

Exact solution of the mean spherical model for simple polar mixtures*

S. A. Adelman and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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Wertheim's solution of the *mean spherical model* (MSM) for pure fluids composed of hard spheres with embedded dipoles [J. Chem. Phys. 55, 4291 (1971)] is extended to multicomponent polar fluid mixtures. The components are restricted to have equal hard sphere radii but may have different dipole moments. The anisotropic part of the pair correlation functions for an m -component fluid characterized by hard sphere diameter d , temperature parameter β , dipole moments $\mu_1, \mu_2, \dots, \mu_m$, and densities $\rho_1, \rho_2, \dots, \rho_m$ are shown to be expressible in terms of the corresponding functions for an effective pure MSM polar fluid with the same hard sphere radius and the same temperature parameter but with an effective dipole moment $\hat{\mu} = [m^{-1}(\mu_1^2 + \mu_2^2 + \dots + \mu_m^2)]^{1/2}$ and an effective density $\hat{\rho} = \hat{\mu}^{-2}(\mu_1^2 \rho_1 + \mu_2^2 \rho_2 + \dots + \mu_m^2 \rho_m)$. The excess thermodynamic properties of the mixture (relative to a pure hard sphere Percus-Yevick fluid) are shown to be those of the effective pure fluid. The dielectric constant of the mixture is also that of the effective pure fluid. The case of polar-nonpolar mixtures is considered by allowing one or more of the dipole moments to vanish. It is found that the potential of mean force and spatial distribution of the nonpolar molecules is independent of the magnitude of the dipoles while the anisotropic correlations between the polar molecules are independent of the presence of the nonpolar species.

I. INTRODUCTION AND SUMMARY OF RESULTS

The *mean spherical model* (MSM) was introduced by Lebowitz and Percus¹ as a generalization to fluid systems with hard sphere interactions of the spherical model for Ising spin systems. The MSM, which is specified in Sec. II, is based on reasonable though somewhat drastic approximations. It invites study because it has the virtue of yielding analytic results for systems of physical interest.

Recently Wertheim² has presented an exact solution of the MSM for a pure polar fluid consisting of hard spheres with embedded permanent dipole moments. The importance of Wertheim's contribution is that it provides remarkably simple analytic expressions for a variety of quantities of interest such as the dielectric constant, Kirkwood's "g" factor,³ and the thermodynamic functions⁴ of the polar fluid. Previously, models did not exist that yielded explicit results for these important quantities. Analysis of the MSM serves to sharpen our understanding of real polar liquids, a most important class of fluids.

In this paper we present an exact solution of the MSM for a multicomponent polar mixture. The model fluid, which is treated in the MSM approximation, consists of a mixture of hard spheres with the molecules of each component bearing a different embedded permanent electric dipole moment. For reasons of mathematical simplicity, we have assumed equal hard sphere diameters for the different components; however many of the conclusions would be unchanged if this assumption were removed. Attention is restricted to an infinite sys-

tem. Our motivation for undertaking this study is that it is the first example of an analytically solved model of a fluid mixture where an anisotropic pair potential is involved. Furthermore while the MSM model is too crude to expect close agreement of its predictions with experiment, the results we obtain may prove useful to those interpreting measurements on real solutions of polar molecules. Finally we note that a most interesting limiting case of the model occurs when the dipole moments of one or more of the species are shrunk to zero. In this limit our model reduces to a multicomponent solution of nonpolar species (hard spheres) in a polar solvent and we are in a position to examine the pair distribution and the potential of mean force between two nonpolar molecules.

Because the mathematical analysis required for solution of the MSM is rather involved, we summarize for the reader the main results of the calculation and point out where the results may be found in the body of the paper.

(1) An exact expression is found for the two particle correlation function $G_{ij} \equiv H_{ij} + 1$ for species i and j [Eq. (4.44)]. The remarkable fact is that these correlation functions are completely determined from the pure polar fluid result of Wertheim. Specifically, the correlation functions H_{ij} of an m -component mixture specified by number densities $\rho_1, \rho_2, \dots, \rho_m$ and dipole moments $\mu_1, \mu_2, \dots, \mu_m$ at a particular temperature are determined by MSM for an effective pure polar fluid with dipole moment

$$\hat{\mu}^2 = m^{-1} \sum_{i=1}^m \mu_i^2 \quad (1.1)$$

at the same temperature and at a density

$$\hat{\rho} = \hat{\mu}^{-2} \sum_{i=1}^m \mu_i^2 \rho_i. \quad (1.2)$$

Thus the multicomponent MSM polar fluid problem (with equal hard sphere radii) is reduced to an effective one-component MSM polar fluid problem.

(2) The excess thermodynamic properties relative to the reference hard sphere system are determined for the internal energy [Eq. (5.3)], the Helmholtz free energy [Eq. (5.5)], and the pressure [Eq. (5.10)]. The expressions for the excess thermodynamic properties of the multicomponent MSM polar fluid system are identical to the expressions for the excess properties in the pure polar MSM system⁴ evaluated at the effective density $\hat{\rho}$ and the effective dipole moment $\hat{\mu}$.

(3) An expression is obtained for the dielectric constant of the polar mixture [Eq. (6.2)] which, again, is identical to the expression for the dielectric constant of the effective pure dipolar fluid.

(4) An explicit expression is obtained for the potential of mean force between any two species at large separation [Eq. (7.2)]. The form of this expression is similar to the one-component result.

(5) The interesting limiting case where the dipole moments of one or more of the components vanish corresponds to a crude model of a polar-nonpolar solution. In this limit we find from the model (Sec. VIII) that (a) the pair correlation functions of the nonpolar species are unaffected by the dipoles on the remaining polar components, (b) the anisotropic part of the pair correlation function of the polar species is unaffected by the presence of the nonpolar species, and (c) the dielectric constant and excess thermodynamic properties of the mixture are unchanged if some or all of the nonpolar molecules are removed under conditions which keep the densities of the polar species and the temperature constant. These results represent important qualitative limitations of the MSM since we would anticipate effects on all these quantities from the expected local segregation of nonpolar species as the polarity of the polar solvent is increased. These limitations are a consequence of the assumed linearity in the MSM between the direct correlation function and the dipole-dipole potential [Eq. (2.4)]. They can be overcome by introducing nonlinearity into the model in a way that will mix the effects of the hard core and dipole-dipole forces. Alternatively, addition of anisotropic forces of appropriate symmetry could couple polar and nonpolar molecules so as to produce the segregation effect even within a linear MSM-type theory. Analytically tractable models which incorporate either or both of these generalizations, however, have not yet been developed.

II. SPECIFICATION OF THE MODEL

The Ornstein-Zernike equation for a multicomponent fluid composed of linear molecules is

$$H_{ij}(X_1, X_2) - C_{ij}(X_1, X_2) = (1/4\pi) \sum_k \int C_{ik}(X_1, X_3) \rho_k H_{kj}(X_3, X_2) dX_3, \quad (2.1)$$

where $X_\alpha = (\mathbf{r}_\alpha, \Omega_\alpha)$ refers to the center of mass position \mathbf{r}_α and orientation $\Omega_\alpha = (\theta_\alpha, \phi_\alpha)$ of molecule α , ρ_k is the number density of species k , and C_{ij} and H_{ij} are, respectively, the direct and indirect correlation functions for species i and j . In matrix notation, which we shall use throughout, Eq. (2.1) is

$$\mathbf{H}(X_1, X_2) - \mathbf{C}(X_1, X_2) = (1/4\pi) \int \mathbf{C}(X_1, X_3) \boldsymbol{\rho} \mathbf{H}(X_3, X_2) dX_3, \quad (2.2)$$

where $\boldsymbol{\rho}$ is a diagonal matrix of species densities and the elements $F_{ij}(X_1, X_2)$ of the correlation function matrix $\mathbf{F}(X_1, X_2)$ (\mathbf{F} equals \mathbf{C} or \mathbf{H} here and below) give the correlation of a molecule of species i with configuration X_1 with a molecule of species j with configuration X_2 .

The MSM model for the case of dipolar mixtures with equal radii is defined by the Ornstein-Zernike equation, Eq. (2.2), and the following closure conditions:

$$\mathbf{V}(X_1, X_2) = \infty \quad \text{or} \quad \mathbf{H}(X_1, X_2) = -\mathbf{1} \quad \text{for} \quad r_{12} < d, \quad (2.3)$$

$$\mathbf{C}(X_1, X_2) = -\beta \mathbf{V}(X_1, X_2) \quad \text{for} \quad r_{12} > d. \quad (2.4)$$

In Eq. (2.3) the elements of the matrix \mathbf{V} are the potential energy terms between species i and j , $\beta = (k_B T)^{-1}$, and $\mathbf{1}$ is a matrix with all elements equal to unity. The restriction of the model to the case where all species have equal hard core radii is made by adopting a single value d for each element in the matrices in Eqs. (2.3) and (2.4). For the more general unequal radii case it would be necessary to introduce different values d_{ij} .

In the case of polar systems under consideration here the potential energy terms are given by

$$V_{ij}(X_1, X_2) = \mu_i(\Omega_i) \cdot \mathbf{T}(\mathbf{r}_{ij}) \cdot \mu_j(\Omega_j), \quad (2.5)$$

where μ_i is the permanent dipole moment of species i and \mathbf{T} is the dipole-dipole tensor:

$$\mathbf{T}(\mathbf{r}) = r^{-3}(\mathbf{U} - 3\mathbf{r}\mathbf{r}r^{-2}), \quad (2.6)$$

where \mathbf{U} is the unit dyadic.

The multicomponent MSM model for dipolar fluids is specified by Eqs. (2.2)–(2.5). In order to solve the multidimensional integral equation, Eq. (2.2), we first reduce it to a set of one-dimensional equations. This is accomplished in the next section by closely following the procedure developed by Blum.⁵

III. REDUCTION OF THE ORNSTEIN-ZERNIKE EQUATION

We expand the correlation functions $F(X_1, X_2)$ in terms of a complete set of angular functions. For isotropic fluids, the correlation functions must be independent of our choice of coordinate system and this invariance simplifies the expansion. Introducing the variable $r_{12} = (r_{12}, \Omega_{12}) \equiv r_2 - r_1$, we find⁶

$$F(X_1, X_2) = \sum_{l_1 l_2 l_3} f(l_1 l_2 l_3; r_{12}) \phi_{l_1 l_2 l_3}(\Omega_1, \Omega_2, \Omega_{12}), \tag{3.1}$$

where

$$\phi_{l_1 l_2 l_3}(\Omega_1 \Omega_2 \Omega_{12}) = \sum_{m_1 m_2 m_3} (-)^{m_1} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} Y_{l_1 m_1}^*(\Omega_1) Y_{l_2 m_2}(\Omega_2) Y_{l_3 m_3}(\Omega_{12}). \tag{3.2}$$

Equations for the expansion coefficients $c(l_1 l_2 l_3; r)$ and $h(l_1 l_2 l_3; r)$ are found by inserting Eqs. (3.1) and (3.2) into Eq. (2.2). After integrating over Ω_3 we obtain

$$\begin{aligned} (4\pi)^{3/2} \sum_{\substack{\lambda_1 \lambda_2 \lambda_3 \\ \mu_1 \mu_2 \mu_3}} (-)^{\mu_1} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ -\mu_1 & \mu_2 & \mu_3 \end{pmatrix} [h(\lambda_1 \lambda_2 \lambda_3; r_{12}) - c(\lambda_1 \lambda_2 \lambda_3; r_{12})] Y_{\lambda_1 \mu_1}^*(\Omega_1) Y_{\lambda_2 \mu_2}(\Omega_2) Y_{\lambda_3 \mu_3}(\Omega_{12}) \\ = 4\pi^2 \sum_{\substack{l_1 l_2 l_3 \\ m_1 m_2 m_3}} \sum_{\substack{L_1 L_2 L_3 \\ M_1 M_2 M_3}} (-)^{m_1 + M_1} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} L_1 & L_2 & L_3 \\ -M_1 & M_2 & M_3 \end{pmatrix} \delta_{l_2 L_1} \delta_{m_2 M_1} Y_{l_1 m_1}^*(\Omega_1) Y_{L_2 M_2}(\Omega_2) \int c(l_1 l_2 l_3; r_{12}) \\ \times \rho h(L_1 L_2 L_3; r_{12}) Y_{l_3 m_3}(\Omega_{13}) Y_{L_3 M_3}(\Omega_{32}) dr_{12}. \end{aligned} \tag{3.3}$$

The integral in Eq. (3.3) is of the Fourier convolution type and thus its Fourier transform can be simply expressed in terms of the transforms

$$\begin{aligned} f(l_1 l_2 l_3; k) Y_{l_3 m_3}(\Omega_k) &= (1/2\pi)^{3/2} \int \exp(i\mathbf{k} \cdot \mathbf{r}_{12}) f(l_1 l_2 l_3; r_{12}) Y_{l_3 m_3}(\Omega_{12}) dr_{12} \\ &= [4\pi i^{l_3} / (2\pi)^{3/2}] Y_{l_3 m_3}(\Omega_k) \int_0^\infty r^2 j_{l_3}(kr) f(l_1 l_2 l_3; r) dr. \end{aligned} \tag{3.4}$$

The transform of Eq. (3.3) is

$$\begin{aligned} \sum_{\substack{\lambda_1 \lambda_2 \lambda_3 \\ \mu_1 \mu_2 \mu_3}} (-)^{\mu_1} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ -\mu_1 & \mu_2 & \mu_3 \end{pmatrix} [h(\lambda_1 \lambda_2 \lambda_3; k) - c(\lambda_1 \lambda_2 \lambda_3; k)] Y_{\lambda_1 \mu_1}^*(\Omega_1) Y_{\lambda_2 \mu_2}(\Omega_2) Y_{\lambda_3 \mu_3}(\Omega_k) = 2^{-3/2} (4\pi)^2 \\ \times \sum_{\substack{l_1 l_2 l_3 \\ m_1 m_2 m_3}} \sum_{\substack{L_2 L_3 \\ M_2 M_3}} (-)^{m_1 + m_2} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_2 & L_2 & L_3 \\ -m_2 & M_2 & M_3 \end{pmatrix} Y_{l_1 m_1}^*(\Omega_1) Y_{L_2 M_2}(\Omega_2) \\ \times Y_{l_3 m_3}(\Omega_k) Y_{L_3 M_3}(\Omega_k) c(l_1 l_2 l_3; k) \rho h(l_2 L_2 L_3; k). \end{aligned} \tag{3.5}$$

Multiplying the above equation by $Y_{l_1 m_1}(\Omega_1) Y_{L_2 m_2}(\Omega_2) Y_{\lambda_3 \mu_3}(\Omega_k)$, integrating over Ω_1, Ω_2 , and Ω_k , and using the formula for the integral of three spherical harmonics⁶ gives

$$\begin{aligned} [h(l_1 L_2 \lambda_3; k) - c(l_1 L_2 \lambda_3; k)] \begin{pmatrix} l_1 & L_2 & \lambda_3 \\ -m_1 & M_2 & \mu_3 \end{pmatrix} = (2\pi)^{3/2} \sum_{\substack{l_2 l_3 L_3 \\ m_2 m_3 M_3}} (-)^{m_2 + \mu_3} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} l_2 & L_2 & L_3 \\ -m_2 & M_2 & M_3 \end{pmatrix} \begin{pmatrix} \lambda_3 & l_3 & L_3 \\ 0 & 0 & 0 \end{pmatrix} \\ \times \begin{pmatrix} \lambda_3 & l_3 & L_3 \\ -\mu_3 & m_3 & M_3 \end{pmatrix} [(2\lambda_3 + 1)(2l_3 + 1)(2L_3 + 1)]^{1/2} c(l_1 l_2 l_3; k) \rho h(l_2 L_2 L_3; k). \end{aligned} \tag{3.6}$$

This equation can be further simplified by multiplying by $\begin{pmatrix} l_1 & L_2 & \lambda_3 \\ -m_1 & M_2 & \mu_3 \end{pmatrix}$ summing over m_1, M_2, μ_3 , using an orthogonality property of the three- j symbol,⁶ and also using the definition of the six- j symbol as a sum of products of four three- j symbols.⁶ The result is

$$\begin{aligned} h(l_1 L_2 \lambda_3; k) - c(l_1 L_2 \lambda_3; k) \\ = (2\pi)^{3/2} \sum_{l_2 l_3 L_3} (-)^{l_2 + \lambda_3} [(2\lambda_3 + 1)(2l_3 + 1)(2L_3 + 1)]^{1/2} \begin{Bmatrix} l_3 & L_3 & \lambda_3 \\ L_2 & l_1 & l_2 \end{Bmatrix} \begin{Bmatrix} l_3 & L_3 & \lambda_3 \\ 0 & 0 & 0 \end{Bmatrix} c(l_1 l_2 l_3; k) \rho h(l_2 L_2 L_3; k). \end{aligned} \tag{3.7}$$

Using the identity⁶

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ l_1 & l_2 & l_3 \end{Bmatrix} \begin{Bmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{Bmatrix} = \sum_{M_1, M_2, M_3} (-)^{l_1+l_2+l_3+m_1+m_2+m_3} \begin{Bmatrix} j_1 & l_2 & l_3 \\ m_1 & M_2 & -M_3 \end{Bmatrix} \begin{Bmatrix} l_1 & j_2 & l_3 \\ -M_1 & m_2 & M_3 \end{Bmatrix} \begin{Bmatrix} l_1 & l_2 & j_3 \\ M_1 & -M_2 & m_3 \end{Bmatrix}$$

and the definition

$$f^{(m)}(l_1 l_2; k) = \sum_{l_3} (2l_3 + 1)^{1/2} \begin{Bmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{Bmatrix} f(l_1 l_2 l_3; k), \tag{3.8}$$

we find, after multiplying Eq. (3.7) by $(2\lambda_3 + 1)^{1/2} \begin{Bmatrix} l_1 & l_2 & \lambda_3 \\ m & -m & 0 \end{Bmatrix}$ and summing over λ_3 , that Eq. (3.7) can be re-written as

$$h^{(m)}(l_1 L_2; k) - c^{(m)}(l_1 L_2; k) = (-)^m (2\pi)^{3/2} \sum_{l_2} c^{(m)}(l_1 l_2; k) \rho h^{(m)}(l_2 L_2; k). \tag{3.9}$$

The Fourier transform of Eq. (3.9) is

$$h^{(m)}(l_1 L_2; r_{12}) - c^{(m)}(l_1 L_2; r_{12}) = (-)^m \sum_{l_2} \int c^{(m)}(l_1 l_2; r_{13}) \rho h^{(m)}(l_2 L_2; r_{32}) dr_3, \tag{3.10}$$

where

$$\begin{aligned} f^{(m)}(l_1 l_2; r_{12}) &= (1/2\pi)^{3/2} \int \exp(-i \mathbf{k} \cdot \mathbf{r}_{12}) f^{(m)}(l_1 l_2; k) d\mathbf{k} \\ &= [4\pi/(2\pi)^{3/2}] \int_0^\infty k^2 j_0(kr_{12}) f^{(m)}(l_1 l_2; k) dk. \end{aligned} \tag{3.11}$$

Equation (3.10) is the desired set of one-dimensional integral equations. We must relate the solutions of these equations, the $f^{(m)}(l_1 l_2; r)$, to the expansion coefficients $f(l_1 l_2 l_3; r)$ of $\mathbf{C}(X_1, X_2)$ and $\mathbf{H}(X_1, X_2)$. To accomplish this we define

$$\begin{aligned} \bar{f}(l_1 l_2 l_3; r_{12}) &= (1/2\pi)^{1/2} \int \exp(-i \mathbf{k} \cdot \mathbf{r}_{12}) f(l_1 l_2 l_3; k) d\mathbf{k} \\ &= [4\pi/(2\pi)^{3/2}] \int_0^\infty k^2 j_0(kr_{12}) f(l_1 l_2 l_3; k) dk. \end{aligned} \tag{3.12}$$

Comparing Eqs. (3.8), (3.11), and (3.12) we see

$$f^{(m)}(l_1 l_2; r_{12}) = \sum_{l_3} (2l_3 + 1)^{1/2} \begin{Bmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{Bmatrix} \bar{f}(l_1 l_2 l_3; r_{12}). \tag{3.13}$$

The inverse of the above equation is

$$\bar{f}(l_1 l_2 l_3; r_{12}) = \sum_m (2l_3 + 1)^{1/2} \begin{Bmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{Bmatrix} f^{(m)}(l_1 l_2; r_{12}). \tag{3.14}$$

Thus if we have a relation between $\bar{f}(l_1 l_2 l_3; r_{12})$ and $f(l_1 l_2 l_3; r_{12})$ we can relate the latter functions to the solutions of Eq. (3.10) through Eq. (3.14). This relation can be obtained by inserting the second form of Eq. (3.4) into the second form of Eq. (3.12). We find

$$\bar{f}(l_1 l_2 l_3; r_{12}) = (2/\pi) \int_0^\infty r^2 \phi_{l_3}(r_1 r_{12}) f(l_1 l_2 l_3; r) dr, \tag{3.15}$$

where

$$\phi_l(x, y) = i^l \int_0^\infty k^2 j_l(kx) j_0(ky) dk.$$

The above integral is evaluated in Appendix A. We find, using Eq. (A7) in Eq. (3.15),

$$\bar{f}(l_1 l_2 l_3; r_{12}) = f(l_1 l_2 l_3; r_{12}) - (1/r_{12}) \int_{r_{12}}^\infty P'_l(r_{12}/r) f(l_1 l_2 l_3; r) dr, \tag{3.16}$$

where $P'_l(x)$ is the derivative of the l th Legendre Polynomial.

The inverse of Eq. (3.16) can be similarly obtained from the inverses of Eqs. (3.4) and (3.12). We find

$$f(l_1 l_2 l_3; r_{12}) = \bar{f}(l_1 l_2 l_3; r_{12}) - (1/r_{12}^2) \int_0^{r_{12}} r P'_l(r/r_{12}) \bar{f}(l_1 l_2 l_3; r) dr. \tag{3.17}$$

As discussed in the Appendix, Eqs. (3.16) and (3.17) only hold for l_3 even. For the MSM dipolar fluid mixture problem we only require $l_3 = 0, 2$ so Eqs. (3.16) and (3.17) are sufficient.

IV. SOLUTION OF THE MODEL

The MSM is defined in Sec. II. In order to solve it for our case we must expand the potential energy

matrix $\mathbf{V}(X_1, X_2)$ in terms of its angular components. Since $\mathbf{V}(X_1, X_2)$ does not depend on the coordinate system, it has an expansion of the form (3.1), i. e.,

$$V(X_1, X_2) = (4\pi)^{3/2} \sum_{l_1 l_2 l_3} v(l_1 l_2 l_3; r_{12}) \phi_{l_1 l_2 l_3}(\Omega_1 \Omega_2 \Omega_{12}). \tag{4.1}$$

For the dipolar case all $v(l_1 l_2 l_3; r) = 0$ except

$$\begin{aligned} v(000; r) &= \infty && \text{for } r < d \\ &= 0 && \text{for } r > d, \end{aligned} \tag{4.2a}$$

$$\begin{aligned} v(112; r) &= 0 && \text{for } r < d \\ &= -(\frac{2}{3})^{1/2} \bar{\mu} \cdot \bar{\mu} r^{-3} && \text{for } r > d. \end{aligned} \tag{4.2b}$$

In Eq. (4.2b) $\bar{\mu}$ is a diagonal matrix with elements equal to the dipole moments of the species in the mixture. For a two-component mixture

$$\bar{\mu} \cdot \bar{\mu} = \begin{pmatrix} \mu_1^2 & \mu_1 \mu_2 \\ \mu_2 \mu_1 & \mu_2^2 \end{pmatrix}.$$

From Eqs. (2.4) and (3.6) and the fact that $v(l_1 l_2 l_3; r) = 0$ unless $(l_1 l_2 l_3) = (000)$ or (112) one can verify that

$$\begin{aligned} F(X_1, X_2) &= (4\pi)^{3/2} [f(000; r_{12}) \phi_{000}(\Omega_1 \Omega_2 \Omega_{12}) \\ &+ f(110; r_{12}) \phi_{110}(\Omega_1 \Omega_2 \Omega_{12}) \\ &+ f(112; r_{12}) \phi_{112}(\Omega_1 \Omega_2 \Omega_{12})] \end{aligned} \tag{4.3}$$

and all other $f(l_1 l_2 l_3; r)$ vanish. The closure conditions listed below follow from Eqs. (2.3), (2.4), (4.2a), and (4.2b):

$$h(000; r) = -1 \quad \text{for } r < d, \tag{4.4a}$$

$$c(000; r) = 0 \quad \text{for } r > d, \tag{4.4b}$$

$$h(110; r) = 0 \quad \text{for } r < d, \tag{4.5a}$$

$$c(110; r) = 0 \quad \text{for } r > d, \tag{4.5b}$$

$$h(112; r) = 0 \quad \text{for } r < d, \tag{4.6a}$$

$$c(112; r) = (\frac{2}{3})^{1/2} \beta \bar{\mu} \cdot \bar{\mu} r^{-3} \quad \text{for } r > d. \tag{4.6b}$$

Using the explicit forms, $P_0(x) = 1$ and $P_2(x) = \frac{1}{2}(3x^2 - 1)$, we verify from Eqs. (3.16) and (3.17) that

$$\bar{f}(000; r) = f(000; r), \tag{4.7}$$

$$\bar{f}(110; r) = f(110; r), \tag{4.8}$$

$$\bar{f}(112; r) = f(112; r) - 3 \int_r^\infty y^{-1} f(112; y) dy, \tag{4.9}$$

$$f(112; r) = \bar{f}(112; r) - 3 r^{-3} \int_0^r y^2 \bar{f}(112; y) dy. \tag{4.10}$$

The Fourier transform of Eq. (3.8) gives us the additional relationships

$$f^{(0)}(00; r) = \bar{f}(000; r), \tag{4.11}$$

$$f^{(0)}(11; r) = (\frac{1}{3})^{1/2} [\sqrt{2} \bar{f}(112; r) - \bar{f}(110; r)], \tag{4.12}$$

$$f^{(\pm 1)}(11; r) = (\frac{1}{3})^{1/2} [\frac{1}{2} \sqrt{2} \bar{f}(112; r) + \bar{f}(110; r)]. \tag{4.13}$$

Note that $f^{(-1)}(11; r) = f^{(+1)}(11; r)$. Consequently we will only consider $f^{(+1)}(11; r)$ below.

Equation (3.10) for the dipolar MSM problem re-

duces to the following uncoupled equations:

$$\begin{aligned} h^{(0)}(00; r_{12}) - c^{(0)}(00; r_{12}) \\ = \int c^{(0)}(00; r_{13}) \rho h^{(0)}(00; r_{32}), \end{aligned} \tag{4.14}$$

$$\begin{aligned} h^{(m)}(11; r_{12}) - c^{(m)}(11; r_{12}) \\ = (-)^m \int c^{(m)}(11; r_{13}) \rho h^{(m)}(11; r_{32}) d r_{32}, \end{aligned}$$

$$m = 0, 1. \tag{4.15}$$

Equations (4.4a), (4.4b), and (4.14) define a hard sphere Percus-Yevick⁷ problem for which solutions are known.⁸ Thus

$$f(000; r) = f(r; \rho), \tag{4.16}$$

where $f(r; \rho)$ is a correlation function for the one-component hard sphere Percus-Yevick fluid with hard sphere diameter d and density $\rho = \text{Tr} \rho$.

To solve the dipolar part of the problem, it proves useful to first make a brief digression and consider the equation

$$\begin{aligned} h(x_{12}; \mathbf{N}) - c(x_{12}; \mathbf{N}) \\ = (6/\pi) \int c(x_{13}; \mathbf{N}) h(x_{32}; \mathbf{N}) dx_{32} \end{aligned} \tag{4.17}$$

with closure conditions

$$c(x; \mathbf{N}) = 0 \quad \text{for } x > 1, \tag{4.18}$$

$$h(x; \mathbf{N}) = -\mathbf{N} \quad \text{for } x < 1. \tag{4.19}$$

Suppose \mathbf{N} is of the form

$$\mathbf{N} = N \lambda^{1/2} \mathbf{I} \lambda^{1/2},$$

where λ is diagonal. For this special choice, $f(x, \mathbf{N})$ takes the simple form

$$f(x; \mathbf{N}) = N f(x; \lambda N) \lambda^{1/2} \mathbf{I} \lambda^{1/2}, \tag{4.20}$$

where $\lambda = \text{Tr} \lambda$ and the functions $f(x; \lambda N)$ satisfy

$$\begin{aligned} h(x_{12}; \lambda N) - c(x_{12}; \lambda N) \\ = (6\lambda N/\pi) \int c(x_{13}; \lambda N) h(x_{32}; \lambda N) dx_{32} \end{aligned} \tag{4.21}$$

with closure conditions

$$c(x; \lambda N) = 0 \quad \text{for } x > 1, \tag{4.22a}$$

$$h(x; \lambda N) = -1 \quad \text{for } x < 1. \tag{4.22b}$$

Thus the $f(x; \lambda N)$ are correlation functions for a hard sphere Percus-Yevick fluid with a density $\rho = 6\lambda N/\pi$ and a diameter $d = 1$.

To verify Eqs. (4.20) and (4.21), we substitute Eq. (4.20) into Eq. (4.17). This gives

$$\begin{aligned} [h(x_{12}; \lambda N) - c(x_{12}; \lambda N)] \lambda^{1/2} \mathbf{I} \lambda^{1/2} \\ = (6/\pi) N \lambda^{1/2} \mathbf{I} \lambda^{1/2} \int c(x_{13}; \lambda N) h(x_{32}; \lambda N) dx_{32}. \end{aligned} \tag{4.23}$$

Using the identity

$$|\lambda| = |\text{Tr} \lambda| = \lambda \tag{4.24}$$

valid for diagonal λ , we recover Eq. (4.17). Com-

paring Eqs. (4.18) and (4.19) with Eqs. (4.20) and (4.22), we also verify the correctness of the closure relations (4.22).

The preceding discussion is helpful since the functions $f^{(m)}(\mathbf{11}; r)$ can be related to the solutions of Eq. (4.17). To see this, we first obtain closure conditions for the $f^{(m)}(\mathbf{11}; r)$. From Eqs. (4.5), (4.6), (4.9), (4.12), and (4.13) we find

$$c^{(0)}(\mathbf{11}; r) = c^{(1)}(\mathbf{11}; r) = 0 \text{ for } r > d, \tag{4.25a}$$

$$h^{(0)}(\mathbf{11}; r) = -2n \text{ for } r < d, \tag{4.25b}$$

$$h^{(1)}(\mathbf{11}; r) = -n, \tag{4.25c}$$

where

$$n = \left(\frac{3}{2}\right)^{1/2} \int_d^\infty r^{-1} h(\mathbf{112}; r) dr. \tag{4.26}$$

Introducing the dimensionless quantities

$$\eta = (\pi d^3/6) \rho \text{ and } x = r/d \tag{4.27}$$

into Eq. (4.15) and pre- and postmultiplying the resulting expression by $\eta^{1/2}$ we obtain an equation of the same form as Eq. (4.17). We also verify that the closure relations (4.25) are reducible to the form in Eq. (4.18). Thus we show

$$\eta^{1/2} f^{(0)}(\mathbf{11}; r) \eta^{1/2} = f(x; 2\eta^{1/2} n \eta^{1/2}), \tag{4.28}$$

$$\eta^{1/2} f^{(1)}(\mathbf{11}; r) \eta^{1/2} = -f(x; -\eta^{1/2} n \eta^{1/2}). \tag{4.29}$$

Using Eqs. (4.6b), (4.25a), (4.12), and (4.13), we can evaluate Eq. (4.10) for $r > d$ as

$$\frac{2}{3} \beta \tilde{\mu} \cdot \tilde{\mu} = -2 \int_0^d r^2 [c^{(0)}(\mathbf{11}; r) + c^{(1)}(\mathbf{11}; r)] dr. \tag{4.30}$$

Pre- and postmultiplying Eq. (4.30) by $\rho^{1/2}$ and using Eqs. (4.27)–(4.29) then gives

$$(4\pi\beta/q) \rho^{1/2} \tilde{\mu} \cdot \tilde{\mu} \rho^{1/2} = \frac{1}{3} [q(2\eta^{1/2} n \eta^{1/2}) - q(-\eta^{1/2} n \eta^{1/2})], \tag{4.31}$$

where

$$q(2\eta^{1/2} n \eta^{1/2}) = 1 - 24 \int_0^1 x^2 c(x; 2\eta^{1/2} n \eta^{1/2}) dx. \tag{4.32}$$

In the above equation, $\mathbf{1}$ is the unit matrix.

Since ρ , $\tilde{\mu}$, and therefore $\rho^{1/2} \tilde{\mu}$ are diagonal, we can write

$$\rho^{1/2} \tilde{\mu} \cdot \tilde{\mu} \rho^{1/2} = \hat{\mu}^2 \hat{\rho}^{1/2} \hat{\rho}^{1/2}, \tag{4.33}$$

where

$$\hat{\rho} = \hat{\mu}^{-2} \rho \hat{\mu}^2 = \hat{\mu}^{-2} \tilde{\mu}^2 \rho \tag{4.34}$$

is a diagonal matrix of effective densities and $\hat{\mu}^2$ is the mean square dipole moment of the species in the mixture, i. e., for an m -component mixture

$$\hat{\mu}^2 = m^{-1} \sum_{i=1}^m \mu_i^2.$$

Combining Eqs. (4.31) and (4.33) gives

$$(4\pi/q) \beta \hat{\mu}^2 \hat{\rho}^{1/2} \hat{\rho}^{1/2} = \frac{1}{3} [q(2\eta^{1/2} n \eta^{1/2}) - q(-\eta^{1/2} n \eta^{1/2})]. \tag{4.35}$$

This expression can be regarded as an equation for $\eta^{1/2} n \eta^{1/2}$. We assume a solution of the form

$$\eta^{1/2} n \eta^{1/2} = \hat{n} \hat{\eta}^{1/2} \hat{\eta}^{1/2}, \tag{4.36}$$

where

$$\hat{\eta} = (\pi d^3/6) \hat{\rho} \tag{4.37}$$

and where \hat{n} is to be determined. If Eq. (4.36) is correct, we can use Eq. (4.20) (since $\hat{\eta}$ is diagonal) and, therefore,

$$f(x; 2\eta^{1/2} n \eta^{1/2}) = 2\hat{\eta} f(x; 2\hat{\eta} \hat{n} \hat{\eta}^{1/2} \hat{\eta}^{1/2}), \tag{4.38}$$

where $\hat{\eta} = \text{Tr } \hat{\eta}$.

Thus if Eq. (4.36) is correct, our multicomponent problem reduces to solving for $f(x; 2\hat{\eta} \hat{n})$, a one-component hard sphere Percus–Yevick correlation function.

To check Eq. (4.36), we combine it with Eqs. (4.20), (4.32), and (4.35). This gives

$$(4\pi/q) \beta \hat{\rho} \hat{\mu}^2 \hat{\rho}^{1/2} \hat{\rho}^{1/2} = \frac{1}{3} [q(2\hat{\eta} \hat{n}) - q(-\hat{\eta} \hat{n})] \hat{\rho}^{1/2} \hat{\rho}^{1/2}, \tag{4.39}$$

where

$$q(z) = 1 - 24z \int_0^1 x^2 c(x; z) dx, \tag{4.40a}$$

with $c(x)$ being the Percus–Yevick hard sphere direct correlation function. Here q is the Percus–Yevick hard sphere inverse compressibility.

Equation (4.39) shows that our assumed solution of Eq. (4.35) is correct. Moreover cancelling the factor $\rho^{1/2} \hat{\rho}^{1/2}$ from both sides of Eq. (4.39) gives an equation identical to one which arose in Wertheim’s solution² of the one-component MSM dipolar fluid:

$$(4\pi/q) \beta \hat{\rho} \hat{\mu}^2 = \frac{1}{3} [q(2\hat{\eta} \hat{n}) - q(-\hat{\eta} \hat{n})], \tag{4.40b}$$

where

$$\hat{\eta} = (\pi d^3/6) \hat{\mu}^{-2} \sum_{i=1}^m \rho_i \mu_i^2 = (\pi d^3/6) \hat{\rho}.$$

In fact comparison of our results with Wertheim’s shows that we have reduced the multicomponent MSM polar fluid problem characterized by densities ρ , dipole moments $\tilde{\mu}$, and hard sphere diameter d to a one-component MSM problem characterized by an effective density $\hat{\rho}$, an effective dipole moment $\hat{\mu}$, and the same hard sphere diameter d . More precisely, we see

$$\eta^{1/2} f^{(m)}(\mathbf{11}; r) \eta^{1/2} = f^{(m)}(\mathbf{11}; r) \hat{\eta}^{1/2} \hat{\eta}^{1/2}, \tag{4.41}$$

where $f^{(m)}(\mathbf{11}; r)$ is the correlation function for the effective pure MSM polar fluid with dipole moment $\hat{\mu}$ and density $\hat{\rho}$ analogous to $f^{(m)}(\mathbf{11}; r)$. That is $f^{(m)}(\mathbf{11}; r)$ satisfies the one-component limits of Eqs. (4.15), (4.25), and (4.31) with the parameters being those of the effective fluid.

Using Eqs. (4.34) and (4.37), Eq. (4.41) can be rewritten as

$$f^{(m)}(11; r) = \hat{\mu}^{-2} \tilde{\mu} | \tilde{\mu} f^{(m)}(11; r). \tag{4.42}$$

Combining Eqs. (4.12), (4.13), and (4.42) shows that similarly

$$f(11l; r) = \hat{\mu}^{-2} \tilde{\mu} | \tilde{\mu} f(11l; r), \tag{4.43}$$

where again $f(11l; r)$ is the effective pure fluid correlation function analogous to $f(11l; r)$.

Thus we have solved the equal radii multicomponent MSM dipolar problem. We have demonstrated that the correlation functions **H** and **C** may be determined from the pure dipolar MSM at a different effective density and dipole moment. Explicit expressions for the correlation functions are easily obtained from the preceding results. For example the correlation function **H** is given by

$$\begin{aligned} H(X_1, X_2) = & h(000; r_{12}) | \\ & + \hat{\mu}^{-2} \mu | \mu [h(110; r_{12}) \phi_{110}(\Omega_1 \Omega_2 \Omega_{12}) \\ & + h(112; r_{12}) \phi_{112}(\Omega_1 \Omega_2 \Omega_{12})], \end{aligned} \tag{4.44}$$

where $h(000; r_{12})$ is the hard sphere Percus–Yevick correlation function⁷⁻⁸ at density ρ and temperature $[k_B \beta]^{-1}$ and $h(110; r_{12})$ and $h(112; r_{12})$ are, respectively, the functions $-\sqrt{1/3} h_{\Delta}(r_{12})$ and $\sqrt{2/3} h_D(r_{12})$ determined by Wertheim² for the pure dipolar MSM fluid at the same temperature bearing effective dipole moment $\hat{\mu}$ and at density $\hat{\rho}$. Explicitly we have^{2,4}

$$\begin{aligned} h_{\Delta}(r) = & 2\hat{n} [h_s(r, 2\hat{n}\hat{\rho}) - h_s(r, -\hat{n}\hat{\rho})], \\ h_D(r) = & \hat{h}_D(r) - 3r^{-3} \int_0^r s^2 \hat{h}_D(s) ds, \end{aligned}$$

with

$$\hat{h}_D(r) = \hat{n} [2h_s(r, 2\hat{n}\hat{\rho}) + h_s(r, -\hat{n}\hat{\rho})],$$

where $h_s(r, \rho)$ is the hard sphere Percus–Yevick correlation function at density ρ . The quantity \hat{n} is determined by implicitly solving Eq. (4.40b) for \hat{n} as a function of β and $\hat{\rho}$.

V. THERMODYNAMICS

Given the results of Sec. IV, it is not surprising that the dielectric constant and the dipolar contribution to the thermodynamic properties of the MSM mixture are just those of the effective MSM pure fluid characterized by $\hat{\rho}$, $\hat{\mu}$, d . The dipolar potential energy per unit volume for a multicomponent mixture is expressed as

$$\begin{aligned} V^{-1} \Delta E = & (V^{-1}/32\pi^2) \sum_{ij} \rho_i \rho_j (4\pi)^{3/2} \\ & \times \int v_{ij}(112; r_{12}) \phi_{112}(\Omega_1 \Omega_2 \Omega_{12}) \\ & \times G_{ij}(X_1, X_2) dX_1 dX_2 \end{aligned}$$

which after performing the angular integrations may be rewritten as

$$\begin{aligned} V^{-1} \Delta E = & 2\pi \int_0^{\infty} r^2 \text{Tr} [\rho^{1/2} v(112; r) \\ & \times \rho^{1/2} \rho^{1/2} h(112; r) \rho^{1/2}] dr. \end{aligned} \tag{5.1}$$

Equation (5.1) can be reduced to

$$V^{-1} \Delta E = (-4\pi/3) \text{Tr}(\rho^{1/2} \tilde{\mu} | \tilde{\mu} \rho^{1/2} \rho^{1/2} n \rho^{1/2}), \tag{5.2}$$

where we have used Eqs. (4.2b) and (4.26).

Finally using Eqs. (4.27), (4.33), (4.36), and (4.37) we simplify Eq. (5.2) to the one-component form:

$$V^{-1} \Delta E = (-4\pi/3) \hat{\rho}^2 \hat{\mu}^2 \hat{n}, \tag{5.3}$$

which is the dipolar potential energy for the effective fluid.

Using the Gibbs–Helmholtz relation

$$\partial \beta \Delta A(\beta) / \partial \beta = \Delta E(\beta), \tag{5.4}$$

we calculate the dipolar Helmholtz free energy per unit volume from Eq. (5.3) as

$$V^{-1} \Delta A = -(4\pi/3\beta) \hat{\rho}^2 \hat{\mu}^2 \int_0^{\beta} \hat{n}(\beta') d\beta'. \tag{5.5}$$

Thus the Helmholtz free energy A of the multicomponent polar fluid in the MSM may be expressed as

$$A = A_0 + \Delta A, \tag{5.6}$$

where A_0 is the Helmholtz free energy of the pure Percus–Yevick hard sphere reference fluid and ΔA is the dipolar excess free energy given by Eq. (5.5). The quadrature in Eq. (5.5) is accomplished, for fixed density and composition, by inversion of Eq. (4.40b).

The internal energy of the multicomponent MSM polar fluid is found by use of the Gibbs–Helmholtz relation, Eq. (5.4), as

$$E = E_0 + \Delta E, \tag{5.7}$$

where the excess dipolar internal energy ΔE is given in Eq. (5.3) and E_0 is the internal energy of the reference fluid.

The pressure p of a multicomponent system is found from the thermodynamic relation

$$p = (\partial A / \partial V)_{T, N_1, \dots, N_m}. \tag{5.8}$$

For the polar multicomponent MSM model with equal radii one obtains from Eqs. (5.3)–(5.5)

$$p = p_0 + \Delta p, \tag{5.9}$$

with the excess dipolar pressure Δp given by the relationship

$$\Delta p = \Delta E / V - \Delta A / V, \tag{5.10}$$

with ΔA and ΔE determined from Eqs. (5.3) and

(5.5), respectively. In Eq. (5.9) p_0 is the pressure of the reference equal-radii hard sphere mixture in the MSM approximation.

In summary the thermodynamics of this polar multicomponent mixture in MSM approximation with equal hard sphere radii at temperature $(k_B\beta)^{-1}$ and composition (ρ_1, \dots, ρ_m) is identical to the thermodynamics of an effective pure polar fluid in the MSM approximation with dipole moment $\hat{\eta}$ at temperature $(k_B\beta)^{-1}$ and density $\hat{\rho}$:

$$\hat{\rho} = \hat{\mu}^{-2} \sum_{i=1}^m \mu_i^2 \rho_i. \tag{5.11}$$

The expressions for ΔE , ΔA , and Δp given by Eqs. (5.3), (5.5), and (5.6), respectively, are identical to the expressions obtained for these quantities in the pure MSM polar fluid.⁴ We shall not further explore the thermodynamics of the MSM polar mixtures here except to note that the model will exhibit phase separations and critical behavior as well as provide quantitative predictions for the thermodynamics of polar solutions. A detailed study of the polar multicomponent MSM thermodynamics and comparison with experiment will be presented in the near future.

For the MSM the compressibility theorem, Eq. (4.40a), predicts that the compressibility of the polar system is exactly equal to the compressibility of the hard-sphere reference system. On the other hand, if the expression for the pressure Eq. (5.9) is employed to compute the compressibility one finds a nonvanishing dipolar contribution. Since the MSM is not exact these two procedures do not lead to equivalent results which is a frequent failing of approximate models of the liquid state.

VI. DIELECTRIC CONSTANT

The dielectric constant ϵ for the mixture can be computed using the arguments Wertheim² gave for the pure fluid case. The result is

$$(\epsilon - 1)/(\epsilon + 2) = \text{Tr} \{ [q(2\eta^{1/2} n \eta^{1/2}) \times q^{-1}(-\eta^{1/2} n \eta^{1/2}) - 1] [q(2\eta^{1/2} n \eta^{1/2}) \times q^{-1}(-\eta^{1/2} n \eta^{1/2}) + 2]^{-1} \}. \tag{6.1}$$

After some algebra Eq. (5.7) can be reduced to

$$\epsilon = q(2\hat{\eta}\hat{n})q^{-1}(-\hat{\eta}\hat{n}), \tag{6.2}$$

which is Wertheim's formula for the dielectric constant of the effective pure fluid. As can be seen from Eq. (4.40b) $\hat{\eta}\hat{n}$ at a given temperature depends only on

$$\hat{\rho}\hat{\mu}^2 = \sum_{i=1}^m \rho_i \mu_i^2. \tag{6.3}$$

Hence ϵ depends only on this quantity. Thus we have the following combination rule for the MSM

dielectric constant of a mixture:

$$\epsilon_{\text{MSM}}^{\text{mix}}(\rho, \mu) = \epsilon_{\text{MSM}}^{\text{pure}} \left(\sum_{i=1}^m \rho_i \mu_i^2 \right). \tag{6.4}$$

The Onsager formula for the dielectric constant ϵ_{ONS} of a rigid polar mixture is given by⁹

$$(\epsilon_{\text{ONS}} - 1)[(2\epsilon_{\text{ONS}} + 1)/3\epsilon_{\text{ONS}}] = (4\pi\beta/3) \sum_{i=1}^m \rho_i \mu_i^2 \tag{6.5}$$

so that the same combination rule as Eq. (6.4) holds for the Onsager theory.

The combination rule is illustrated in Fig. 1. There we plot the composition dependence of the Wertheim and Onsager dielectric constants for a two-component fluid with $\rho = \rho_1 + \rho_2 = 10^{22}$ molecules/cc, $T = 300$ °K, $\mu_1 = 1$ D, and $\mu_2 = 3$ D.

VII. THE ASYMPTOTIC POTENTIAL OF MEAN FORCE

The potential of mean force $w_{ij}(X_1 X_2)$ between two species i and j in a multicomponent mixture is defined by

$$w_{ij} = -\beta^{-1} \ln G_{ij} = -\beta^{-1} \ln(H_{ij} + 1). \tag{7.1}$$

At large interparticle separations h_{ij} is small and accordingly $w_{ij}^\infty \sim -\beta^{-1} H_{ij}$, where the superscript infinity indicates that the relation is only correct for large separations. Employing Eq. (4.44) and Wertheim's results for the pure fluid leads to the asymptotic expression

$$w^\infty(X_1, X_2) = (4\pi)^{3/2} v(112; r_{12}) \phi_{112}(\Omega_1 \Omega_2 \Omega_{12}) \times [q(2\hat{\eta}\hat{n})q(-\hat{\eta}\hat{n})]^{-1} = (4\pi)^{3/2} (\frac{2}{3})^{1/2} \bar{\mu} | \bar{\mu}$$

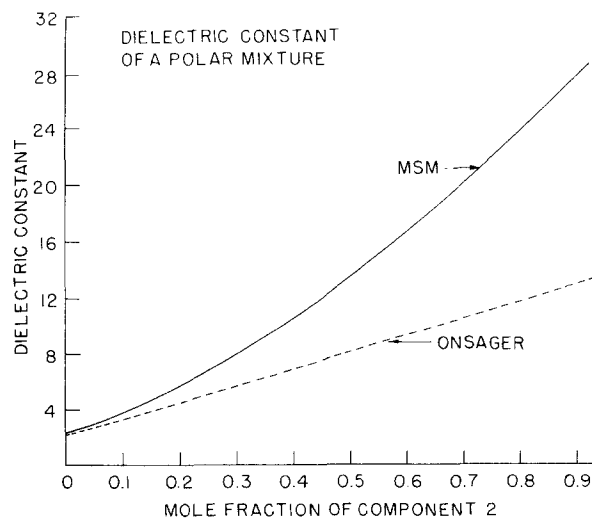


FIG. 1. MSM (continuous line) and Onsager (dotted) line dielectric constants for a binary polar fluid mixture as a function of mole fraction of component 2. Components 1 and 2 have dipole moments 1 and 3 D, respectively. The total number density is constant at 10^{22} molecules cc⁻¹ and the temperature is 300 °K.

$$\times r_{12}^{-3} \phi_{112}(\Omega_1 \Omega_2 \Omega_{12}) [q(2\hat{\eta}\hat{n})q(-\hat{\eta}\hat{n})]^{-1}. \quad (7.2)$$

This result is only correct for an infinite system. For a system in a finite volume w^∞ will contain nonnegligible boundary contributions that depend upon sample shape in a manner similar to that encountered in the pure polar fluid.¹⁰ Note that

$$w_{ij}^\infty/w_{ki}^\infty = v_{ij}(112; r)/v_{ki}(112; r) = \mu_i \mu_j / \mu_k \mu_l, \quad (7.3)$$

with a similar relationship holding for the angular dependent part of the correlation functions exhibited in Eq. (4.44).

VIII. LIMITATIONS OF THE MODEL

In this section we discuss important qualitative limitations of the MSM as a theory of polar solutions. First we consider the interesting limiting case where the dipole moments of one or more components of the mixture vanish. This case is of interest since it is a prototype model for the behavior of nonpolar species in polar solvents. One might expect some "hydrophobic bonding," i. e., local segregation of the nonpolar molecules from the polar species. Our result Eq. (4.44) for the pair correlation function H_{ij} shows that this does not occur in the MSM. At all concentrations the nonpolar molecules are simply distributed like hard spheres at the total density ρ . Furthermore the potential of mean force w_{ij} for the nonpolar species, computed according to Eqs. (7.1) and (4.44) will be independent of the strength of the dipoles on the remaining polar components. Accordingly if we think of a hydrophobic bonding as increased attraction in the potential of mean force between nonpolar species as the dipole moments of the polar solvent components are increased, we must conclude that the polar MSM will not exhibit this propensity for nonpolar species to gather together.

Also if we consider the correlation functions of the polar components in the MSM mixture we find that the dipolar components of the correlation functions of the polar species does not depend on the presence of any nonpolar species. This occurs because $\hat{\rho}$ and $\hat{\mu}$ always appear in the combination $\hat{\rho}\hat{\mu}^2$ which is independent of the density of the nonpolar species. It follows that the dielectric constant and excess thermodynamic properties of the solution are unchanged if some or all of the nonpolar molecules are removed in a process which leaves the densities of the polar species unchanged. Similar results can be found in the work of Waisman and Lebowitz¹¹ on the MSM for charged hard sphere systems which includes the possibility of adding a neutral species.

These results are unrealistic. We expect that the polar species will influence the nonpolar

species, and vice versa, in a more important manner than exhibited by the MSM. Indeed, when anisotropic forces are present, it is possible for the asymptotic potential of mean force for the nonpolar species to behave exactly like the asymptotic potential of mean force of the polar species.¹² As long as the short-range potential energy of the nonpolar species (here taken to be an isotropic hard core) does not contain symmetry components $v(110; r)$ or $v(112; r)$, the MSM, where the direct correlation function is linear in the pair potential, will not exhibit the interplay between short-range and dipolar forces that are expected to be of importance in real polar fluids. These conclusions about the defects of the polar mixture MSM would stand if unequal hard core radii were permitted or indeed any choice made for the $v_{ij}(000; r)$ component of the pair potential. To improve the situation one must either introduce anisotropy in the nonpolar part of the pair potential v_{ij} or introduce a nonlinear relation between the direct correlation function C_{ij} and v_{ij} .

Anderson and Chandler have developed a device to introduce nonlinear character into the MSM and their own closely related linear fluid theory. This procedure, which they call the EXP approximation,¹³ involves exponentiation of the perturbation part of the pair distribution function given by the linear theory. The EXP method has been shown to substantially improve the quantitative predictions of the linear theories as well as certain of their qualitative features without adding any computational labor.¹⁴ Unfortunately, EXP does not eliminate the qualitative difficulties discussed in this section.

According to the EXP approximation, the correlation functions H , given by the linear theory in Eq. (4.44), are represented as

$$H_{ij}(X_1, X_2) = h(000; r_{12}) \exp\{\hat{\mu}^{-2} \mu_i \mu_j [h(110; r_{12}) \times \phi_{110}(\Omega_1 \Omega_2 \Omega_{12}) + h(112; r_{12}) \phi_{112} \times (\Omega_1 \Omega_2 \Omega_{12})]\}.$$

For nonpolar species the EXP approximation predicts

$$H_{ij}^{\text{EXP}}(\text{nonpolar } i \text{ or } j) = h(000; r),$$

which again reveals no effect of the polar species on the correlation functions of the nonpolar species. Similarly, in the EXP approximation, the anisotropic part of the polar species correlation functions remain unaffected by the presence of nonpolar species. The EXP approximation will however lead to qualitatively different behavior for the polar species correlation functions at small separation. The EXP approximation will also lead to substantially different formulas for the dielectric constant and the excess thermodynamic properties of

the polar mixture. It will not be possible to put these new expressions into the form of an effective pure polar fluid.

APPENDIX

We wish to perform the integration

$$\phi_l(x, y) = i^l \int_0^\infty k^2 j_l(kx) j_0(ky) dk. \quad (\text{A1})$$

We begin with the integral representation

$$j_l(kx) = [(-i)^l / 2] \int_{-1}^1 e^{ikxu} P_l(u) du, \quad (\text{A2})$$

where $P_l(u)$ is the l th Legendre polynomial, and the explicit form

$$j_0(ky) = \text{sinky} / ky. \quad (\text{A3})$$

Inserting Eqs. (A2) and (A3) in Eq. (A1), interchanging integration orders and introducing a

$$\lim_{\epsilon \rightarrow 0} e^{-\epsilon k}$$

factor for convergence gives

$$\phi_l(x, y) = \lim_{\epsilon \rightarrow 0} (2y)^{-1} \int_{-1}^1 P_l(u) du \times \int_0^\infty k \text{sinky} e^{ik(ux+i\epsilon)} dk. \quad (\text{A4})$$

The inner integral can be rewritten as

$$(ix)^{-1} \frac{d}{du} \int_0^\infty dk \text{sinky} e^{ik(ux+i\epsilon)} = (2ix)^{-1} \frac{d}{du} \left(\frac{1}{ux+y+i\epsilon} - \frac{1}{ux-y+i\epsilon} \right).$$

Inserting this in Eq. (A4) and then integrating by parts gives

$$\phi_l(x, y) = \lim_{\epsilon \rightarrow 0} (4ixy)^{-1} \left[P_l(u) \left(\frac{1}{ux+y+i\epsilon} - \frac{1}{ux-y+i\epsilon} \right) \right]_{-1}^1 - \int_{-1}^1 P_l'(u) \left(\frac{1}{ux+y+i\epsilon} - \frac{1}{ux-y+i\epsilon} \right) du. \quad (\text{A5})$$

Using $P_l(-u) = (-1)^l P_l(u)$ and the identity

$$\lim_{\epsilon \rightarrow 0} [1/(x+y+i\epsilon)] = P[1/(x+y)] - i\pi\delta(x+y)$$

we can reduce Eq. (A5) to the following form for the case of even l

$$\phi_l(x, y) = (\pi/2xy) \{ \delta(x-y) - \delta(x+y) - \int_0^1 P_l'(u) [\delta(xu-y) - \delta(xu+y)] \}. \quad (\text{A6})$$

For odd l , Eq. (A5) reduces to a more complicated form involving principal valued integrals. Since we only require $l=0, 2$ for the dipolar problem we will not consider this further. Since we only require $\phi_l(x, y)$ for positive x, y in Eq. (3.15), we can further simplify Eq. (A6) to

$$\phi_l(x, y) = (\pi/2xy) [\delta(x-y) - x^{-1} \Theta(x-y) P_l'(y/x)] \quad (\text{A7})$$

In Eq. (A7), $\Theta(x-y)$ is the unit step function.

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