

Generalized mean spherical approximations for polar and ionic fluids

J. S. Høye

Mechanics Department, State University of New York, Stony Brook, New York 11790

J. L. Lebowitz

Belfer Graduate School of Science, Yeshiva University, New York, New York 10016

G. Stell

Mechanics Department, State University of New York, Stony Brook, New York 11790

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Generalized mean spherical approximations are solved for polar and ionic fluids. They are generalizations of previous mean spherical results in the sense that more general forms for the direct correlation function $c(12)$ are considered than heretofore. In the case of a polar fluid, $c(12)$ outside a hard-sphere core is taken to be a sum of an ideal dipole term, a Yukawa term, and two short-ranged terms, one of which is a shielded dipolar interaction, the other of which is a shielded "classical Heisenberg" interaction. In the ionic case, $c(12)$ outside the core is taken to be the sum of Coulomb and Yukawa terms. In both cases, the coefficients of all terms can be independently adjusted. Two applications of our generalized mean spherical results are discussed. The first generates improved approximations with built-in thermodynamic consistency. The second is a more straightforward use of the generalization to provide mean spherical approximations for a wider class of potentials.

I. INTRODUCTION

In the statistical mechanical theory of fluids, it is usually assumed that the atoms (or molecules) interact via a pair potential $\phi(12)$ that becomes infinite as the distance r between particles goes to zero and vanishes as r goes to infinity. For such potentials, the probability density associated with finding two particles a distance r apart approaches zero as $r \rightarrow 0$. If one further assumes the fluid particles to have impenetrable cores of diameter R , this pair density $g_2(12)$ is identically zero for $r < R$. For many potentials one also expects the direct correlation function $c(12)$ to approach $-\beta\phi(12)$ as $r \rightarrow \infty$, where $\beta^{-1} = kT$, T the absolute temperature, as long as one is not at a critical point.¹ The simplest approximation that embodies these expectations for particles with impenetrable cores of diameter R is the mean spherical approximation of Lebowitz and Percus² (MSA),

$$c(12) = -\beta\phi(12), \quad \text{for } r > R. \quad (\text{I.1})$$

The $c(12)$ and $g_2(12) - 1 = h(12)$ are related by the Ornstein-Zernike³ (OZ) equation

$$h(12) = c(12) + \int \rho(3) c(13) h(23) d(3). \quad (\text{I.2})$$

The impenetrability of the cores imposes the condition

$$g_2(12) = 0, \quad \text{for } r < R. \quad (\text{I.3})$$

For a single-component fluid with spherically symmetric potential $\phi(12) = v(r)$, the $g_2(12)$ is just the radial distribution function $g(r)$, $\rho(3)$ is just the number density ρ , and $\int d(3)$ represents integration over a volume element $d\mathbf{r}_3$; for orientation-dependent $\phi(12)$ or many-component systems, $g(12)$ and $\int d(3) \rho(3)$ represent appropriate generalizations of these concepts, as discussed below.

Equation (I.3) is exact and (I.2) can be taken to be a

definition of $c(12)$ in terms of $h(12)$. For potentials that decay relatively slowly as $r \rightarrow \infty$, (I.1) can be expected to be at its worst in the region, immediately outside the core, where $\phi(12)$ is at its largest.^{1,4} The error incurred may result in an extreme lack of thermodynamic consistency in the MSA; various ways of computing the thermodynamics from $h(12)$ can lead to very different answers. For the charged-sphere case solved by Waisman and Lebowitz,⁵ only the route via integration of the internal energy to get the free energy gives satisfactory results.⁵ For the dipolar-sphere case, solved by Wertheim,⁶ even this route is unsatisfactory; Eq. (I.1) does not give very satisfactory agreement for interesting values of the physical parameters with known^{4,7} thermodynamic results no matter how one computes the thermodynamics from $h(12)$. On the other hand, the dielectric constant obtained from the MSA seems likely to be good. Furthermore, the MSA is the only approximate integral equation for the pair distribution function of a fluid which can be solved exactly for interesting systems (the P.Y. equation for hard spheres is a special case of the MSA) and, as already noted, yields very good results for some quantities. It therefore appears very desirable to find ways of improving the MSA without giving up its good features of solubility and simplicity.

In this paper we begin a study of one means of improving (I.1) in the intermediate r region. It is based upon the analytic solution of the OZ equation for $c(12)$ of more general form than (I.1) and owes much, both technically and conceptually, to previous work of Waisman,^{8,9} upon which we lean very heavily. Our solutions, which we shall refer to as generalized mean spherical approximations (GMSA), permit rectification of the MSA defect of thermodynamic inconsistency.

We consider both ionic and polar systems. In Sec. II, we give an analytic solution to our GMSA for a system of

dipolar spheres that generalizes Wertheim's⁶ solution of the MSA for that system and is given in terms of Waisman's solution⁹ of his own GMSA for hard spheres. In Sec. III, we solve a GMSA for a symmetric mixture of charged spheres. As in the case of our dipolar-sphere equation, the solution is expressed in terms of previous results of Waisman.⁹

For dipolar nonpolarizable spheres, the pair potential has the form

$$\begin{aligned} \phi(12) &= \infty, & \text{for } r < R, \\ \phi(12) &= -m^2 D(12)/r^3, & \text{for } r > R, \end{aligned} \quad (\text{I. 4})$$

where

$$D(12) = 3(\hat{r} \cdot \hat{s}_1)(\hat{r} \cdot \hat{s}_2) - \hat{s}_1 \cdot \hat{s}_2.$$

Here m is the magnitude of the dipole moment, \hat{s}_i is a unit vector in the direction of the dipole moment of particle i , \hat{r} is the unit vector $\mathbf{r}_{12}/|\mathbf{r}_{12}|$, and $r = |\mathbf{r}_{12}|$. For this system, we solve in Sec. II the Ornstein-Zernike equation in the form

$$h(12) = c(12) + \rho/4\pi \int c(13)h(23)d(3), \quad (\text{I. 5a})$$

where $d(i) = d\mathbf{r}_i d\Omega_i$ with $d\Omega_i$ the element of solid angle, $4\pi = \int d\Omega_i$, and

$$\begin{aligned} h(12) &= -1, & r < R, \\ c(12) &= c_s(r) + c_\Delta(r)\Delta(12) + c_D(r)D(12), \end{aligned} \quad (\text{I. 5b})$$

where $\Delta(12) = \hat{s}_1 \cdot \hat{s}_2$ and for $r > R$,

$$\begin{aligned} c_s(r) &= S e^{-\kappa r}/r, \\ c_\Delta(r) &= A e^{-\lambda r}/r, \\ c_D(r) &= \beta m^2/r^3 + B \{-3(1 + \lambda R) e^{-\lambda R}/r^3 \lambda^2 \\ &\quad + \lambda[(\lambda r)^{-1} + 3(\lambda r)^{-2} + 3(\lambda r)^{-3}] e^{-\lambda r}\}. \end{aligned} \quad (\text{I. 5c})$$

When $S = A = B = 0$, (I. 5) reduces to the MSA solved by Wertheim. [Wertheim's formal solution actually permits $c_s(r)$ to be arbitrary for $r > R$, cf. Rushbrooke, Stell, and Høye.¹⁰] Our solution to (I. 5) can be effected with the parameters S , A , B , κ , and λ all unspecified functions of ρ , β , and m . Hence (I. 5) can be used with arbitrary side conditions on those parameters. We briefly discuss the question of their choice in Sec. IV.

In the case of charged spheres, we treat an over-all neutral mixture of species of equal diameter R and charge e_i immersed in a continuum of dielectric constant ϵ . The interaction potential between a particle of species i and one of species j is then of the form

$$\phi_{ij}(r) = \phi_{ji}(r) = \infty, \quad \text{if } r < R, \quad (\text{I. 6a})$$

$$\phi_{ij}(r) = \phi_{ji}(r) = e_i e_j / \epsilon r, \quad \text{if } r > R, \quad (\text{I. 6b})$$

and one has the charge-neutrality constraint

$$\sum \rho_i e_i = 0. \quad (\text{I. 6c})$$

This is generally referred to as the primitive-model electrolyte. We consider the GMSA

$$g_{ij}(r) = 0, \quad r < R, \quad (\text{I. 7a})$$

$$c_{ij}(r) = -\beta \phi_{ij} + B e^{-\lambda r}/r, \quad r > R, \quad (\text{I. 7b})$$

where g_{ij} and c_{ij} refer to the radial distribution function and direct correlation function between particles of species i and j . The OZ equation then takes the form

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int c_{ik}(r') h_{kj}(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (\text{I. 7c})$$

where $h_{ij}(r) = g_{ij}(r) - 1$.

With no extra labor, we can follow Waisman⁸ and consider also the case of "shielded charged spheres" obtained by replacing (I. 6b) by

$$\phi_{ij}(r) = \phi_{ji}(r) = e_i e_j A e^{-\mu r}/r, \quad \sum \rho_i e_i = 0. \quad (\text{I. 8})$$

This reduces to (I. 6b) when $A = \epsilon^{-1}$ and $\mu = 0$.

When $B = 0$, these equations have been solved by Waisman and Lebowitz⁵ and by Waisman.^{8a} We discuss the choice of B and λ in Sec. IV. [The more general case in which we add to the right side of (I. 7b) a term $e_i e_j A' e^{-\lambda' r}/r$ appears to be solvable also.^{8b}]

Our solutions of (I. 5) and (I. 7) can also be employed for a different purpose than that discussed above. If we continue to use (I. 1), then (I. 7) continues to represent the original MSA assumptions, but now for a $\phi(12)$ that includes a Yukawa as well as a Coulomb term. This is of obvious general interest, because real ions are not perfectly hard charged spheres, and the Yukawa term provides us with a means of either "softening" the repulsion hard core or of adding an attractive tail to mimic the variety of weakly attractive terms found in real interionic potentials. In typical applications of (I. 7) to ionic solution theory, the availability of the Yukawa term takes on special added importance, associated with the fact that $\phi(12)$ represents the ion-ion potential of mean force at infinite dilution rather than the bare interionic potential itself. It has long been surmised on heuristic grounds that one must include in $\phi(12)$ a soft short-ranged "Gurney-Frank" term¹¹ of roughly the same qualitative form as a Yukawa,¹² even if no such term exists in the underlying bare potential. Recently it has been confirmed on the basis of a statistical-mechanical investigation¹³ that such a term must indeed be expected to arise; moreover, a careful systematic analysis of experimental data by Friedman and his co-workers¹⁴ has yielded estimates of its size for a variety of real ionic pairs. These estimates can be used to estimate appropriate B and λ in (I. 7b), which can alternatively be estimated from simple model results of Ref. 13.

The situation with regard to the significance of (I. 5) used with (I. 1) is similar. It is of obvious general interest because it provides a potential core that can be softened and made anisotropic, thus coming that much closer to real polar molecules, which clearly do not have perfectly hard and spherically symmetric cores; the Yukawa term can also mimic the symmetric attractive forces completely lacking in the dipolar hard-sphere interaction but present in the interactions between real polar molecules. Of special interest is the fact that (I. 5) includes highly anisotropic short-range terms that can be made very strongly attractive for certain orientations while not for others. Such terms appear to be nec-

essary in order to capture the effects of hydrogen bonding found in some polar fluids. While one cannot expect the simple symmetry of our Δ and D terms in (I.5) to adequately reflect the complicated orientation-dependent short-range forces found in, say, H_2O or HF , the analogous terms that would be naturally associated with inclusion of quadrupolar forces might begin to capture the most important geometric features of those molecules, and it is not unreasonable to expect that the MSA will ultimately prove soluble with such terms added. Even as it now stands, (I.5c) used with (I.1) is already of considerable theoretical interest as a model potential that can be used to explore and extend Boltzmann's theory of dissociation, formulated in Vol. II, Chap. VI of his famous Gas Theory.¹⁵ (His model of chemical bonding is based on the use of short-ranged attractive interactions that can "saturate" as a result of geometry constraints. Our dipolar and Heisenberg terms can never fully saturate, but they have the geometry that could be used to enhance the formation of chains or rings of particles and discourage other configurations.)

We note finally that the use of our GMSA to treat a broader class of $\phi(12)$ than heretofore considered can be combined with our idea of using the GMSA for self-consistency. In the case of a charged system, for example, we can use (I.7) with

$$\phi_{ij}(r) = \phi_{ji}(r) = e_i e_j / \epsilon r + b e^{-\lambda_0 r} / r,$$

instead of (I.6b), with the B and λ in (I.7b) differing from $-\beta b$ and λ_0 by terms determined to satisfy the self-consistency conditions discussed in Sec. IV B. Analogous remarks hold for our dipolar GMSA.

II. SOLUTION OF THE GMSA FOR DIPOLAR SPHERES

By studying the Fourier transform of the dipole-dipole interaction, one discovers in a rather straightforward way that the solution can be expressed in terms of the solution given by Waisman for the $c(12)$ of Yukawa form for $r > R$.

The dipole-dipole interaction, with a small- r cut-off, is

$$\begin{aligned} \phi_D(12) &= 0, & r < \sigma \\ \phi_D(12) &= -\frac{m^2}{r^3} D(12), & r > \sigma \end{aligned} \quad (II.1)$$

where $D(12) = 3(\hat{r} \cdot \hat{s}_1)(\hat{r} \cdot \hat{s}_2) - \hat{s}_1 \cdot \hat{s}_2$. It has a Fourier transform,

$$\begin{aligned} \bar{\phi}_D(12) &= \int e^{i\mathbf{k}\cdot\mathbf{r}} \phi_D(12) d\mathbf{r}, \\ \bar{\phi}_D(12) &= 4\pi m^2 \left(\frac{\sin z}{z^3} - \frac{\cos z}{z^2} \right) \bar{D}(12) = \bar{\psi}(k) \bar{D}(1, 2), \end{aligned} \quad (II.2)$$

where $\bar{D}(12) = 3(\hat{k} \cdot \hat{s}_1)(\hat{k} \cdot \hat{s}_2) - \hat{s}_1 \cdot \hat{s}_2$ and $z = k\sigma$. One notes that $\bar{\psi}(k)$ is the same as the Fourier transform of the spherically symmetric square-well potential

$$\begin{aligned} \psi(r) &= \frac{m^2}{\sigma^3}, & r < \sigma, \\ \psi(r) &= 0, & r > \sigma. \end{aligned} \quad (II.3)$$

This is a special case of a more general relation derived

in Appendix A. We merely note here that while (II.1) is zero for $r < \sigma$, (II.3) is zero outside this region, i.e., there is a kind of "inversion" relation with regard to Fourier transforms between a spherical symmetric potential and one with the dipolar angular dependence $D(12)$. An arbitrary dipole potential $f(r)D(1, 2)$ can be obtained by "summing over" (i.e., integrating) (II.1) for different σ , and correspondingly an arbitrary spherically symmetric potential can be obtained by summing over (II.3) for different σ . We now look at the Ornstein-Zernike equation for dipolar spheres,

$$h(12) = c(12) + \rho \int c(13)h(32) \frac{d\Omega_3}{4\pi} d\mathbf{r}_3. \quad (II.4)$$

Following Wertheim, we seek a $c(12)$ and $h(12)$ that can be written for all r as

$$\begin{aligned} c(12) &= c_\Delta \Delta(12) + c_D D(12) + c_s(r), \\ h(12) &= h_\Delta \Delta(12) + h_D D(12) + h_s(r). \end{aligned} \quad (II.5)$$

Values given $c(12)$ in (I.5) for $r > R$ are

$$\begin{aligned} c_s &= S e^{-kr} / r, \\ c_\Delta &= A e^{-\lambda r} / r, \\ c_D &= \frac{\beta m^2}{r^3} + B \left\{ -3(1 + \lambda R) e^{-\lambda R} / r^3 \lambda^2 \right. \\ &\quad \left. + \lambda [(\lambda r)^{-1} + (\lambda r)^{-2} + 3(\lambda r)^{-3}] e^{-\lambda r} \right\}, \end{aligned} \quad (II.6a)$$

while for $r < R$,

$$h_s = 1, \quad h_\Delta = h_D = 0. \quad (II.6b)$$

Fourier transformation of (II.4) and (II.5) gives

$$\bar{h} = \bar{c} + (\rho / 4\pi) \int \bar{c} \bar{h} d\Omega_3, \quad (II.7)$$

$$\begin{aligned} \bar{c} &= \bar{c}_\Delta \bar{\Delta}(12) + \bar{c}_D \bar{D}(12) + \bar{c}_s, \\ \bar{h} &= \bar{h}_\Delta \bar{\Delta}(12) + \bar{h}_D \bar{D}(12) + \bar{h}_s. \end{aligned} \quad (II.8)$$

As noted by Wertheim, we have the convolution rules

$$DD = \frac{1}{3}(D + 2\Delta), \quad \Delta D = \frac{1}{3}D, \quad \Delta\Delta = \frac{1}{3}\Delta, \quad (II.9)$$

where $DD \equiv (1/4\pi) \int D(1, 2)D(2, 3)d\Omega_2$, etc. Introducing

$$J_1 = D + \Delta \text{ and } J_2 = 2\Delta - D, \quad (II.10)$$

we have

$$J_1 J_1 = J_1; \quad J_2 J_2 = J_2; \quad J_1 J_2 = 0. \quad (II.11)$$

We now set

$$\begin{aligned} \bar{c} &= \bar{c}_1 J_1 + \bar{c}_2 J_2 + \bar{c}_s, \\ \bar{h} &= \bar{h}_1 J_1 + \bar{h}_2 J_2 + \bar{h}_s, \end{aligned} \quad (II.12)$$

where we introduce

$$\begin{aligned} \bar{c}_1 &= \frac{1}{3}(\bar{c}_\Delta + 2\bar{c}_D), & \bar{c}_\Delta &= \bar{c}_1 + 2\bar{c}_2, \\ \bar{c}_2 &= \frac{1}{3}(\bar{c}_\Delta - \bar{c}_D), & \bar{c}_D &= \bar{c}_1 - \bar{c}_2, \end{aligned} \quad (II.13)$$

and similar expressions for \bar{h}_1 and \bar{h}_2 . When we put (II.12) into (II.7), making use of (II.11), we get

$$\begin{aligned} \bar{h}_1 J_1 + \bar{h}_2 J_2 + \bar{h}_s &= \bar{c}_1 J_1 + \bar{c}_2 J_2 + \bar{c}_s \\ &\quad + \rho \bar{c}_1 \bar{h}_1 J_1 + \rho \bar{c}_2 \bar{h}_2 J_2 + \rho \bar{c}_s \bar{h}_s. \end{aligned} \quad (II.14)$$

The coefficients of each of the angular dependent parts J_1 and J_2 must vanish, so we get the following three equations, which uncouple $\bar{c}_s, \bar{c}_1, \bar{h}_1$ and $\bar{h}_s, \bar{c}_2, \bar{h}_2$:

$$\begin{aligned} \tilde{h}_s &= \tilde{c}_s + \rho \tilde{c}_s \tilde{h}_s, \\ \tilde{h}_1 &= \tilde{c}_1 + \rho \tilde{c}_1 \tilde{h}_1, \\ \tilde{h}_2 &= \tilde{c}_2 + \rho \tilde{c}_2 \tilde{h}_2. \end{aligned} \quad (\text{II. 15})$$

In (II.15), J_1 and J_2 do not appear. Therefore, as noted before, \tilde{c}_1 , \tilde{c}_2 , \tilde{h}_1 , \tilde{h}_2 may be considered as Fourier transforms of *spherically symmetric* functions. As a result, it turns out that the boundary conditions (II.6) transform to those of the MSA for a hard-sphere plus Yukawa potential. When $A=B=0$, one sees from this that the MSA for polar fluids can be expressed in terms of the solution for hard spheres. Similarly, but less obviously, the solution to Eq. (II.7) can be expressed in terms of the solution for $c(12)$ which is of the Yukawa form for $r > R$. To see this, let us transform the boundary conditions (II.6). The c_Δ and h_Δ come from spherically symmetric functions (with respect to \mathbf{r}) so they remain unchanged; thus, the spherically symmetric functions \hat{c}_Δ and \hat{h}_Δ , whose Fourier transforms are \tilde{c}_Δ and \tilde{h}_Δ are

$$c_\Delta = c_\Delta, \quad \hat{h}_\Delta = h_\Delta. \quad (\text{II. 16a})$$

But c_D and h_D have to be transformed, and we now make use of the relation between (II.2) and (II.3). Suppose $B=0$; from (II.6), one can conclude that $c_D D(12)$ (c_D is for the moment unknown for $r < \sigma$) can be written as a sum (becoming an integral) over terms given by (II.1) all having $(0 <) \sigma < R$. Accordingly, the transformed c_D , which we will denote by \hat{c}_D , can be written as a sum (becoming an integral) over terms given by (II.3) which all also have $\sigma < R$. Therefore, we have the boundary condition

$$\hat{c}_D = 0, \quad \text{for } r > R. \quad (\text{II. 16b})$$

For $B \neq 0$, it is most convenient to work backwards. We seek c_D such that

$$\hat{c}_D = B e^{-\lambda r} / r, \quad r > \sigma. \quad (\text{II. 16c})$$

The details of this evaluation are given in Appendix A. The c_D that we find is that which appears in (I.5). From (II.6), one also sees that $h_D D(12)$ can be written as a sum (becoming an integral) over terms given by (II.1) all having $\sigma > R$. Therefore the corresponding transformed quantity \hat{h}_D can be written as a sum (becoming an integral) over terms given by (II.3) all also having $\sigma > R$. Accordingly, for $r < R$, \hat{h}_D will be some constant which we shall denote by $-3K$:

$$\hat{h}_D = -3K, \quad \text{for } r < R. \quad (\text{II. 17a})$$

Using Eq. (A2), one can easily see that K can also be written as

$$\int_R^\infty h_D(r) r^{-1} dr = K. \quad (\text{II. 17b})$$

These transformed boundary conditions we put into (II.13) introducing the appropriate corresponding hatted quantities for c_1 , c_2 , h_1 , and h_2 . The boundary conditions for these quantities become

$$\begin{aligned} \hat{c}_1 &= \frac{1}{3}(\hat{c}_\Delta + 2\hat{c}_D), & \hat{c}_2 &= \frac{1}{3}(\hat{c}_\Delta - \hat{c}_D), & \text{for } r > R \\ \hat{h}_1 &= -2K, & \hat{h}_2 &= K, & \text{for } r < R. \end{aligned} \quad (\text{II. 18})$$

To go further we change to the new variables,

$$\begin{aligned} \hat{H}_1 &= 2K\hat{H}_1, & \hat{C}_1 &= 2K\hat{C}_1, \\ \hat{H}_2 &= -K\hat{H}_2, & \hat{C}_2 &= -K\hat{C}_2, \end{aligned} \quad (\text{II. 19})$$

thereby changing the boundary conditions (II.18) to

$$\begin{aligned} \hat{C}_1 &= (\hat{c}_\Delta + 2\hat{c}_D)/6K, & \hat{C}_2 &= (\hat{c}_\Delta - \hat{c}_D)/-3K, & \text{for } r > R, \\ \hat{H}_1 &= -1, & \hat{H}_2 &= -1, & \text{for } r < R. \end{aligned} \quad (\text{II. 20})$$

These are exactly the boundary conditions for the case of hard spheres with an added Yukawa term in the MSA. With these new variables, (II.15) becomes

$$\begin{aligned} \tilde{H}_0 &= \tilde{C}_0 + \rho \tilde{C}_0 \tilde{H}_0, \\ \tilde{H}_1 &= \tilde{C}_1 + 2K\rho \tilde{C}_1 \tilde{H}_1, \\ \tilde{H}_2 &= \tilde{C}_2 + (-K\rho) \tilde{C}_2 \tilde{H}_2, \end{aligned} \quad (\text{II. 21})$$

where we have set $h_s = H_0$, $c_s = C_0$ for notational symmetry. Accordingly, the solution for the Fourier transforms are [using (II.19) and (II.13)],

$$\begin{aligned} \tilde{c}_\Delta &= 2K\tilde{C}_1 + 2(-K)\tilde{C}_2, \\ \tilde{c}_D &= 2K\tilde{C}_1 - (-K)\tilde{C}_2, \end{aligned} \quad (\text{II. 22})$$

$$\begin{aligned} \tilde{h}_\Delta &= 2K\tilde{H}_1 + 2(-K)\tilde{H}_2, \\ \tilde{h}_D &= 2K\tilde{H}_1 - (-K)\tilde{H}_2, \end{aligned} \quad (\text{II. 23})$$

where the \tilde{C}_1 , \tilde{H}_1 and \tilde{C}_2 , \tilde{H}_2 are the Fourier transforms of the \hat{C}_1 , \hat{H}_1 and \hat{C}_2 , \hat{H}_2 of Eq. (II.20), from which we have

$$\begin{aligned} \hat{C}_1(r) &= B_1 e^{-\lambda r} / r, & r > R, \\ B_1 &= (A + 2B)/6K, & r > R, \end{aligned}$$

and

$$\begin{aligned} \hat{C}_2(r) &= B_2 e^{-\lambda r} / r, & r > R, \\ B_2 &= (B - A)/3K. & r > R. \end{aligned}$$

The OZ equation for a direct correlation function of this form has been solved by Waisman.⁸ Thus, (II.22) and (II.23) give the solution of our equation in terms of the solution of Waisman's equation.

For the Fourier transform at $k=0$, one can introduce the functions $q_i = 1 - n_i \hat{C}_i(0)$, where n_i is the coefficient appearing in front of $\hat{C}_i \hat{H}_i$ in (II.21). We note that q_i is the "a" appearing in Waisman's Eq. (3c). From (II.21), it follows that

$$n_i \tilde{H}_i(0) = \tilde{n}_i \tilde{C}_i(0) [1 - \tilde{n}_i \tilde{C}_i(0)]^{-1} = (1/q_i) - 1. \quad (\text{II. 24})$$

When $S=A=B=0$, the q_i reduce to the hard-sphere values⁶

$$q_i = \frac{(1 + 2x_i)^2}{(1 - x_i)^4}; \quad x_i = \frac{\pi}{6} n_i R^3. \quad (\text{II. 25})$$

In general, the q_i for $i=1, 2$ depend upon m , β , λ , etc., as well as x_i , but for our purposes only the x_i dependence need be exhibited. It is understood that $q_i(x_i)$ is to be evaluated at the m , β , A , B , and λ associated with the \tilde{C}_i of (II.24).

For $k=0$, we get, putting (II.22) and (II.23) into (II.8),

$$\rho\bar{c}(12) = -[q_1(2\xi) - q_2(-\xi)]\bar{D}(12) + [3 - q_1(2\xi) - 2q_2(-\xi)]\Delta(12) + c_s, \quad (\text{II. 26})$$

$$\rho\bar{h}(12) = -\{[q_1(2\xi) - q_2(-\xi)]/q_1(2\xi)q_2(-\xi)\}\bar{D}(12) + [1/q_1(2\xi) + 2/q_2(-\xi) - 3]\bar{\Delta}(12) + \bar{h}_s, \quad (\text{II. 27})$$

where

$$\xi = (\pi/6)K\rho R^3.$$

From (II. 1), (II. 2), and (II. 6), one sees that for $k=0$ one must have $\rho\bar{c}_D = -4\pi/3\beta m^2\rho = -3y$. Accordingly, we can use (II. 26) to determine the unknown K via the relation

$$3y = q_1(2\xi) - q_2(-\xi). \quad (\text{II. 28})$$

Equations (II. 26) and (II. 27) are consistent with the following general expressions for a polar fluid, valid for $k=0$,

$$\rho\bar{c}(12) = -3y\bar{D}(12) + 3(1-y/z)\bar{\Delta}(12) + \dots, \quad (\text{II. 29a})$$

$$\rho\bar{h}(12) = A\bar{D}(12) + (B - 2zA)\bar{\Delta}(12) + \dots, \quad (\text{II. 29b})$$

where A , B , and z are related by the equations

$$A = -3z^2/[y(1+2z)(1-z)] \quad \text{and} \quad B = 3(z/y - 1), \quad (\text{II. 30})$$

and the unexhibited terms in (II. 29) can be shown¹⁶ to make no contribution to the dielectric constant. In our approximation [(II. 26) and (II. 27)], we thus have

$$z = [q_1(2\xi) - q_2(-\xi)][q_1(2\xi) + 2q_2(-\xi)]^{-1}. \quad (\text{II. 31})$$

Together with the exact¹⁶ relation between the dielectric constant and z ,

$$\frac{\epsilon - 1}{\epsilon + 2} = z, \quad (\text{II. 32})$$

this gives

$$\epsilon = q_1(2\xi)/q_2(-\xi). \quad (\text{II. 33})$$

From (II. 17b), it also follows that for dipolar spheres the parameter K is directly related to u , the configurational energy per particle via the simple relation

$$\beta u = -3yK, \quad (\text{II. 34})$$

since for dipolar spheres

$$u = \frac{1}{2}\rho \int h(12)\phi_D(12)dr \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi},$$

which can be reduced to

$$u = -\frac{1}{3}\rho m^2 \int h_D(r)r^{-3}dr. \quad (\text{II. 35})$$

as noted in Appendix B.

Let us consider u and β times the free energy per particle $\beta f = \psi$ as functions of the reciprocal temperature. Then, starting at the higher temperature end where $\beta=0$, we have the general relation

$$\psi(\beta) - \psi(0) = \int_0^\beta u(\beta')d\beta'. \quad (\text{II. 36})$$

According to (II. 34), we have from this

$$\beta f(\beta) - \psi(0) = -3y \int_0^\beta K(\beta')d\beta'. \quad (\text{II. 37})$$

These equations can be generalized without difficulty to apply to the case in which the hard-sphere potential is replaced by any spherically symmetric potential with hard core at diameter R ; in particular, (II. 33) and the functions $q_i(x)$ remain unchanged. A generalization in another direction is obtained if one remains with a system of dipolar spheres but considers either the exact $\bar{c}(12)$ and $\bar{h}(12)$ defined by (II. 7) or any approximation that retains the structure of (II. 29), (II. 30), and (II. 32). Then defining $q_i(x)$ through (II. 24) will yield (II. 33), where the $q_i(x)$, $x \geq 0$ is well defined. As long as $q_2(x)$ can be uniquely continued into the negative- x domain (as it can for the MSA and GMSA considered here) so that $q_2(x)$ is well defined for $x < 0$, Eq. (II. 33) continues to hold.

III. SOLUTION OF GMSA FOR CHARGED AND SHIELDED CHARGED SPHERES

Let \mathbf{E} , \mathbf{U} , ρ be n matrices (n is the number of species) with

$$E_{ij} = e_i e_j, \quad U_{ij} = 1, \quad \rho_{ij} = \rho_i \delta_{ij}. \quad (\text{III. 1})$$

It follows from the charge neutrality condition $\sum \rho_i e_i = 0$ that

$$\mathbf{U}\rho\mathbf{E} = \mathbf{E}\rho\mathbf{U} = 0, \quad (\text{III. 2})$$

while

$$\mathbf{U}\rho\mathbf{U} = \rho\mathbf{U}, \quad \mathbf{E}\rho\mathbf{E} = \gamma\mathbf{E}; \quad \rho = \sum \rho_i, \quad \gamma = \sum \rho_j e_j^2. \quad (\text{III. 3})$$

The OZ equation and GMSA approximation (I. 7) can be put in a simple form by setting

$$\mathbf{h} = h_s(r)\mathbf{U} + h_a(r)\mathbf{E}, \quad (\text{III. 4a})$$

$$\mathbf{c} = c_s(r)\mathbf{U} + c_a(r)\mathbf{E}; \quad (\text{III. 4b})$$

$$h_s(r) = c_s(r) + \rho \int c_s(\mathbf{r}-\mathbf{r}')h_s(\mathbf{r}')d\mathbf{r}', \quad (\text{III. 5a})$$

$$h_a(r) = c_a(r) + \gamma \int c_a(\mathbf{r}-\mathbf{r}')h_a(\mathbf{r}')d\mathbf{r}', \quad (\text{III. 5b})$$

with the boundary conditions

$$h_s(r) = -1, \quad \text{for } r < R; \quad c_s(r) = Be^{-\gamma r}/r, \quad \text{for } r > R, \quad (\text{III. 6a})$$

$$h_a(r) = 0, \quad \text{for } r < R; \quad c_a(r) = -\beta\phi(r), \quad \text{for } r > R, \quad (\text{III. 6b})$$

where

$$\begin{aligned} \phi(r) &= (\epsilon r)^{-1}, & \text{for Coulomb charges,} \\ \phi(r) &= Ae^{-\mu r}/r, & \text{for shielded charges.} \end{aligned} \quad (\text{III. 7})$$

The solution of Eqs. (III. 6) and (III. 7) is essentially contained in the work of Waisman and of Waisman and Lebowitz,^{5,8,9} (Note that some of the species may be uncharged.)

IV. THERMODYNAMIC SELF-CONSISTENCY

A. Polar systems

There are three obvious paths to thermodynamic functions from $g(12)$. The first is via integration of the in-

ternal energy with respect to β or λ as in (II. 36). The exact $h(12)$ will no longer have the functional form given by (II. 5), but it is clear that if we write $h(12)$ as the sum of the terms shown in (II. 5) plus a remainder term $R(12)$, where $h_\Delta(r)$, $h_D(r)$, and $h_s(r)$ are taken to be unspecified functions of r , Eq. (II. 36) is an exact expression for the free energy—i. e., neither h_Δ , h_s , nor $R(12)$ contribute. Similarly, it is easy to see that the exact relation between $\partial\beta p/\partial\rho$ and $h(12)$ or $c(12)$ is given by

$$\partial\beta p/\partial\rho = 1 - \rho \int c_s(r) dr = \left[1 + \rho \int h_s(r) dr \right]^{-1}. \quad (IV. 1)$$

This gives a second path to thermodynamics. Finally, the virial theorem discussed in Appendix B provides a third path. For dipolar spheres it is of the form given by (B9) and (B7),

$$\beta p = \rho + \frac{4\pi}{6} \rho R^3 [h_s(R) + 1] - 3y\rho K, \quad (IV. 2)$$

where

$$K = \int_R^\infty h_D(r) r^{-1} dr, \quad y = \frac{4\pi}{9} \beta m^2 \rho.$$

The requirement that ϵ and f be prescribed functions and that (II. 36), (IV. 1), and (IV. 2) be consistent will determine four independent relations among the five available parameters S , A , B , κ , and λ . We thus have more than enough parameters to both satisfy the most obvious self-consistency requirements and reproduce the best available approximations for f and ϵ . For f , a simple Padé approximation is available¹⁰; for ϵ , the best currently available approximation is probably that of the MSA.⁶ Using these (and letting the remaining relations among parameters be dictated by technical convenience) represents one possible choice of parameters; others are possible. We hope to continue our investigation of this question in future publications.

B. Charged systems

For charged systems, the same three general routes from the correlation functions to thermodynamics are available.⁵ For our GMSA, we can be much more specific about our choice of parameters than in the polar case because the equations are much simpler in struc-

ture. There are only two available parameters [Eq. (III. 6)], B and λ , and one expects them to be uniquely determined if we require all three routes to give the same equation of state and further prescribe that the equation come from the MSA “energy” equation⁵ (obtained from integration of the internal energy with respect to β or e to get the free energy) supplemented by the Carnahan–Starling hard-sphere equation used by Waisman.⁸ The MSA equation is adequate in the 1–1 electrolyte case, where poor values of $g_{ij}(r)$ for $r \approx R$ represent the major deficiency of the MSA.^{4,5} Larsen¹⁷ reports that the MSA internal energy remains accurate to within 10% or so even for the extremely high ρ and e/ϵ values that are characteristic of fused salts, but again the $g_{ij}(r)$ values are poor for r/R slightly greater than unity.¹⁷ In our GMSA, the $g_{ij}(r)$ values for $1 < r/R < 2$ can be expected to be much more accurate if the above self-consistency constraints are imposed.

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APPENDIX A: COMPUTATION OF $c(r)D(12)$ WHICH HAS FOURIER TRANSFORM $\tilde{c}(k)\tilde{D}(12)$, WHERE $\tilde{c}(k)$ IS THE TRANSFORM OF $\hat{c}(r) = 1/re^{-\lambda r} (r > \sigma)$

This computation can be done most easily by applying the following formula of Wertheim⁶:

$$c(r) = \hat{c}(r) - \frac{3}{r^3} \int_0^r \hat{c}(r') r'^2 dr', \quad (A1)$$

or

$$\hat{c}(r) = c(r) - 3 \int_r^\infty c(r') r'^{-1} dr'. \quad (A2)$$

To show that the Fourier transform of $c(r)D(12)$ is just $\tilde{c}(k)\tilde{D}(12)$, where $c(r)$ is given by (A1), we write¹⁶

$$\tilde{c}(k) = 4\pi \int_0^\infty [-j_2(kr)] c(r) r^2 dr = -4\pi \int_0^\infty j_2(kr) \hat{c}(r) r^2 dr + 4\pi \int_0^\infty j_2(kr) \frac{3}{r^3} \left(\int_0^r \hat{c}(r') r'^2 dr' \right) r^2 dr, \quad (A3)$$

where $j_2(z) = 3 \sin z/z^3 - 3 \cos z/z^2 - \sin z/z$.

The last integral can be integrated partially,

$$\begin{aligned} \tilde{c}(k) &= -4\pi \int_0^\infty j_2(kr) \hat{c}(r) r^2 dr - 4\pi \left(\frac{3 \sin(kr)}{(kr)^3} - \frac{3 \cos(kr)}{(kr)^2} \right) \int_0^r \hat{c}(r') r'^2 dr \Big|_0^\infty + 4\pi \int_0^\infty \left(\frac{3 \sin(kr)}{(kr)^3} - \frac{3 \cos(kr)}{(kr)^2} \right) \hat{c}(r) r^2 dr \\ &= 4\pi \int_0^\infty \frac{\sin(kr)}{kr} \hat{c}(r) r^2 dr = \tilde{\hat{c}}(k) \end{aligned} \quad (A4)$$

Let $\hat{c}(r)$ be given by

$$\hat{c}(r) = \begin{cases} \frac{1}{r} e^{-\lambda r}, & r > \sigma, \\ 0, & r < \sigma. \end{cases}$$

Application of (A1) then gives

$$\begin{aligned} c(r) &= \frac{1}{r} e^{-\lambda r} - \frac{3}{r^3} \int_{\sigma}^r \frac{1}{r'} e^{-\lambda r'} r'^2 dr' \\ &= \frac{1}{r} e^{-\lambda r} + \frac{3}{r^3} \int_0^r \frac{1}{\lambda^2} (1 + \lambda r) e^{-\lambda r} \\ &= -\frac{3}{\lambda^2} (1 + \lambda \sigma) e^{-\lambda \sigma} \frac{1}{r^3} + \lambda \left(\frac{1}{\lambda r} + \frac{3}{(\lambda r)^2} + \frac{3}{(\lambda r)^3} \right) e^{-\lambda r}, \quad r > \sigma. \\ c(r) &= 0, \quad r < \sigma. \end{aligned} \tag{A5}$$

APPENDIX B: THE VIRIAL THEOREM APPLIED TO A POLAR FLUID OF DIPOLAR SPHERES

For molecules of cylindrical symmetry, the virial theorem has the form

$$\beta p = \rho - \frac{\beta \rho^2}{6} \int [h(12) + 1] \mathbf{r} \cdot \nabla \phi(12) d\mathbf{r} \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi}. \tag{B1}$$

For such a fluid, let us write the pair potential as

$$\begin{aligned} \phi(12) &= \phi_0(12) + \phi_D(12); \\ \phi_D(12) &= -\frac{m^2}{r^3} [3(\hat{r}_1 \hat{s}_1)(\hat{r}_2 \hat{s}_2) - \hat{s}_1 \hat{s}_2]. \end{aligned} \tag{B2}$$

Introducing polar coordinates $x_1, x_2, x_3 \rightarrow r, \theta, \phi$ one finds $\mathbf{r} \cdot \nabla = r(\partial/\partial r)$. Accordingly,

$$\mathbf{r} \cdot \nabla \phi_D(12) = r \frac{\partial}{\partial r} \phi_D(12) = -3\phi_D(12), \tag{B3}$$

$$\beta p = \rho - \frac{\beta \rho^2}{6} \int [h(12) + 1] \mathbf{r} \cdot \nabla \phi_0(12) d\mathbf{r} \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi} + \beta \rho u_D. \tag{B4}$$

Here u_D is the internal energy per particle from the dipolar part of the interaction,

$$u_D = \frac{1}{2} \rho \int h(12) \phi_D(12) d\mathbf{r} \frac{d\Omega_1}{4\pi} \frac{d\Omega_2}{4\pi}. \tag{B5}$$

The $h(12)$ can be expanded¹⁶ (in spherical harmonics with respect to \hat{s}_1 and \hat{s}_2);

$$\begin{aligned} h(12) &= h_s(r) + h_\Delta(r)(\hat{s}_1 \hat{s}_1) + h_D(r) \\ &\quad \times [3(\hat{r}_1 \hat{s}_1)(\hat{r}_2 \hat{s}_2) - \hat{s}_1 \hat{s}_2] + \dots, \end{aligned} \tag{B6}$$

and it can be shown without difficulty that only the h_D term in (B6) contributes to u_D :

$$u_D = -\frac{1}{3} \rho m^2 \int h_D(r) \frac{1}{r^3} d\mathbf{r}, \tag{B7}$$

and only h_s contributes to the second term on the right side of (B4). Specializing $\phi_0(12)$ to the case of hard spheres of diameter R we get, as is well known,

$$-\beta \int [h_s(r) + 1] \mathbf{r} \cdot \nabla \phi_0 d\mathbf{r} = 4\pi [h_s(R+) + 1] R^3, \tag{B8}$$

where $h_s(R+)$ is the value of $h_s(r)$ at contact. Then, using the definition (II.17) of K , one finds comparing with (B7) that $\beta u_D = -3yK$ (with $y = (4\pi/9) \beta \rho m^2$). So

$$\beta p = \rho + \frac{4\pi}{6} \rho^2 R^3 (h_s(R+) + 1) - 3y\rho K. \tag{B9}$$

As an example, consider now the MSA for a polar fluid of dipolar hard spheres [$c(12) = -\beta\phi_D(12)$, for $r > R$]. Then $h_s(r)$ is as for pure hard spheres. Therefore, when (B9) is used, the excess pressure p_{ex} due to the dipolar interaction will be

$$\beta p_{ex} = \beta \rho u_D = -3y\rho K. \tag{B10}$$

By means of the energy relation one obtains (for the MSA) the free energy (noting that u_D in this case depends on β and ρ only through y)

$$f = \frac{1}{\beta} \int_0^\beta u_D d\beta = \frac{1}{y} \int_0^y u_D dy, \tag{B11}$$

and excess pressure

$$\beta p_{ex} = \beta \rho^2 \frac{\partial f}{\partial y} = \beta \rho y \frac{\partial f}{\partial y} = \beta \rho (u_D - f). \tag{B12}$$

Accordingly, these two ways of obtaining the excess pressure differ by a term $\beta \rho f$, as can be seen from comparing (B10) and (B12).

¹More precisely, one expects $c(12) + \beta\phi(12) \rightarrow Ah^2(12) + O[h^3(12)] + O[h^2(12)/r]$, where A is a functional of the functional derivative of $c(12)$ with respect to the one-point density function $\rho(3)$. For most potentials, one cannot hope to express A as a purely thermodynamic quantity, but for spherically symmetric potentials that fall off like a power of r as $r \rightarrow \infty$, one has

$$A = \frac{\rho^4}{2} \left(\frac{\partial^2 \beta \mu}{\partial \rho^2} \right)^2,$$

where μ is chemical potential. For such potentials, one also expects $h(12) \rightarrow -(1/\rho \times \partial \rho / \partial \beta \mu)^2 \beta \phi(12)$ and hence $c(12) \rightarrow -\beta \phi(12)$. For dipolar systems, one similarly concludes $c(12) + \beta\phi(12) \rightarrow A/r^6$, so that $c(12) \rightarrow -\beta\phi(12)$ again as $r \rightarrow \infty$. These asymptotic estimates, obtained by J. Groeneveld and G. Stell (unpublished work) are reliable only for $\kappa r \gg 1$, where κ is the characteristic inverse correlation length in the problem. At a critical point, one has $\kappa = 0$, and a quite different sort of asymptotic analysis of $c(12) + \beta\phi(12)$ is appropriate. This is given by G. Stell in Phys. Rev. B **1**, 2265 (1970).

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