigma_{ij}$ .

Consider now the form of  $J_{ij}(r)$  for  $r < \sigma_{ij}$ . From (1.23) and since

$$\hat{h}_{ij}^{mnl}(r) = 0, \quad m, n, l \neq 0; \quad r < \sigma_{ij},$$

$$\hat{h}_{ij}^{000}(r) = -1, \quad r < \sigma_{ij}, \quad (1.24)$$

we get from Eq. (1.23),

$$J(r) = \begin{pmatrix} J^{00} & 0 \\ 0 & J^{11} \end{pmatrix} + \begin{pmatrix} 0 & J^{01} \\ J^{10} & 0 \end{pmatrix} r + \begin{pmatrix} \pi & 0 \\ 0 & J^{11} \end{pmatrix} r^2, \quad (1.25)$$

where the constants are explicitly given by

$$J_{ij}^{00} = 2\pi \int_0^{\infty} dr r h_{ij}^{000}(r),$$

$$J_{in}^{01} = -J_{ni}^{10} = -(2\pi/\sqrt{3}) \int_0^{\infty} dr h_{in}^{011}(r),$$

$$J_{nn}^{11} = (3/2)(2/15)^{1/2} 2\pi \int_0^{\infty} dr h_{nn}^{112}(r)/r,$$

$$I^{11} = -2\pi \left\{ (1/\sqrt{3}) \int_0^{\infty} dr r h_{nn}^{110}(r) + (1/\sqrt{30}) \int_0^{\infty} dr h_{nn}^{112}(r) \right\}. \quad (1.26)$$

From the inverse of the definition (1.11) we get the following relations:

$$Q_{ij}^{mn}(\sigma_{ij}) = 0, \\ A_{ij}^{00} = Z_i \alpha_j^0, \quad j < n-1, \\ A_{in}^{01} = Z_i \alpha_n^1, \quad j = n, \\ A_{nj}^{10} = A_{nn}^{11} = 0. \quad (1.27)$$

Then, as before<sup>22</sup> we know that

$$D_{ij}^{\infty} = \sum_{k=1}^n \rho_k A_{ik}^{\infty} A_{jk}^{\infty}, \quad (1.28)$$

which, after some manipulations, yields

$$\sum_{k=1}^{n-1} \rho_k (a_k^0)^2 + \rho_n (a_n^1)^2 = \alpha_0^2, \quad (1.29)$$

which is the condition that gives the relation for the ion-ion coupling parameter  $\alpha_0$ . We get another relation for the ion-dipole interaction from the inverse Fourier transform of Eq. (1.11) for the ion-dipole term:

$$-\sum_{j=1}^{n-1} \rho_j a_j^0 K_{nj}^{10} + a_n^1 (1 - \rho_n K_{nn}^{11}) = \alpha_2 \alpha_0, \quad (1.30)$$

where we have introduced

$$K_{ij}^{mn} = \int_{\lambda_{ij}}^{\sigma_{ij}} dr Q_{ij}^{mn}(r). \quad (1.31)$$

The relation for the dipole-dipole strength parameter  $\alpha_2$  is obtained in a manner similar to Wertheim.<sup>26</sup> The results are

$$(1 - \rho_n K_{nn}^{11})^2 + \rho_n \sum_k \rho_k (K_{nk}^{10})^2 = y_1^2 + \rho_n \alpha_2^2, \quad (1.32)$$

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

$$b_2 = \rho_n \sigma_n^3 J_{nn}^{11},$$

$$\beta_6 = 1 - b_2/6,$$

$$\beta_{12} = 1 + b_2/12. \quad (1.33)$$

From Eq. (1.23), we deduce the form of the function  $Q(r)$  which is a second degree polynomial in  $r$ , which is zero at  $r = \sigma_{ij}$ ,

$$Q_{ij}^{mn}(r) = (1/2)(r - \sigma_{ij})(r - \lambda_{ji})\alpha_j^{mn} + (r - \sigma_{ij})\beta_{ij}^{mn}. \quad (1.34)$$

Furthermore, since  $C_{ij}(r)$  is a symmetric function from the inverse transform of Eqs. (1.11) and (1.28), we get the important symmetry relations

$$P_{ij}^{mn} \equiv Q_{ij}^{mn}(\lambda_{ji}) = Q_{ji}^{mn}(\lambda_{ij}) \equiv P_{ji}^{mn}, \quad (1.35)$$

or

$$P_{ij}^{mn} = \sigma_i \beta_{ij}^{mn} - Z_i a_j^0 = \sigma_j \beta_{ji}^{mn} - Z_j a_i^0 = P_{ji}^{mn},$$

$$P_{in} = \sigma_i \beta_{in}^{mn} - Z_i a_n^1 = \sigma_n \beta_{ni}^{mn} = P_{ni}^{mn}, \quad (1.36)$$

where the new parameters  $P_{ij}^{mn}$  have been introduced to simplify the notation.

The set of equations (1.23) has been solved in previous work.<sup>22</sup> However, to find all the parameters in these equations we still need another set of  $n+1$  equations to compute the parameters  $a_i^0, a_n^1$ . These can be obtained either from Eq. (1.23) or from the fact that the direct correlation function  $C_{ij}(r)$  at the origin,  $r=0$ , must be analytic and bounded. One easily gets,<sup>27,28</sup>

$$\beta_{ii}^{mn} + \sigma_i \alpha_i^{mn}/2 = -(1/2) \sum_k \rho_k [P_{ki}^{mn}]^2 \quad (i=1, \dots, n), \quad (1.37)$$

then

$$P_{ij}^{00} = (\pi/\Delta_1) \sigma_i \sigma_j - (1/2) \rho_n \sigma_n^2 \sigma_i \eta_j m_i / D \beta_6 + 2a_j^0 D_i^G / \beta_6,$$

$$P_{in}^{01} = -\sigma_i \beta_3 m_i / (D \beta_6^2) + 2a_n^1 D_i^G / \beta_6,$$

$$P_{nj}^{10} = \sigma_n \{ \eta_j + \Omega^{10} a_j^0 / \beta_6^2 \} / D,$$

$$1 + (1/2) \rho_n \sigma_n P_{nn}^{11} = \{ \beta_3 / \beta_6 + \rho_n \sigma_n^2 \Omega^{10} a_n^1 / (2 \beta_6^2) \} / D, \quad (1.38)$$

where

$$a_j^0 = \beta_6 \{ Z_j \beta_6 / 2 - D_j^G - (\pi \sigma_j^2 / 2 \Delta_1) \sum_k \rho_k \sigma_k D_k^G \} / (\sigma_j D_a),$$

$$a_n^1 = \beta_6 \{ \sigma_n B^{10} / 2 + \Omega^{10} \beta_3 / (D \beta_6^2) \} / (2 D_a), \quad (1.39)$$

with the following definitions:

$$\Delta_1 = 1 - (\pi/6) \sum_k \rho_k \sigma_k^3,$$

$$m_j = J_{nj}^{10} + \pi / (6 \Delta_1) \sum_k \rho_k \sigma_k^3 J_{nk}^{10},$$

$$B^{10} = \sum_k \rho_k Z_k m_k,$$

$$S_m = (\pi/2 \Delta_1) \sum_k \rho_k \sigma_k^2 m_k,$$

$$\eta_j = [m_j + \sigma_j S_m] / \beta_6,$$

$$D = 1 + \rho_n \sigma_n^2 / (4 \beta_6^2) \sum_k \rho_k (\sigma_k m_k)^2,$$

$$D_k^F = [\beta_6 (N_k \sigma_k + Z_k) - \rho_n \sigma_n^3 B^{10} \sigma_k m_k / 12] / 2,$$

$$\Omega^{10} = \sum_k \rho_k \sigma_k m_k D_k^F,$$

$$D_{ac} = \sum_k \rho_k (D_k^F)^2,$$

$$D_a = \left\{ D_{ac} - \rho_n \sigma_n^2 \sum_{k,l} \rho_k \rho_l [(N_k \sigma_k + Z_k) m_l \sigma_l - (N_l \sigma_l + Z_l) m_k \sigma_k] / 32 \right\} / D,$$

$$B_j = \sum_k \rho_k Z_k J_{kj}^{00},$$

$$N_j = B_j + \pi \sum_k \rho_k \sigma_k^2 (\sigma_k B_k + (3/2) Z_k) / (6 \Delta_1),$$

$$P_D = (1/\beta_6) \sum_k \rho_k \sigma_k D_k^F,$$

$$P_\eta = \sum_k \rho_k (\sigma_k \beta_3 + \sigma_n \beta_6) D_k^F m_k + \beta_6^2 P_D S_m \sigma_n, \quad (1.40)$$

and also

$$D_j^G = D_j^F - \rho_n \sigma_n^2 \Omega^{10} \sigma_j m_j / (4 D \beta_6^2).$$

From the above results we find the following simple sum rules for the coefficients  $P_{ij}^{00}$  and  $P_{in}^{01}$ :

$$Z_j \beta_6 / 2 = \sum_k (\delta_{kj} + (1/2) \rho_k \sigma_j P_{kj}^{00}) D_k^F \quad (1.41)$$

and

$$\sigma_n B^{10} / 2 = \sum_k \rho_k P_{kn}^{01} D_k^F. \quad (1.42)$$

For the equal size case these two relations reduce the previously found ones<sup>22</sup>

$$1 + P^{00}/2 = \beta_6/(2D_F),$$

$$P^{01} = b_1/(2D_F), \quad (1.43)$$

where for the equal size case

$$D_F = [\beta_6(1 + b_0) - b_1^2/12]/2.$$

The symmetry requirements for the direct correlation  $C_{ij}(r)$  imply

$$P_{ij}^{00} = P_{ji}^{00} \quad (1.44)$$

and

$$P_{jn}^{01} = P_{nj}^{10}. \quad (1.45)$$

Starting from the sum rule (1.41) and (1.42) and using the scaling factor

$$\Gamma = (1/\beta_6) \sum_k \rho_k a_k^0 D_k^F \quad (1.46)$$

we find

$$D_j^F = [\beta_6(Z_j - \pi\sigma_j^2 P_D/\Delta_1)/2 - S_m A_{nj} \sigma_j \sigma_n] / [1 + \sigma_j \Gamma - P_\eta A_{nj}/(\beta_6 D_{ac})] \quad (1.47)$$

and

$$m_j = [P_\eta D_j^F - S_m \sigma_n \sigma_j \beta_6 D_{ac}] / [D_{ac}(\sigma_n \beta_6 + \sigma_j \beta_3)], \quad (1.48)$$

where

$$A_{nj} = \rho_n \sigma_j^2 \sigma_n^2 B^{10} / [8(\sigma_n \beta_6 + \sigma_j \beta_3)].$$

We have used the relation

$$B^{10} = 2 \left[ \sum_k \rho_k (1 + \sigma_k \Gamma) m_k D_k^F + \beta_6 S_m P_D \right] / (D \beta_6), \quad (1.49)$$

which comes directly from the sum rule (1.42).

We express  $D_k^F$  and  $m_k$  in terms the three parameters  $\Gamma$ ,  $B^{10}$ ,  $b_2$ , and constants which are independent of  $k$ . This is basically the formal solution of our problem.

The  $\mathbf{K}$  matrix in Eqs. (1.30) and (1.32) is given by

$$-K_{ij}^{00} = \sigma_i^3 \pi / 6 \Delta_1 + (\sigma_i^2 / 2) \times \sum_k (\delta_{ik} - \rho_k \sigma_k^2 \sigma_i \pi / 6 \Delta_1) \beta_{kj}^{00} + \sigma_i^3 \pi \chi_1 a_j^0 / 12 \Delta_1$$

$$-K_{in}^{01} = (\sigma_i^2 / 2) \sum_k (\delta_{ik} - \rho_k \sigma_k^2 \sigma_i \pi / 6 \Delta_1) \times \beta_{kn}^{01} + \sigma_i^3 \pi \chi_1 a_n^1 / 12 \Delta_1,$$

$$-K_{nj}^{10} = \sigma_n^2 \beta_{nj}^{10} / 2 \beta_6 + \sigma_n^3 B^{10} a_j^0 / (12 \beta_6),$$

$$1 - \rho_n K_{nn}^{11} = 1 / \beta_6 \{ [1 + \rho_n \sigma_n^2 \beta_{nn}^{11} / 2] + \rho_n \sigma_n^3 B^{10} a_n^1 / 12 \}, \quad (1.50)$$

where

$$\beta_{ij}^{00} = (P_{ij}^{00} - Z_i a_j^0) / \sigma_i \quad (j = 1, n-1),$$

$$\beta_{in}^{01} = (P_{in}^{01} - Z_i a_n^1) / \sigma_i,$$

$$\beta_{nj}^{10} = P_{nj}^{10} / \sigma_n \quad (j = 1, \dots, n),$$

$$\chi_1 = \sum_k \rho_k Z_k \sigma_k, \quad (1.51)$$

and elements of the matrix  $\mathbf{P}$  are defined by Eq. (1.38). Finally

the parameters  $a_j^0$  and  $a_n^1$  are given by Eq. (1.38).

We have to solve the set of three equations:

$$\sum_{k=1}^{n-1} \rho_k (a_k^0)^2 + \rho_n (a_n^1)^2 = \alpha_0^2, \quad (1.29)$$

$$- \sum_{j=1}^{n-1} \rho_j a_j^0 K_{nj}^{10} + a_n^1 (1 - \rho_n K_{nn}^{11}) = \alpha_2 \alpha_0, \quad (1.30)$$

$$(1 - \rho_n K_{nn}^{11})^2 + \rho_n \sum_k \rho_k (K_{nk}^{10})^2 = \gamma_1^2 + \rho_n \alpha_2^2 \quad (1.32)$$

for the three unknown parameters  $\Gamma$ ,  $B^{10}$ , and  $b_2$ . The procedure is to start with some convenient guess, for example, taking the mean ionic size  $\bar{\sigma} = \sum_k \rho_k \sigma_k / (\sum_k \rho_k)$  for all the ions, then, as seen in next section, we can compute everything analytically. With the values of  $\Gamma$ ,  $B^{10}$ , and  $b_2$ , using Eqs. (1.47), (1.48), and the definitions (1.40) we can generate a set of six nonlinear equations for the parameters  $D$ ,  $\Omega^{10}$ ,  $S_m$ ,  $P_D$ ,  $D_{ac}$ , and  $D_a$ , which have to be solved numerically. Once we have them, substituting back to Eqs. (1.47) and (1.48), we calculate  $P_{ij}^{mn}$ ,  $a_j$ , and finally the matrix  $\mathbf{K}$  needed in the closure relations (1.29), (1.30), and (1.32), which is then solved by numerical methods (Newton-Raphson, for example). As a test of our equations we have carried out this program.

## II. THE LIMIT OF EQUAL IONIC SIZE

We find that if the ions have the same size, we can get an explicit solution for the problem. The model becomes a mixture of ions with arbitrary charge but equal size  $\sigma$  and a dipole whose size  $\sigma_n$  is different from that of the ions. The results are very similar to the case of equal size for ions and dipole and unit charge. In order to be consistent with our previous results, we keep the notations of Sec. I.

The key step in the solution is to find the scaling relations. In this case, from Eq. (1.48), we have

$$m_k = Z_k B^{10} / \eta \quad (2.1)$$

and from Eq. (1.47),

$$N_k = Z_k b_0 / \sigma, \quad (2.2)$$

where  $B^{10}$  and  $b_0$  are our intended scaling parameters. Based on these, Eq. (1.38) can be written as

$$P_{kj}^{00} = \pi \sigma_k \sigma_j / \Delta_1 + Z_j Z_k (\beta_6 / D_F - 2) / [\eta \sigma]$$

$$P_{jn}^{01} = Z_j b_1 / [2 D_F \sqrt{\rho_n \eta \sigma}],$$

$$P_{nj}^{10} = Z_j b_1 (\beta_6 + a_1 D_F) / [\sqrt{\rho_n \eta \sigma \Delta}],$$

$$1 + (1/2) \rho_n \sigma_n P_{nn}^{11} = [2 \beta_3 \beta_6 + (\sigma_n / \sigma) D_F a_2 b_1] / [2 \Delta], \quad (2.3)$$

and after some algebra, from (1.50) we obtain

$$K_{kj}^{00} = \frac{\pi \sigma_k^2}{2 \Delta_1} \left[ \sigma_j + \frac{\sigma_k}{3} + \sigma_k \sigma_j \xi_2 \frac{\pi}{60} \right] + Z_k Z_j (\beta_6 / D_F - 2 - a_1) / [2 \eta],$$

$$K_{jn}^{01} = Z_j (b_1 / 2 D_F - a_2) / [2 \sqrt{\rho_n \eta}],$$

$$K_{nj}^{10} = Z_j b_1 \sigma_n (1 + a_1 \Lambda) / [2 \Delta \sqrt{\rho_n \eta \sigma}],$$

$$1 - \rho_n K_{nn}^{11} = (\beta_3 + a_2 b_1 \Lambda \sigma_n / 2 \sigma) / \Delta, \quad (2.4)$$

where

$$\begin{aligned}
D_F &= [\beta_6(1 + b_0) - \sigma_n b_1^2 / (12\sigma)] / 2, \\
\Delta &= b_1^2 / 4 + \beta_6^2, \\
\Lambda &= (1 + b_0) / 2 + \beta_6 \sigma_n / (6\sigma), \\
a_1 &= (\Delta - 2\beta_6 D_F) / (2D_F^2), \\
a_2 &= b_1(\Delta / 2 + \sigma \beta_3 D_F / \sigma_n) / (2D_F^2 \beta_6), \\
\eta &= \sum_k \rho_k Z_k^2, \\
b_1 &= \sqrt{\rho_n / \eta} \sigma_n \sigma B^{10}.
\end{aligned} \quad (2.5)$$

The  $\mathbf{Q}$  matrix is also explicitly given. The coefficients of Eq. (1.34) are now

$$\begin{aligned}
\alpha_{ij}^{\infty} &= \frac{2\pi}{\Delta_1} \left[ 1 + \sigma_j \xi_2 \frac{\pi}{2\Delta_1} \right], \\
\alpha_{jn}^{01} &= 0, \\
\alpha_{nj}^{10} &= 6Z_j b_1 [1 - \beta_6 + a_1(\Lambda - D_F)] / [\sqrt{\rho_n} \eta \sigma \Delta \sigma_n^2], \\
\alpha_{nn}^{11} &= 12\{\beta_3(1 - \beta_6) + \sigma_n a_2 b_1(\Lambda - D_F) / 2\sigma\} / (\rho \sigma_n^3 \Delta),
\end{aligned} \quad (2.6)$$

where

$$\xi_2 = \sum_i \rho_i \sigma_i^2.$$

From Eqs. (2.4) and (1.51), we have

$$\begin{aligned}
\beta_{kj}^{\infty} &= \pi \sigma_j / \Delta_1 + Z_k Z_j [\beta_6 / D_F - 2 - a_1] / [\eta \sigma^2], \\
\beta_{nj}^{01} &= Z_j [b_1 / 2D_F - a_2] / [\sqrt{\rho_n} \eta \sigma^2], \\
\beta_{nj}^{10} &= Z_j b_1 [\beta_6 + a_1 D_F] / [\sqrt{\rho_n} \eta \sigma_n \sigma \Delta], \\
1 + (1/2) \rho_n \sigma_n^2 \beta_{nn}^{11} &= [2\beta_3 \beta_6 + (\sigma_n / \sigma) D_F a_2 b_1] / [2\Delta].
\end{aligned} \quad (2.7)$$

The three equations for  $b_0$ ,  $b_1$ , and  $b_2$  are given explicitly

$$d_0^2 = a_1^2 + a_2^2, \quad (2.8a)$$

$$\sigma_n a_1 b_1 / 2\sigma + \beta_3 a_2 = d_0 \Delta A, \quad (2.8b)$$

$$\sigma_n^2 b_1^2 / 4\sigma^2 + \beta_3^2 = y_1^2 \Delta^2 + \Delta^2 A^2, \quad (2.8c)$$

where

$$A = d_2 - \sigma_n d_0 b_1 \Lambda / (2\Delta \sigma). \quad (2.9)$$

As was previously found there is an explicit solution of the problem of all equal sizes case in terms of a cubic.<sup>30</sup> This is also true in the present case. The key equation to get the cubic from equations above is

$$- [b_0 \beta_3 + b_1^2 \sigma_n / (6\sigma)] = 2y_1 d_0 D_F^2. \quad (2.10)$$

Using Eq. (2.8a), we have

$$c_6 b_1^6 + c_4 b_1^4 + c_2 b_1^2 + c_0 = 0, \quad (2.11)$$

where

$$\begin{aligned}
c_6 &= y_1^2 / 144, \\
c_4 &= \{y_1^2 [9(1 + \sigma_n \beta_6 / 3\sigma)^2 / 4 + 3(\beta_6 + \beta_3 \sigma / \sigma_n) \\
&\quad + 3\sigma \beta_3 b_0 / \sigma_n] - \sigma_n^2 / \sigma^2\} / 36, \\
c_2 &= y_1^2 \{[\beta_6 + \sigma \beta_3 (1 + b_0) / \sigma_n]^2 / 4 \\
&\quad - b_0 \beta_6^2 (1 + \sigma_n \beta_6 / 3\sigma) / 2\} - b_0 \sigma_n \beta_3 / 3\sigma, \\
c_0 &= b_0^2 (\beta_6^4 y_1^2 - \beta_3^2).
\end{aligned} \quad (2.12)$$

The cubic is also a quadratic equation for  $b_0$ . Simply by rearranging Eq. (2.11) we have

$$q_2 b_0^2 + q_1 b_0 + q_0 = 0, \quad (2.13)$$

where

$$\begin{aligned}
q_2 &= (\beta_6^4 y_1^2 - \beta_3^2) + y_1^2 \sigma^2 \beta_3^2 b_1^2 / (4\sigma_n^2), \\
q_1 &= y_1^2 \sigma \beta_3 b_1^4 / 12\sigma_n + b_1^2 y_1^2 [\sigma \beta_3 (\beta_6 + \sigma \beta_3 / \sigma_n) / 2\sigma_n \\
&\quad - \beta_6^2 (1 + \sigma_n \beta_6 / 3\sigma) / 2] - \sigma_n \beta_3 b_1^2 / 3\sigma, \\
q_0 &= y_1^2 b_1^6 / 144 + b_1^4 \{y_1^2 [9/4(1 + \sigma_n \beta_6 / 3\sigma)^2 \\
&\quad + 3(\beta_6 + \sigma \beta_3 / \sigma_n)] - \sigma_n^2 / \sigma^2\} / 36 \\
&\quad + y_1^2 b_1^2 (\beta_6 + \sigma \beta_3 / \sigma_n)^2 / 4.
\end{aligned} \quad (2.14)$$

Since the quadratic and even cubic equation are analytically solvable, we need to solve only one equation numerically and we can choose the correct physical branch.

The formulas can be simplified if the same scaling as in the Appendix are used. We have

$$a_1 = \beta_6 \sigma \Gamma / D_F, \quad (2.15)$$

$$a_2 = b_1 [\beta_6 \sigma \Gamma + (\beta_6 + \sigma \beta_3 / \sigma_n)] / (2D_F), \quad (2.16)$$

where

$$\begin{aligned}
D_F &= \beta_6 D / [2(1 + \sigma \Gamma)], \\
D &= 1 + b_1^2 / (4\beta_6^2).
\end{aligned} \quad (2.17)$$

In this case,  $b_0$  is related to  $\Gamma$  by

$$\begin{aligned}
b_0 &= -\sigma \Gamma / (1 + \sigma \Gamma) + b_1^2 \\
&\quad \times [1 / (1 + \sigma \Gamma) + \sigma_n \beta_6 / 3\sigma] / (4\beta_6^2).
\end{aligned} \quad (2.18)$$

Then the cubic for  $b_1^2$  can be written as

$$(b_1/2)^6 + C_4 (b_1/2)^4 + C_2 (b_1/2)^2 + C_0 = 0, \quad (2.19)$$

where

$$\begin{aligned}
C_4 &= 2\beta_6^2 + S^2 - \sigma_n^2 / (\sigma y_1)^2, \\
C_2 &= \beta_6^4 + 2\beta_6^2 S^2 + 4\sigma_n \beta_3 S / (\sigma y_1^2), \\
C_0 &= \beta_3^2 S^2 (1/\epsilon_w - 1) / y_1^2,
\end{aligned} \quad (2.20)$$

and

$$S = \beta_6 \sigma \Gamma / [\beta_6 \sigma \Gamma + (\beta_6 + \sigma \beta_3 / \sigma_n)].$$

### III. THERMODYNAMIC PROPERTIES AND DIELECTRIC CONSTANT

One of the features of the MSA is that the thermodynamic properties can be formulated without knowing the explicit expression of the pair correlation functions. Høye and Stell<sup>33</sup> have developed a general formulism for an arbitrary mixture of spherical particles. To get general expansions<sup>34</sup> for these quantities we start from the internal energy

$$\begin{aligned}
\beta \Delta E / V &= 2\pi \beta \sum_{ij} \rho_i \rho_j \sum_{mnl} (2l + 1)^{-1} \\
&\quad \times \int_{\sigma_{ij}}^{\infty} dr r^2 h_{ij}^{mnl}(r) V_{ij}^{mnl}(r),
\end{aligned} \quad (3.1)$$

where  $V_{ij}^{mnl}$  is radial coefficient of the interaction potential which is given by Eqs. (1.13), (1.14), and (1.15). From Eq. (1.26) and (1.40), we have

$$\beta\Delta E/V = \left[ \alpha_0^2 \sum_i \rho_i Z_i N_i - 2\alpha_0 \alpha_2 \rho_n B^{10} - 2\alpha^2 \rho_n b_2 / \sigma_n^3 \right] / (4\pi). \quad (3.2)$$

The free energy is given by

$$-\beta\Delta A/V = -\beta\Delta E/V + J + J', \quad (3.3)$$

where

$$J = (2/3)\pi\beta \sum_{jk} \rho_j \rho_k \sum_{mnl} (2l+1)^{-1} \times \int_{\sigma_{ij}}^{\infty} dr r^3 h_{ij}^{mnl}(r) \frac{\partial V_{ij}^{mnl}(\gamma)}{\partial \gamma} \quad (3.4)$$

and

$$J' = (\pi/3) \sum_{kj} \sum_{mnl} \rho_k \rho_j \sigma_{kj}^3 (2l+1)^{-1} [h_{kj}^{mnl}(r=\sigma_{kj}^+)]^2. \quad (3.5)$$

The contact values of correlation functions are obtained from Eq. (1.23),

$$h_{ij}^{000}(\sigma_{ij}) = (\beta_{ij}^{00} + \sigma_i \alpha_j^{00}/2) / (2\pi\sigma_{ij}), \quad (3.6)$$

$$h_{in}^{110}(\sigma_{in}) = \sqrt{3}(\beta_{in}^{10} + \sigma_i \alpha_n^{10}/2) / (2\pi\sigma_{in}), \quad (3.7)$$

$$h_{nn}^{110}(\sigma_n) = (\beta_{nn}^{11} + \sigma_n \alpha_n^{11}/2 + 2q') / (2\sqrt{3}\pi\sigma_n), \quad (3.8)$$

$$h_{nn}^{112}(\sigma_n) = \sqrt{10}(\beta_{nn}^{11} + \sigma_n \alpha_n^{11}/2 - q') / (2\sqrt{3}\pi\sigma_n), \quad (3.9)$$

where

$$q' = -b_2\beta_{24}/(\beta_{12})^2, \quad (3.10)$$

where  $b_2$ ,  $\beta_{24}$ , and  $\beta_{12}$  are the corresponding results for the  $\chi = 1$  case and the coefficients  $\alpha_{ij}^{mn}$ ,  $\beta_{ij}^{mn}$  are defined by Eqs. (1.34) and (1.51). Using again Eqs. (1.13), (1.14), (1.15), (1.26), and (1.40) we have

$$-\beta\Delta A/V = \left[ -2\alpha_0^2 \sum_j \rho_j Z_j N_j + 2\alpha_0 \alpha_2 \rho_n B^{10} \right] / (12\pi) + J'. \quad (3.11)$$

From Høye and Stell's paper,<sup>23</sup> we get

$$-\beta\rho_k\mu_k = \beta\Delta E_k/V. \quad (3.12)$$

Using Eq. (3.2) we get

$$\beta\mu_i = Z_i [\alpha_0^2 N_i - \alpha_0 \alpha_2 \rho_n m_i] / (4\pi) \quad (3.13)$$

and

$$\beta\mu_n = [-\alpha_0 \alpha_2 B^{10} - 2\alpha_2^2 b_2 / \sigma_n^3] / (4\pi). \quad (3.14)$$

The excess Gibbs free energy is

$$\beta\Delta G/V = \beta \sum_k \rho_k \mu_k + \beta\rho_n \mu_n = \beta\Delta E/V. \quad (3.15)$$

Thus the excess Gibbs free energy equals the excess internal energy. This is a result valid for the MSA. The pressure is given by

$$\beta P = \beta(E - A)/V. \quad (3.16)$$

For equal ionic size case, the formulas are of much simpler form

$$\beta\Delta E/V = [d_0^2 b_0 / \sigma^3 - 2d_0 d_2 b_1 / (\sigma^2 \sigma_n) - 2b_2 d_2^2 / \sigma_n^3] / (4\pi),$$

$$\beta\mu_k = Z_k^2 d_0 (d_0 b_0 - d_2 b_1 \sigma / \sigma_n) / (4\pi \eta \sigma^3),$$

$$\beta\mu_n = -d_2 (2d_2 b_2 - d_0 b_1 \sigma_n^2 / \sigma^2) / (4\pi \rho_n \sigma_n^3),$$

$$-\beta\Delta A/V = [-2d_0^2 b_0 / \sigma^3 + 2d_2 d_0 b_1 / (\sigma^2 \sigma_n) + J'] / (12\pi), \quad (3.17)$$

where

$$J' = (\beta_0/D_F - 2 - a_1)^2 / \sigma^3 + (\sigma + \sigma_n) b_1^2 \times [\beta_3 + a_1(3\Lambda - 2D_F)]^2 / (\Delta^2 \sigma^2 \sigma_n^2) + 4\{[\beta_3^2 + \sigma_n b_1 a_2(3\Lambda - 2D_F)/2\sigma] / \Delta - 1\}^2 / \sigma_n^2 + 2[b_2 \beta_{24} / (\beta_{12})^2]^2 / \sigma_n^3. \quad (3.18)$$

Adelman's dielectric constant can be written as

$$\epsilon_A = \left\{ (1 - \rho_n K_{nn}^{11})^2 + \rho_n \sum_k \rho_k [K_{nk}^{10}]^2 \right\} / y_1^2. \quad (3.19)$$

For equal ionic size case, we have

$$\epsilon_A = \{ (2\beta_3 + (\sigma_n/\sigma) a_2 b_1 \Lambda)^2 + (\sigma_n^2/\sigma^2) b_1^2 (1 + a_1 \Lambda)^2 \} / [4y_1^2 \Delta^2]. \quad (3.20)$$

Wertheim's dielectric constant is

$$\epsilon_W = \beta_3^2 \beta_{12}^2 / \beta_6^6. \quad (3.21)$$

Since we have computed explicitly all the coefficients of the Wertheim-Baxter functions (1.34), then using Eq. (1.23) we can compute all pair correlations between ions and dipoles. The procedure is described in detail in Refs. 31 and 32.

#### IV. THE LOW DENSITY EXPANSION

Although the equal ionic size results we got are very simple, there are still three algebraic equations to be solved. It is desirable to have a completely explicit solution in the low ionic density region. Starting from the Eqs. (2.8b), (2.8c), and (2.10), we can write

$$\begin{aligned} F_1(d_0, d_2) &= d_0, \\ F_2(d_0, d_2) &= -d_0 d_2, \\ F_3(d_0, d_2) &= d_2^2. \end{aligned} \quad (4.1)$$

When  $d_0 \rightarrow 0$ , we expand using Taylor's series

$$F_n(d_0, d_2) = F_n(0, d_2) + d_0 \left. \frac{\partial F_n}{\partial d_0} \right|_{d_0=0} + (d_0^2/2) \left. \frac{\partial^2 F_n}{\partial d_0^2} \right|_{d_0=0} + \dots \quad (4.2)$$

Comparing the coefficients of both sides, we obtain

$$\partial^n b_m / \partial^n d_0, \quad m = 0, 1, 2, \quad n = 1, 2, 3. \quad (4.3)$$

The expansion yields

$$\begin{aligned} b_0 &= -\kappa/2 + \kappa^2 b_0^{(2)}/2, \\ b_1 &= b_1^{(1)}\kappa + b_1^{(2)}\kappa^2/2, \\ b_2 &= b_2^{(0)} + b_2^{(2)}\kappa^2/2 + b_2^{(3)}\kappa^3/6, \end{aligned} \quad (4.4)$$

where

$$\kappa = d_0/\sqrt{\epsilon}. \quad (4.5)$$

$\epsilon$  is Wertheim's dielectric constant (2.18), and

$$\begin{aligned} b_0^{(2)} &= \{1 - d_2^2 \beta_{12}^6 \sigma_n / [3\sqrt{\epsilon} \sigma \beta_6 (\beta_6 + \sigma \beta_3 / \sigma_n)^2]\}, \\ b_1^{(1)} &= d_2 \beta_{12}^2 \beta_6 / (\beta_6 + \sigma \beta_3 / \sigma_n), \end{aligned}$$

$$\begin{aligned} b_1^{(2)} &= -d_2 \beta_{12}^2 \beta_6 [\beta_6 \sqrt{\sigma_n / \sigma} + \beta_3 \sqrt{\sigma / \sigma_n}]^2 / [\beta_3 (\beta_6 + \sigma \beta_3 / \sigma_n)^2], \\ b_2^{(2)} &= -3\beta_{12}^5 \{[\sigma_n^2 \beta_6^2 / \sigma^2 - 2\beta_3^2] (b_1^{(1)})^2 / 2\beta_6 + \sqrt{\epsilon} \sigma_n \beta_6^3 d_2 [1 + \sigma_n \beta_6 / 3\sigma] b_1^{(1)} / \sigma\} / [4\beta_3 \beta_{12}^6 + 2\beta_6 \beta_{24}], \\ b_2^{(3)} &= \frac{-3\beta_3 \beta_6^2 \beta_{12}^7}{2[2\beta_3 \beta_{12}^6 + \beta_{24} \beta_6^6]} \{[\sigma_n^2 \beta_6^2 / \sigma^2 - 2\beta_3^2] [1 + b_1^{(1)} / \sqrt{\epsilon}] b_1^{(2)} / 2\beta_6^6 - 3d_2 b_1^{(1)} \sigma_n / (4\beta_6^2 \sigma) \\ &\quad + d_2 (1 + \sigma_n \beta_6 / 3\sigma) \sigma_n b_1^{(2)} / (\beta_6^2 \sigma) + b_2^{(2)} [(4\beta_{12} \beta_6 + \beta_3 \beta_6 + 10\beta_3 \beta_{12}) / (9\beta_6^6) \\ &\quad - (4\beta_{24} \beta_{12} + \beta_6 \beta_{12} + 10\beta_{24} \beta_6) / (36\beta_{12}^6)]\}. \end{aligned} \quad (4.6)$$

All the thermodynamic properties and correlation functions can be expressed as functions of the three parameters  $b_0$ ,  $b_1$ , and  $b_2$ ,<sup>31</sup> as will be seen below.

For the all equal size case,  $\sigma = \sigma_n$ , the coefficients are much simpler:

$$\begin{aligned} b_0 &= -\kappa/2 + \kappa^2/2 [1 - \beta_{12}^2 d_2^2 / 12\beta_6 \sqrt{\epsilon}], \\ b_1 &= \kappa d_2 \beta_6 \beta_{12} (1 - \kappa \beta_6 \beta_{12} / \beta_3) / 2, \\ b_2 &= b_2^{(0)} + b_2^{(2)} \kappa^2 / 2 + b_2^{(3)} \kappa^3 / 6, \end{aligned} \quad (4.7)$$

where  $b_2^{(0)}$  is the corresponding solution for pure dipole, and

$$\begin{aligned} b_2^{(2)} &= -d_2^2 \beta_6 \beta_{12}^7 [3\beta_6^2 + 2\beta_3 (8\beta_{12} \beta_{24} - 3\beta_3)] / [32(2\beta_3 \beta_{12}^6 + \beta_{24} \beta_6^6)], \\ b_2^{(3)} &= \frac{d_2^2 \sqrt{\epsilon} \beta_{12}^5 \beta_3}{4[2\epsilon \beta_{12}^6 + \beta_3 \beta_{24}]} \{(\beta_6^2 - 2\beta_3^2) \beta_{12}^2 [1/d_2 + \beta_6 \beta_{12} / (2\sqrt{\epsilon})] / (2\beta_6^5 \beta_3) + 3\beta_{12} / 8\beta_6 + 4\beta_{24} \beta_{12} / (3\beta_6 \beta_3) \\ &\quad + 2b_2^{(2)} [(4\beta_{12} \beta_6 + \beta_3 \beta_6 + 10\beta_3 \beta_{12}) / (9\beta_6^6) - (4\beta_{24} \beta_{12} + \beta_6 \beta_{12} + 10\beta_{24} \beta_6) / (36\beta_{12}^6)] / d_2^2\}. \end{aligned} \quad (4.8)$$

For the thermodynamic properties, we get

$$\begin{aligned} \beta \Delta E / V &= [-b_2^{(2)} d_2^2 \kappa^2 - 2b_2^{(0)} d_2^2 - \kappa d_0 d_2^2 \beta_6 \beta_{12}] / 4\pi, \\ \beta A / V &= [-\kappa d_0 d_2^2 \beta_6 \beta_{12} + \kappa^2 d_2^2 \beta_{12}^2 \beta_3^2 / 2\beta_6^2 + d_2^2 \kappa^2 \beta_{12}^4 / 4] + 2(b_2^{(0)} \beta_{24} / \beta_{12}^2)^2 / (12\pi). \end{aligned} \quad (4.9)$$

Note that  $\beta_n$ ,  $\epsilon$ , and  $d_2$  are the value at  $d_0 = 0$ . Using parameters appropriate for an aqueous solution with ion size equal (2.76 Å), we find that this expansion is accurate up to 0.1 M in ionic concentration,  $T = -298$  K,  $\rho_n = 0.033$ ,  $\sigma_+ = \sigma_- = \sigma_n = 2.76$  Å.

## V. THE HIGH COUPLING LIMIT

The recent works of Rosenfeld and Blum<sup>9,10</sup> explored rather completely the behavior of ionic fluids in the high coupling limit. In this limit, the MSA and the HNC internal energy are the same, and also the problem reveals very simple feature. We find that the elements of Baxter matrix  $\mathbf{Q}$  has only one instead of two parameters. The reason is that in this limit there is only one independent equation for  $\mathbf{Q}$ , at the same time there appears another relation for the two param-

eters of the elements of  $\mathbf{Q}$ . The equal size case, we get, directly from Eqs. (1.29) and (1.33),

$$\begin{aligned} Q_{ii}(r) &= Q'_{ii}(r-1) \quad \text{for ion-ion}, \\ Q_{in}(r) &= Q'_{in}(r-1) \quad \text{for ion-dipole}, \\ Q_{nn}(r) &= Q'_{nn}(r-1) \quad \text{for dipole-dipole}. \end{aligned} \quad (5.1)$$

Actually there are two limits for the ion-dipole mixture, one is  $d_0 \rightarrow \infty$  the other is the  $d_2 \rightarrow \infty$ , it turns out that the results are different.

Let us consider the first one,  $d_0 \rightarrow \infty$ , immediately, we find

$$\beta_n = 1, \quad n = 3, 6, 12 \quad (5.2)$$

and



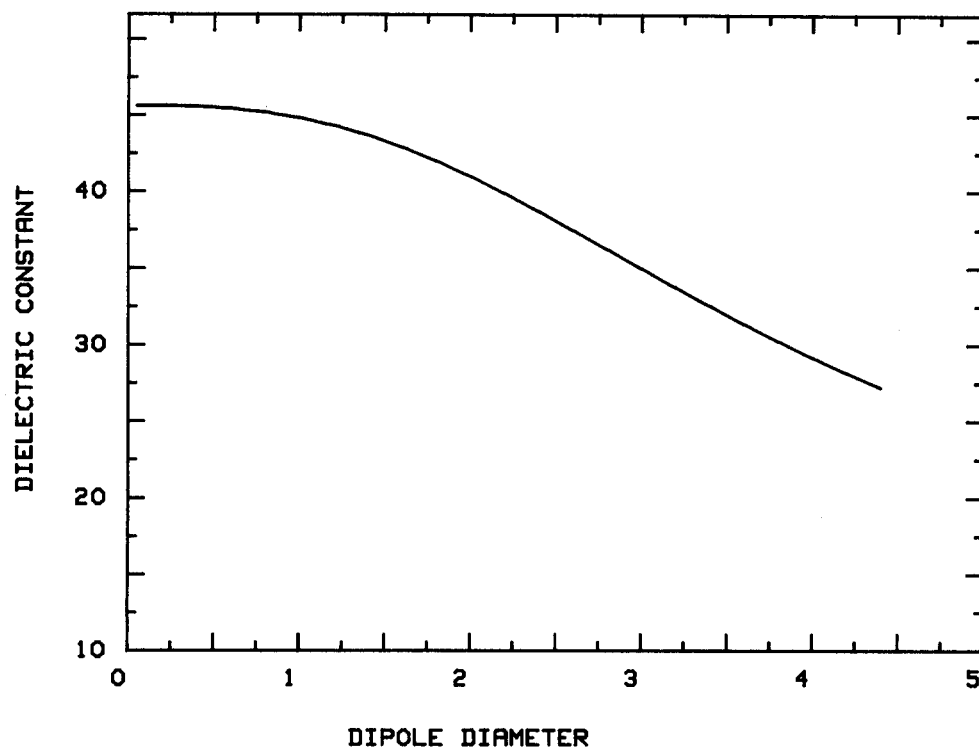


FIG. 1. Plot of the dielectric constant as a function of the diameter of the dipole. The ionic concentration is 0.3 M, and the dipole density emulates water  $\rho_n = 0.033$ ,  $T = 298$  K,  $\sigma = 2.7$  Å,  $\mu = 1.85$  D, and  $|Z_1| = |Z_2| = 1$ .

$$\begin{aligned} b_2 &= 0, \\ b_1 &= 12d_2/d_0, \\ b_0 &= -\sqrt{d_0}/(\sqrt{2} + \sqrt{d_0}), \end{aligned} \quad (5.3)$$

when  $d_2 \rightarrow \infty$ ,

$$\begin{aligned} \beta_6 &= \sqrt{3/d_2}, \\ b_1 &= d_0/d_2, \\ b_0 &= -d_0^2/(18d_2^2), \end{aligned} \quad (5.4)$$

It is interesting to note that in both limits,  $b_1 \rightarrow 0$ , which seems to indicate that the ions and the dipole solvent are immiscible in this limit.

## VI. RESULTS AND DISCUSSION

Indeed the analytical results of the previous sections provide the framework for computing the properties of realistic nonprimitive models of ionic solutions. However, the

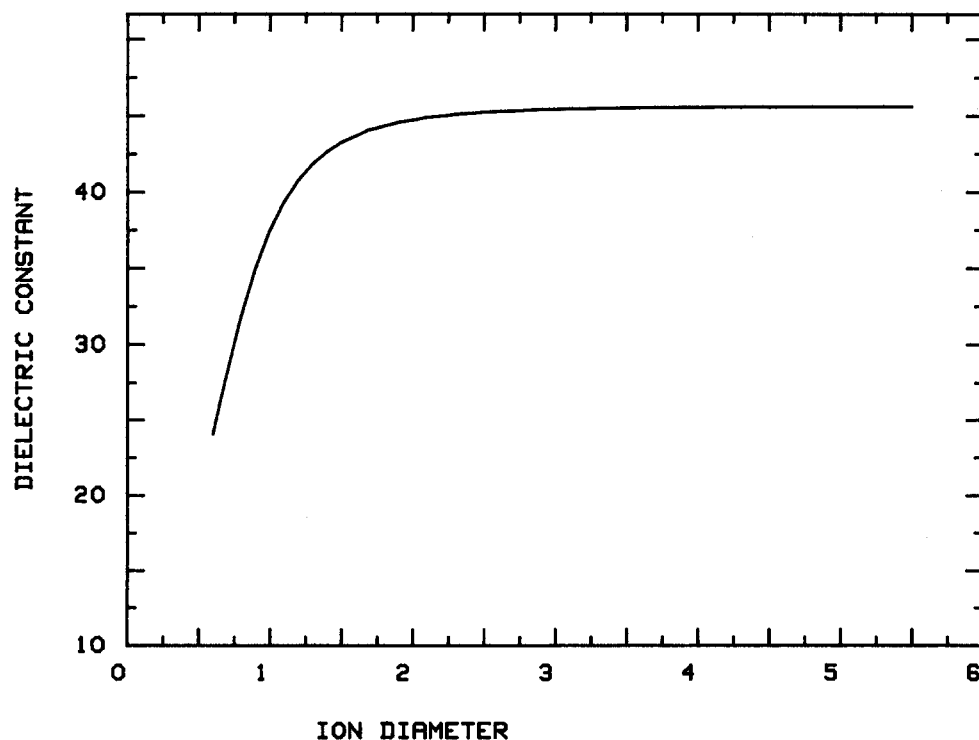


FIG. 2. Plot of the dielectric constant as a function of the ionic diameter. The volume fraction of ions is kept constant  $\rho_i = \pi/6000$ ,  $T = 298$  K,  $\rho_n = 0.0175$ ,  $\sigma_n = 1$  Å,  $\mu = 1.85$  D, and  $|Z_1| = |Z_2| = 1$ .

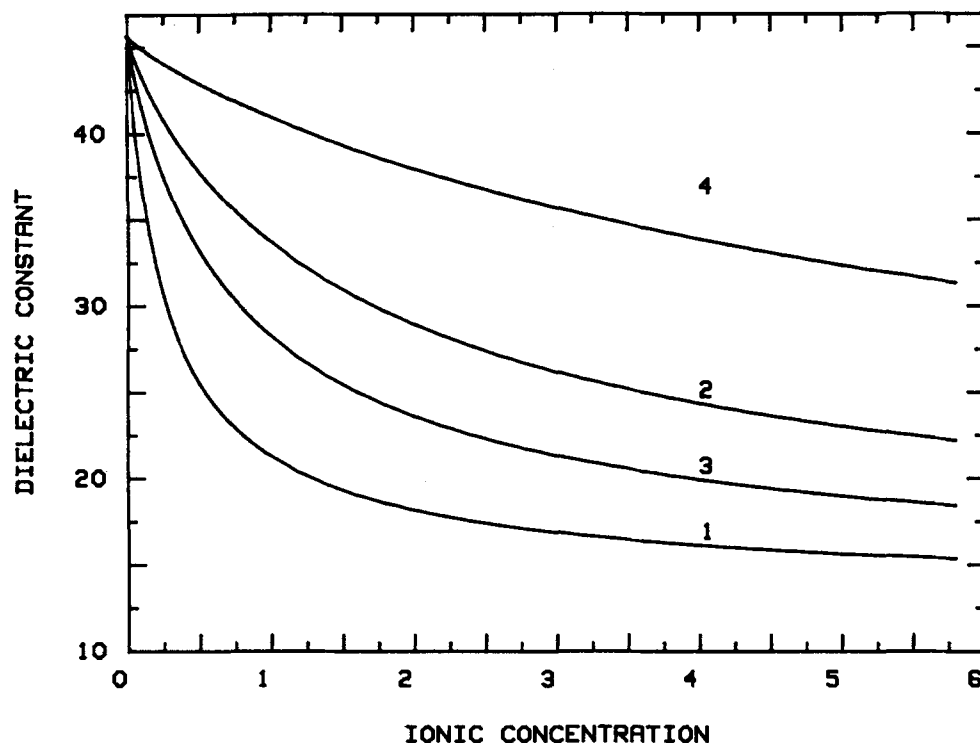


FIG. 3. Plot of the dielectric constant as a function of the ionic concentration (in  $M/\ell$ ). The ratios of ion and dipole diameter are 2.76/4.00 (line 1), 2.76/2.76 (line 2), 5.76/2.76 (line 3), and 17.76/2.76 (line 4). The density of dipolar solvent is that of water and  $T = 298$  K,  $\mu = 1.85$  D, and  $|Z_1| = |Z_2| = 1$ .

equations for the most general case are still not very easy to handle, certainly not as easy as the case of the primitive model, where the thermodynamics can be calculated with the aid of a hand calculator.<sup>3</sup>

The situation here is certainly not that simple, but it is surely true that for a very dilute solution, one must recover the primitive model equations as is shown explicitly in the

Appendix. But there are also two other regions in which this should happen; if the size of ions becomes very large (for example, in micellar solution) or the dipolar size shrinks to zero, in effect becoming a dielectric continuum. We have performed calculation for these cases using the easier case of equal ionic diameters. Figures 1 and 2 show the variations of the Adelman's

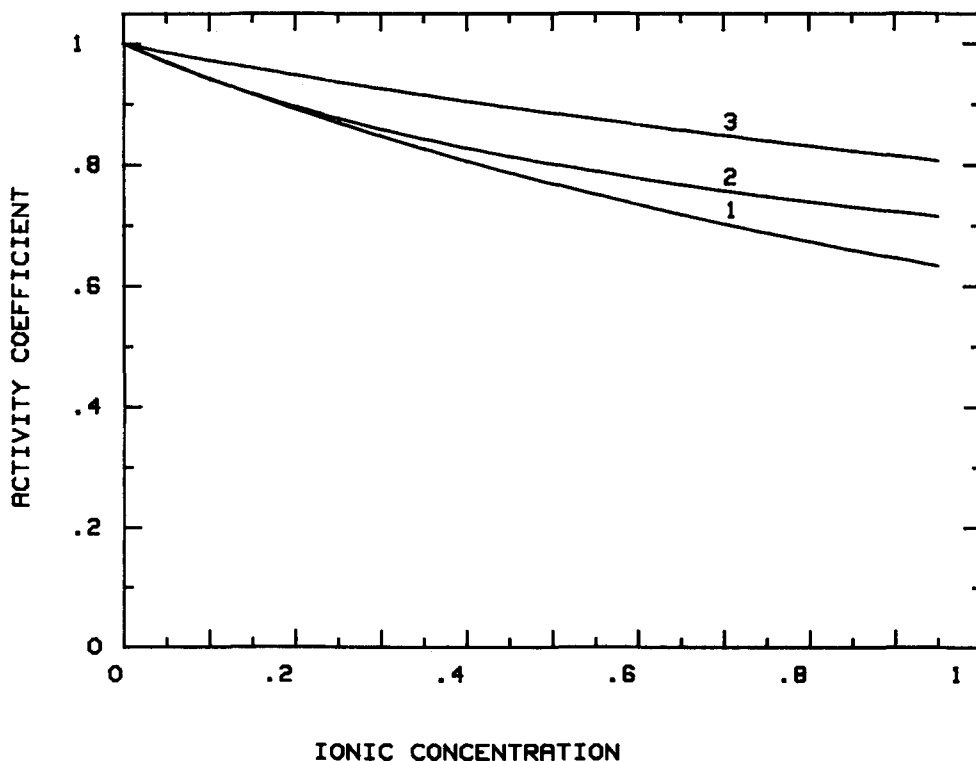


FIG. 4. Plot of the activity coefficient of dipolar solvent as a function of the ionic concentration (in  $M/\ell$ ). The ratios of ion and dipole diameter are 2.76/2.76 (line 1), 2.76/4.76 (line 2), 4.76/2.76 (line 3), the density of dipolar solvent is that of water, and  $T = 298$  K,  $\mu = 1.85$  D, and  $|Z_1| = |Z_2| = 1$ .

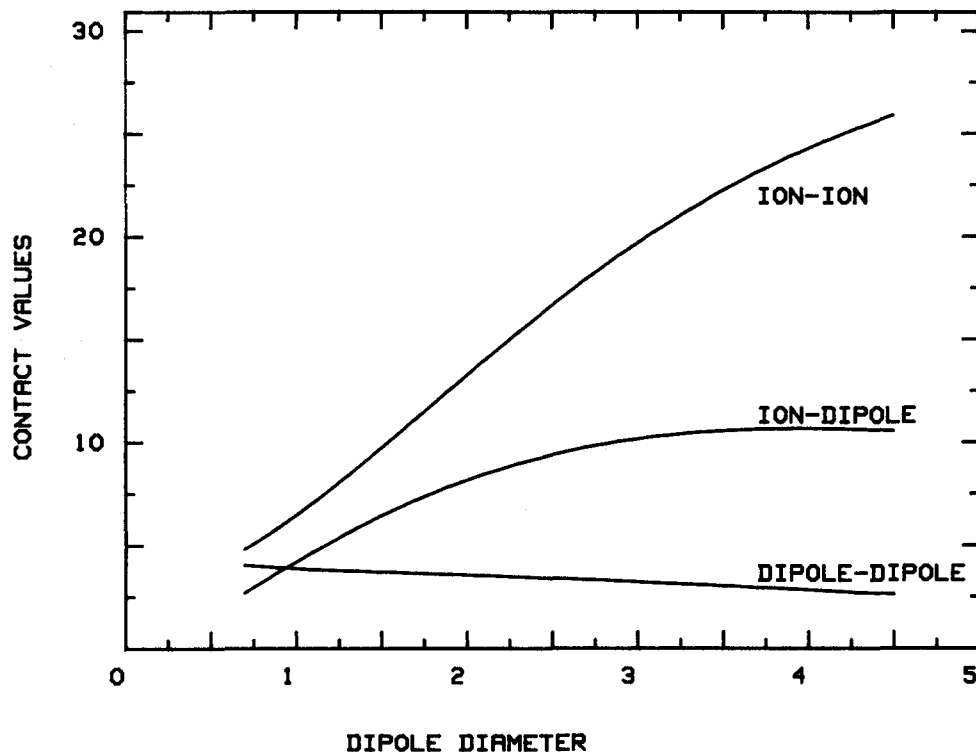


FIG. 5. Plot of the contact values  $h_{12}^{00}$ ,  $h_{in}^{110}$ , and  $h_{nn}^{112}$  as a function of the diameter of dipolar solvent. The concentration of the ions is 1 M, the density of dipolar solvent is that of water and  $T = 298$  K,  $\sigma = 2.76$  Å,  $\mu = 1.85$  D, and  $|Z_1| = |Z_2| = 1$ .

$$\epsilon_A = \{ (2\beta_3 + (\sigma_n/\sigma)a_2b_1\Lambda)^2 + (\sigma_n^2/\sigma^2)b_1^2(1+a_1\Lambda)^2 \} / [4\gamma_1^2\Delta], \quad (2.17)$$

with the ratio  $\sigma/\sigma_n$  of the solute/solvent diameter.

For given size ratios, we have computed also the variation of the Adelman's dielectric constant with ionic concentrations which is depicted in Fig. 3. Figure 4 shows the vari-

ation of the solvent activity coefficient for the same circumstances.

Another interesting quantity is the contact probability of two ions. This is relevant in the theory of electron exchange interactions. The results are shown in Fig. 5 for anion-cation, ion-dipole, dipole-dipole pair correlations. We must, however, point out that for these quantities the MSA

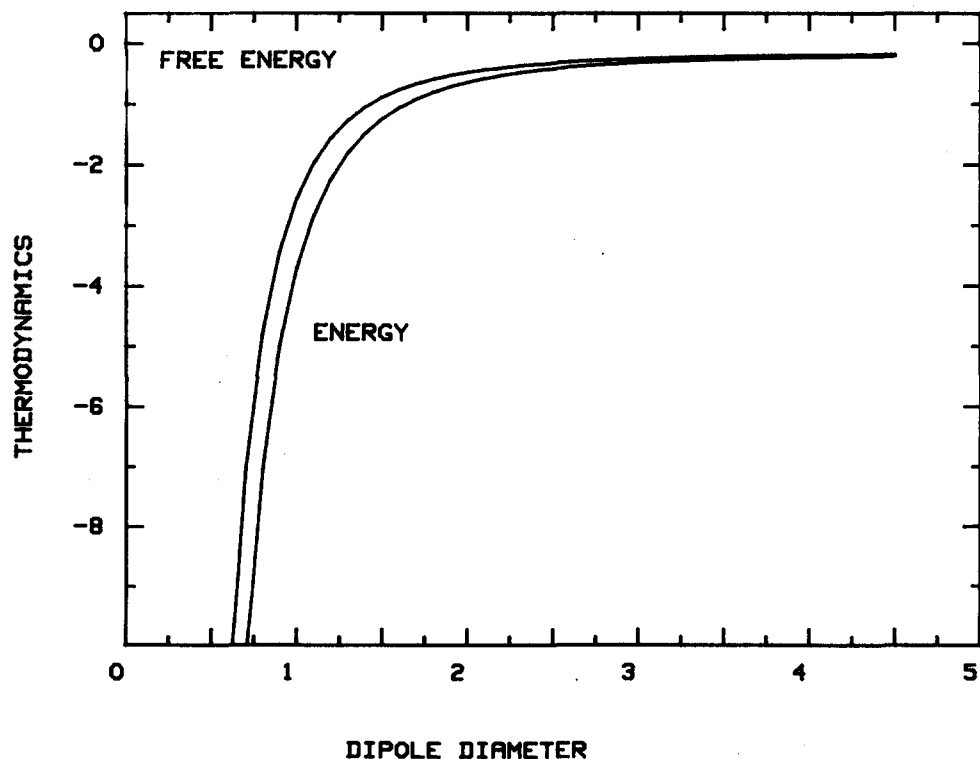


FIG. 6. Plot of the thermodynamic properties as a function of the diameter of dipolar solvent. The concentration of the ions is 1 M, the density of dipolar solvent is that of water, and  $T = 298$  K,  $\sigma = 2.76$  Å,  $\mu = 1.85$  D, and  $|Z_1| = |Z_2| = 1$ .

are not accurate. Finally, results for internal energy and free energy are shown in Fig. 6 for the case of 1 M solution as a function of the diameter of the solvent.

## ACKNOWLEDGMENTS

This work is supported by NSF Grant CHE 85-03503 and PRF Grant 154763-AC7.

## APPENDIX: THE EQUAL SIZE CASE UNDER THE NEW SCALING

If we go over to the complete equal size case, we find a much simpler form than previous work.<sup>31,32</sup> This also serves as a check of our present solution. Let  $\sigma_n$  and  $\sigma_i$  be equal to  $\sigma$  and define

$$b_1 = \sqrt{\rho_n/\eta} \sigma^2 B^{10} \quad (\text{A1})$$

and

$$\eta = \sum_k \rho_k Z_k^2, \quad (\text{A2})$$

then we have

$$\begin{aligned} m_k &= Z_k B^{10}/\eta, \\ D_k^F &= Z_k \Delta/[2(1 + \sigma\Gamma)\beta_6], \\ D_a &= \eta\Delta/[4(1 + \sigma\Gamma)^2], \\ a_1 &= \sigma\Gamma\beta_6/D_F, \\ a_2 &= b_1(\sigma\Gamma\beta_6 + 2\beta_{12})/(2\beta_6 D_F), \end{aligned} \quad (\text{A3})$$

where

$$\begin{aligned} D_F &= \Delta/[2(1 + \sigma\Gamma)\beta_6], \\ \Delta &= b_1^2/4 + \beta_6^2. \end{aligned} \quad (\text{A4})$$

The three algebraic equations can be written as

$$a_1^2 + a_2^2 = d_0^2, \quad (\text{A5a})$$

$$a_1 b_1/2 + \beta_3 a_2 = d_0 \Delta A, \quad (\text{A5b})$$

$$b_1^2/4 + \beta_3^2 = y_1^2 \Delta^2 + \Delta^2 A^2, \quad (\text{A5c})$$

where

$$\begin{aligned} A &= d_2 - d_0 b_1 \Lambda / 2\Delta, \\ \Lambda &= D_F [1 + (1 + \sigma\Gamma)\beta_6/3]/\beta_6, \\ d_0^2 &= \eta \sigma^2 \alpha_0^2, \\ d_2^2 &= \rho_n \alpha_2^2. \end{aligned} \quad (\text{A6})$$

The cubic equation for  $b_1^2$  now reads

$$(b_1/2)^6 + c_4(b_1/2)^4 + c_2(b_1/2)^2 + c_0 = 0, \quad (\text{A7})$$

where

$$\begin{aligned} c_4 &= 2\beta_6^2 - 1/y_1^2 + S^2, \\ c_2 &= \beta_6^4 + 4S\beta_3/y_1^2 + 2\beta_6^2 S^2, \\ c_0 &= S^2(\beta_6^4 - \beta_3^2/y_1^2), \end{aligned} \quad (\text{A8})$$

where

$$S = \sigma\Gamma\beta_6^2/(\sigma\Gamma\beta_6 + 2\beta_{12}). \quad (\text{A9})$$

If we use the following relation

$$\begin{aligned} b_0 &= -\sigma\Gamma/(1 + \sigma\Gamma) + b_1^2[1/(1 + \sigma\Gamma) \\ &\quad + \beta_6/3]/(4\beta_6^2), \end{aligned} \quad (\text{A10})$$

we can recover the equations previously obtained for this case.<sup>11</sup>

If we look carefully at Eqs. (A5a) and (A5c), the first equation gives

$$\begin{aligned} -\sigma\Gamma(1 + \sigma\Gamma) + b_1^2[(1 + \sigma\Gamma)/4\beta_6^2 \\ + (1 + \sigma\Gamma)/3\beta_6\beta_3] = d_0\Delta/(2\epsilon\beta_6^2). \end{aligned} \quad (\text{A11})$$

When dipole moment of the solvent approaches to zero the  $b_1$  is zero, then Eq. (A11) goes immediately to that of the primitive model gotten by Waisman and Lebowitz<sup>1</sup> with the definition

$$b_0 = -\sigma\Gamma/(1 + \sigma\Gamma) \quad (\text{A12})$$

and both sides of the other two equations in Eq. (A5) equal zero.

<sup>1</sup>E. Waisman and J. L. Lebowitz, *J. Chem. Phys.* **52**, 4307 (1970); **56**, 3086, 3093 (1972).

<sup>2</sup>L. Blum, *Mol. Phys.* **30**, 1529 (1975).

<sup>3</sup>L. Blum and J. S. Høye, *J. Phys. Chem.* **81**, 1311 (1977).

<sup>4</sup>K. Hiroike, *Mol. Phys.* **33**, 1195 (1977).

<sup>5</sup>L. Blum and A. H. Narten, *J. Chem. Phys.* **56**, 5197 (1972).

<sup>6</sup>M. Gillan, *J. Phys. C* **7**, L1 (1974).

<sup>7</sup>A. H. Narten, L. Blum, and R. H. Fowler, *J. Chem. Phys.* **60**, 3378 (1974).

<sup>8</sup>G. Senatore and L. Blum, *J. Phys. Chem.* **89**, 2676 (1985).

<sup>9</sup>Y. Rosenfeld and L. Blum, *J. Phys. Chem.* **89**, 5149 (1985).

<sup>10</sup>Y. Rosenfeld and L. Blum, *J. Chem. Phys.* **85**, 1556 (1986).

<sup>11</sup>L. Blum, *Chem. Phys. Lett.* **26**, 200 (1974), *J. Chem. Phys.* **61**, 2129 (1974).

<sup>12</sup>S. A. Adelman and J. M. Deutch, *J. Chem. Phys.* **60**, 3935 (1974).

<sup>13</sup>D. Y. C. Chan, D. Mitchell, and B. Ninham, *J. Chem. Phys.* **70**, 2949 (1979).

<sup>14</sup>S. L. Carnie and D. Y. C. Chan, *J. Chem. Phys.* **73**, 2946 (1980).

<sup>15</sup>P. Garisto, P. Kusalik, and G. N. Patey, *J. Chem. Phys.* **79**, 6294 (1983).

<sup>16</sup>D. Levesque, J. Weis, and G. N. Patey, *J. Chem. Phys.* **72**, 1887 (1980).

<sup>17</sup>P. H. Fries and G. N. Patey, *J. Chem. Phys.* **82**, 429 (1985).

<sup>18</sup>G. N. Patey and J. P. Valleau, *J. Chem. Phys.* **63**, 2334 (1975).

<sup>19</sup>C. W. Outhwaite, *Mol. Phys.* **31**, 1345 (1976).

<sup>20</sup>C. W. Outhwaite, *Mol. Phys.* **33**, 1229 (1977).

<sup>21</sup>D. Henderson, J. Barojas, and L. Blum, *Rev. Mex. Fis.* **30**, 139 (1984).

<sup>22</sup>L. Blum, *J. Stat. Phys.* **18**, 451 (1978).

<sup>23</sup>L. Blum and A. J. Torruella, *J. Chem. Phys.* **56**, 303 (1972).

<sup>24</sup>L. Blum, *J. Chem. Phys.* **57**, 1862 (1972); **58**, 3295 (1973).

<sup>25</sup>A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Princeton, 1960).

<sup>26</sup>M. S. Wertheim, *J. Chem. Phys.* **55**, 4291 (1971).

<sup>27</sup>J. S. Høye and L. Blum, *J. Stat. Phys.* **16**, 399 (1977).

<sup>28</sup>L. Blum and J. S. Høye, *J. Stat. Phys.* **19**, 317 (1978).

<sup>29</sup>F. Vericat and L. Blum, *J. Stat. Phys.* **22**, 593 (1980).

<sup>30</sup>W. P. Hernandez and L. Blum, *J. Stat. Phys.* **24**, 451 (1981).

<sup>31</sup>F. Vericat and L. Blum, *Mol. Phys.* **45**, 1067 (1982).

<sup>32</sup>L. Blum and F. Vericat, in *The Chemical Physics of Solvation*, edited by R. R. Dogonadze, E. Kalman, A. A. Kornishev, and J. Ulstrup (Elsevier, Amsterdam, 1985).

<sup>33</sup>J. S. Høye and G. Stell, *J. Chem. Phys.* **67**, 429 (1977).

<sup>34</sup>F. Vericat and R. Grigera, *An. Quim.* **68**, 27 (1980).