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# Comparison of Two Theories for the Two Particle Distribution Function of Polar Fluids*

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Two recent theories for the two particle distribution function of polar fluids are compared. The formal theory of Nienhuis and Deutch [J. Chem. Phys. **55**, 4213 (1971)] is valid for arbitrary sample geometry and arbitrary short-range forces accompanying the dipole–dipole interactions. The theory of M. S. Wertheim [J. Chem. Phys. **55**, 4291 (1971)] presents an exact result for the mean spherical model (MSM) of a fluid of hard spheres with embedded dipole moment in an infinite system and in a finite spherical system. Perfect agreement is found when the approximations of the MSM are introduced into the Nienhuis–Deutch theory. This lends strong support to the conclusions that have been drawn about the long-range and shape dependent nature of the two particle distribution function for polar systems. Finally an expression is given for the excess free energy of a dipolar fluid in the MSM.

## I. INTRODUCTION

A recent issue of this journal contained two articles dealing with the two particle distribution function, $n_2$, of polar fluids. One of these articles was by us[1]; the other by M. S. Wertheim.[2] The two particle distribution function of polar liquids has a long-range part that arises because of the long-range dipole–dipole interaction between the molecules. Since these two articles are the first attempt to evaluate the long-range nature of the two particle distribution function it is of interest to examine the relationship between the two theories. The main purpose of this paper is to show that the theory presented by Wertheim[2] and that presented by us[1] are in essential agreement. This agreement lends strong support to the central conclusions about the long-range and shape dependent character of the two particle distribution function of polar fluids.

The two theories are not identical in their scope. Werthein[2] has adopted a particular model for the polar fluid, the so-called mean spherical model (MSM). He has solved this model exactly for two particular sample geometries, an infinite system and a finite volume spherical system. The molecules are assumed to be hard spheres with a central point dipole. In the MSM an approximation is made at the outset to the exact direct correlation function $C(1, 2)$. The approximation consists in replacing $C(1, 2)$ by $[-\beta v]$ for $|r_1-r_2|>R$ where $R$ is the hard sphere diameter, $\beta=(kT)^{-1}$, and $v$ is the dipole–dipole potential. For hard spheres, i.e., $v=0$, the MSM is the Percus–Yevick model for the hard spheres system.

Our theory[1] does not adopt a particular model of the fluid nor is the short-range nature of the intermolecular forces specified beyond the assumption of pairwise additivity. This permits us to formally include the effects of angular dependent short-range forces, which is an important feature of real liquids. Furthermore, our theory deals with all sample geometries including the infinite system and the sphere in vacuum. All the consequences of our theory are determined once the short-range part of the two particle correlation function $G_2^{(0)}$ is known. A calculation of this complex quantity requires one to adopt a particular model for the fluid, for example, the MSM.

It is clear that the two theories are attractively complimentary. Our theory which is a more general formulation has the disadvantage that calculation of quantities of interest, such as the dielectric constant, requires knowledge of the short-range correlation function $G_2^{(0)}$. Wertheim's theory achieves the explicit calculation of quantities of interest at the expense of adopting a reasonable, but restrictive, model.

The succeeding sections of the paper are organized as follows: In Sec. II we present the relevant results of our theory; in Sec. III we present the relevant results of Wertheim's theory. The interested reader is referred to Refs. (1) and (2), respectively, for the detailed derivations of these results. In Sec. IV we demonstrate that the results of the two theories are in agreement for the infinite volume case. In Sec. V we show that the central result of the two theories are in agreement when finite volume effects must be taken into account in the case where the sample geometry is a sphere in vacuum.

The final section of the paper explores the thermodynamics of the MSM dipolar fluid. In the second article of our series on the structure of dipolar fluids,[3] we showed how knowledge of the two particle correlation function may be used to determine the thermodynamic properties of dipolar systems. The Helmholtz free energy of the polar fluid may be related to the Halmholtz free energy of a reference fluid and a particular integral involving the two particle correlation function of the dipolar system. In the reference system molecules interact with exactly the same short-range forces present in the dipolar system, but the molecules have zero dipole moment. Explicit calculations cannot be carried out until one adopts an expression for the short-range part of the correlation function $G_2^{(0)}$, which in our theory determines the long-range part of the correlation function. In our previous article[3] we adopted a form for $G_2^{(0)}$ implied by the Onsager model. As stated in that paper, "the chief defect of the Onsager model is that it does not adequately take into account the short-range angular dependent forces present in real liquids." Wertheim's calculation of the MSM provides us with a better approximation for $G_2^{(0)}$, since at least the hard core part of the short-range forces is taken into account in a more realistic manner. We present an expression for the Helmholtz free energy of a dipolar system when the MSM form of $G_2^{(0)}$ is employed to compute the two particle correlation function.

## II. RESULTS OF THE NIENHUIS–DEUTCH THEORY

In this section we summarize the results of the Nienhuis–Deutch theory[1] in a way that permits easy comparison with Wertheim's results. The two particle correlation function is defined by

$$n_2(1,2)=[\rho/\Omega]^2+G_2(1,2), \tag{2.1}$$

where (1, 2) denotes the position and orientation of dipoles one and two, i.e., $(\mathbf{r}_1\boldsymbol{\omega}_1;\ \mathbf{r}_2,\ \boldsymbol{\omega}_2)$, $\rho$ is the density, and $\Omega=\int d\boldsymbol{\omega}_1$. The correlation function $G_2$ may be separated into two terms

$$G_2(1,2)=G_2^{(0)}(1,2)+G_2^{(1)}(1,2). \tag{2.2}$$

The term $G_2^{(0)}$ is strictly of short range, has a unique definition in terms of a graphical expansion, and is the same for all sample geometries $V$. The term $G_2^{(1)}$ has a long-range character and is given by

$$G_2^{(1)}(1,2)=(\beta\rho^2/\epsilon\Omega^2)\boldsymbol{\mu}_{\rm eff}(1)\cdot[\mathsf{T}(\mathbf{r}_1,\mathbf{r}_2)+\mathbf{R}_v^*(\mathbf{r}_1,\mathbf{r}_2;\epsilon^{-1})]\cdot\boldsymbol{\mu}_{\rm eff}(2)=(\rho/\Omega)^2h^{(1)}(1,2), \tag{2.3}$$

where for convenience we introduce the reduced correlation functions by the definitions

$$G_2^{(1)}=(\rho/\Omega)^2h^{(1)} \quad\text{and}\quad G_2^{(0)}=(\rho/\Omega)^2h^{(0)}. \tag{2.4}$$

In Eq. (2.3) $\mathsf{T}$ is the dipole–dipole tensor

$$\mathsf{T}(\mathbf{r},\mathbf{r}')=[3(\mathbf{r}-\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^5]-(\mathsf{I}/|\mathbf{r}-\mathbf{r}'|^3) \tag{2.5}$$

and $\epsilon$ the dielectric constant of the fluid determined by

$$\epsilon-1=(4\pi/3)\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_{\rm eff}. \tag{2.6}$$

The quantity $\mathbf{R}_v^*(\mathbf{r},\mathbf{r}';\epsilon^{-1})\cdot\mathbf{p}$ has the interpretation of the reaction field established at point $\mathbf{r}$ in $V$ by a dipole $\mathbf{p}$ at $\mathbf{r}'$ in $V$, when $V$ is empty and the surrounding is filled with a dielectric continuum characterized by the dielectric constant $\epsilon^{-1}$. The effective dipole moments are determined by the short-range part of the correlation function $h^{(0)}$ according to

$$\boldsymbol{\mu}_{\rm eff}(1)=\boldsymbol{\mu}(1)+(\rho/\Omega)\int d(2)h^{(0)}(1,2)\boldsymbol{\mu}(2), \tag{2.7}$$

and in general $\boldsymbol{\mu}_{\rm eff}$ need not be parallel to $\boldsymbol{\mu}$. Since $h^{(0)}$ determines $\boldsymbol{\mu}_{\rm eff}$ which in term determines $\epsilon$, it follows that knowledge of $h^{(0)}$ completely determines $h^{(1)}$ and hence $n_2$.

These results are valid for arbitrary sample shapes $V$. It should be noted that since $h^{(0)}$ is of short range and independent of sample geometry, $\boldsymbol{\mu}_{\rm eff}$ and $\epsilon$ are the same for all sample geometries. In our original work we considered the more general situation of a molecular sample of volume $V$ surrounded by a continuim dielectric region $W$ of dielectric constant $\epsilon_0$. The results summarized here are for the special case when this surrounding region is not present, i.e., $W=0$.

## III. RESULTS OF THE WERTHEIM THEORY

Wertheim presents[2] an exact expression for the correlation function

$$h(1,2)=G_2(1,2)(\rho/\Omega)^{-2} \tag{3.1}$$

in an infinite system for the MSM in the case where the molecules interact as point dipoles embedded in hard spheres of radius $R$. The exact expression for $h(1,2)$ is

$$h(1,2)=h_s(r)+h_D(r)D(1,2)+h_\Delta(r)\Delta(1,2), \tag{3.2}$$

where

$$\Delta(1,2)=\mathbf{s}_1\cdot\mathbf{s}_2, \tag{3.3}$$

$$D(1,2)=3r^{-2}(\mathbf{s}_1\cdot\mathbf{r})(\mathbf{s}_2\cdot\mathbf{r})-(\mathbf{s}_1\cdot\mathbf{s}_2), \tag{3.4}$$

$\mathbf{s}_1$ ($\mathbf{s}_2$) is a unit vector in the direction of dipole one (two), and $r=|\mathbf{r}_1-\mathbf{r}_2|$. Note that

$$\mathbf{s}_1\cdot\mathsf{T}(\mathbf{r}_1,\mathbf{r}_2)\cdot\mathbf{s}_2=r^{-3}D(1,2). \tag{3.5}$$

The quantity $h_s(r)=h_s(r,\rho)$ is the pair correlation function for a hard sphere fluid at density $\rho$ computed from the Percus–Yevick equation; closed form solutions are available for this equation.[4]

The quantity $h_\Delta(r)$ vanishes for $r<R$ and, for $r>R$, is equal to

$$h_\Delta(r)=2\kappa[h_s(r,2\kappa\rho)-h_s(r,-\kappa\rho)], \tag{3.6}$$

where, here, one of the terms $h_s(r,-\kappa\rho)$ refers to a solution of the Percus–Yevick equation for hard spheres at a negative density equal to $(-\kappa\rho)$. The constant $\kappa$ is found from solving the equation (at a particular $\rho$ and $\beta$),

$$y=\tfrac{1}{3}[q(2\xi)-q(-\xi)], \tag{3.7}$$

where

$$y=[4\pi\beta\mu^2\rho/9], \tag{3.8}$$

$$\xi=\kappa\eta, \tag{3.9}$$

and

$$\eta=[\pi R^3\rho/6]. \tag{3.10}$$

The function $q(\eta)$ is inverse compressibility which for hard spheres, in the Percus–Yevick approximation, is given by

$$[q(\eta)]^{-1}=1+4\pi\rho\int_0^\infty r^2h_s(r,\rho)\,dr=\frac{(1-\eta)^4}{(1+2\eta)^2}. \quad (3.11)$$

Finally, the function $h_D(r)$ vanishes for $r<R$ and is given by

$$h_D(r)=\hat{h}_D(r)-3r^{-3}\int_0^r s^2\hat{h}_D(s)\,ds \quad (3.12)$$

for $r>R$, with

$$\hat{h}_D(r)=\kappa[2h_s(r,2\kappa\rho)+h_s(r,-\kappa\rho)]. \quad (3.13)$$

In fact, Eqs. (3.6) and (3.12) are also valid for $r<R$ since for these values they give zero.

For the MSM both the functions $h_\Delta(r)$ and $h_D(r)$ are determined once solutions to the Percus–Yevick equation $h_s(r,\rho)$ for positive and negative densities are known. Both $h_s(r)$ and $h_\Delta(r)$ are of short range. The function $h_D(r)$ is of long range and asymptotic to

$$-3r^{-3}\int_0^\infty s^2\hat{h}_D(s)\,ds, \quad (3.14)$$

which by use of Eqs. (3.13), (3.11), (3.7), and (3.8) may be shown to be equal to

$$(\beta\mu^2/r^3)[1/q(2\kappa\eta)q(-\kappa\eta)]. \quad (3.15)$$

It follows from Eqs. (3.2) and (3.5) that the asymptotic form of $h(1,2)$ in MSM is

$$\lim_{r\to\infty} h(1,2)=\beta[q(2\kappa\eta)q(-\kappa\eta)]^{-1}\boldsymbol{\mu}(1)\cdot\mathbf{T}(\mathbf{r}_1,\mathbf{r}_2)\cdot\boldsymbol{\mu}(2). \quad (3.16)$$

In summary, Eqs. (3.13) and (3.12) determine $h_D(r)$ and Eqs. (3.6) determines $h_\Delta(r)$ in terms of the hard sphere $h_s(r)$ obtained from the Percus–Yevick equation. These functions specify $h(1,2)$ according to Eq. (3.2). It should be emphasized that Wertheim's result quoted in this section applies only to an infinite volume system; for finite volumes the results must be modified.[2]

The dielectric constant is determined by Wertheim in the MSM to be

$$\epsilon=[q(2\xi)/q(-\xi)], \quad (3.17)$$

which can be put in the alternative form

$$\epsilon=[3y/q(-\xi)]+1 \quad (3.18)$$

by use of Eq. (3.7).

## IV. COMPARISON OF THE TWO THEORIES FOR THE INFINITE VOLUME SYSTEM

We now wish to show that the two theories are in agreement. We shall demonstrate this agreement in the following manner. In order to apply our theory we must have an expression for $h^{(0)}$, the short-range part of the two particle correlation function. We shall select, as $h^{(0)}$, the short-range part of Wertheim result for $h(1,2)$ in the MSM. We shall then use exclusively the results of our theory, presented in Sec. II, for an infinite volume system, to compute all other results for the MSM presented in Sec. III. This means that we must use the MSM $h^{(0)}$ and our theory, to (a) compute the dielectric constant and find agreement with Eqs. (3.17) or (3.18), (b) compute $h^{(1)}$ and find agreement with Eq. (3.16), (c) show that $h=h^{(0)}+h^{(1)}$ is identical to the exact expression for $h$, Eq. (13.2), found by Wertheim for the MSM in the infinite volume system.

The short-range function $h^{(0)}$ for the MSM is formed by subtracting the long-range asymptotic part of $h(1,2)$, Eq. (3.16), from the exact expression for $h(1,2)$, Eq. (3.2). Thus,

$$h^{(0)}(1,2)=h_s(r)+h_\Delta(r)\Delta(1,2)+\{h_D(r)-[\beta\mu^2/r^3q(2\xi)q(-\xi)]\}D(1,2), \quad (4.1)$$

where $\xi=\kappa\eta$ and we have made use of Eq. (3.5).

The functions $h_\Delta(r)$ and $q(x)$ are defined by Eqs. (3.6) and (3.11), respectively; the function $h_D(r)$ is defined by Eqs. (3.12) and (3.13); and the factor $\xi$ has exactly the same meaning as in Sec. III. We proceed to use this form of $h^{(0)}$ in the results of our theory presented in Sec. II.

In order to compute the dielectric constant in our theory according to Eq. (2.6) we must know $\boldsymbol{\mu}_{\text{eff}}$. This quantity is defined by Eq. (2.7). For the MSM, $h^{(0)}$ is given by Eq. (4.1); an elementary calculation yields

$$\boldsymbol{\mu}_{\text{eff}}(1)=\boldsymbol{\mu}(1)\left\{1+[y/q(2\xi)q(-\xi)]+\tfrac{4}{3}\pi\rho\int_0^\infty r^2h_\Delta(r)\,dr\right\}, \quad (4.2)$$

where the singularity at the origin in the last term of the expression for $h^{(0)}$, Eq. (4.1), is taken into account according to the prescription,[1]

$$\int_{|\mathbf{r}-\mathbf{r}'|<L} d\mathbf{r}'\,\mathbf{s}_1\cdot\mathbf{T}(\mathbf{r},\mathbf{r}')\cdot\mathbf{s}_2=\int_{|\mathbf{r}-\mathbf{r}'|<L} d\mathbf{r}'\,D(1,2)r^{-3}=-\tfrac{4}{3}\pi\mathbf{s}_1\cdot\mathbf{s}_2. \quad (4.3)$$

The last term in Eq. (4.2) may be evaluated by use of Eqs. (3.6) and (3.11) with the result

$$\boldsymbol{\mu}_{\text{eff}}(1)=\boldsymbol{\mu}(1)\left([y/q(2\xi)q(-\xi)]+\tfrac{1}{3}\{[q(2\xi)]^{-1}+[2/q(-\xi)]\}\right). \quad (4.4)$$

In the MSM, $y$ is related to $q(-\xi)$ and $q(2\xi)$ according to Eq. (3.7). It follows that

$$\boldsymbol{\mu}_{\text{eff}}(1)=\boldsymbol{\mu}(1)q(-\xi)^{-1}, \quad (4.5)$$

so that in the MSM $\mu_{\text{eff}}$ is parallel to $\mu$.

According to Eq. (2.6) the dielectric constant in our theory will be given by

$$\epsilon-1=(4\pi/3)\beta\rho\boldsymbol{\mu}\cdot\boldsymbol{\mu}_{\text{eff}}=3yq(-\xi)^{-1}, \quad (4.6)$$

in agreement with Wertheim's result, Eq. (3.18), the alternative form for the dielectric constant, Eq. (3.17), follows immediately by use of Eq. (3.7).

Our next task is to show that the MSM short range $h^{(0)}$, when employed in our formalism, regenerates the appropriate long-range part of the two particle correlation function found by Wertheim for the MSM. For an infinite system, according to our theory, the long-range part of $h(1, 2)$ is given by

$$h^{(1)}(1, 2) = (\beta/\epsilon)\,\boldsymbol{\mu}_{\mathrm{eff}}(1)\cdot\mathbf{T}(\mathbf{r}_1, \mathbf{r}_2)\cdot\boldsymbol{\mu}_{\mathrm{eff}}(2). \quad (4.7)$$

If we substitute for $\boldsymbol{\mu}_{\mathrm{eff}}$ the expression we have found in Eq. (4.5) and use the form for $\epsilon$ given in Eq. (3.17) we obtain exactly the asymptotic result [Eq. (3.16)] found by Wertheim for the MSM. It follows immediately that $h = h^{(0)} + h^{(1)}$ is identical to the exact expression for $h(1, 2)$, Eq. (3.2).

In our theory the dielectric constant may be computed in alternative manner from a fluctuation formula. For a sphere embedded in an infinite dielectric continuim of the same dielectric constant this formula is

$$\begin{aligned}(\epsilon-1)[(2\epsilon+1)/3\epsilon] &= (\beta/3V)\langle M^2\rangle_\infty(4\pi)\\ &= 3y[1+(N-1)\langle \mathbf{s}_1\cdot\mathbf{s}_2\rangle_\infty] \quad (4.8)\end{aligned}$$

[see Eq. (1.5) of Ref. 1], where the bracket denotes an average over the distribution function appropriate to an infinite system and the average is performed over a sphere with radius $A$,

$$(\mu-1)\langle \mathbf{s}_1\cdot\mathbf{s}_2\rangle_\infty = (\rho/\Omega^2)\int_{|\mathbf{r}|<A} d\mathbf{r}\,d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2\,\mathbf{s}_1\cdot\mathbf{s}_2 h(1, 2). \quad (4.9)$$

A simple calculation employing Eq. (3.2) for $h = h^{(0)} + h^{(1)}$ leads to the result

$$(\epsilon-1)[(2\epsilon+1)/3\epsilon] = y\{[q(2\xi)]^{-1} + [2/q(-\xi)]\}, \quad (4.10)$$

which may be shown by use of Eq. (3.7) to lead to the expression for the dielectric constant presented in Eq. (3.17).

In this section we have demonstrated the agreement between our general theory and Wertheim's results for the MSM in the case of an infinite system. In the next section we turn to a comparison between the two theories in the case of a finite spherical system.

## V. COMPARISON OF THE TWO THEORIES FOR A FINITE SPHERICAL SYSTEM

For large separation, the potential of mean force $w(1, 2)$ between two dipoles is related to $h$ by the formula

$$h(1, 2) \sim -\beta w(1, 2). \quad (5.1)$$

Wertheim presents an exact formula for $w(1, 2)$ for the MSM in the case of a spherical sample of radius $A$. Wertheim's result is

$$\begin{aligned}w(1, 2) = {}& \left(\frac{\epsilon-1}{3y}\right)\left(\frac{\epsilon-1}{3y\epsilon}\right)(\boldsymbol{\mu}_1\cdot\nabla_1)(\boldsymbol{\mu}_2\cdot\nabla_2)\\ &\times\left[r_{12}^{-1} + \frac{\epsilon-1}{A}\sum_{L=1}^{\infty}\frac{L+1}{L+1+2\epsilon}\left(\frac{r_1r_2}{A^2}\right)^L P_L(\cos\theta_{12})\right].\end{aligned} \quad (5.2)$$

We shall show that our theory leads to an identical expression for the potential of mean force for this finite system geometry. In our theory $w(1, 2)$ at large separations is given by

$$-\beta w(1, 2) \sim h^{(1)}(1, 2) \quad (5.3)$$

or

$$\begin{aligned}w(1, 2) = -\epsilon^{-1}\boldsymbol{\mu}_{\mathrm{eff}}(1)\cdot[&\mathbf{T}(\mathbf{r}_1, \mathbf{r}_2)\\ &+\mathbf{R}_v^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon^{-1})]\cdot\boldsymbol{\mu}_{\mathrm{eff}}(2). \quad (5.4)\end{aligned}$$

The effective dipole moment and the dielectric constant do not depend on sample shape, so for the MSM we may use the result for $\boldsymbol{\mu}_{\mathrm{eff}}$ presented in the last section in the form

$$\boldsymbol{\mu}_{\mathrm{eff}} = [(\epsilon-1)/3y]\boldsymbol{\mu}, \quad (5.5)$$

where we have used Eqs. (4.5) and (4.6). It follows that

$$\begin{aligned}w(1, 2) = {}& [(\epsilon-1)/3y][(\epsilon-1)/3y\epsilon]\boldsymbol{\mu}(1)\\ &\cdot[\nabla_1\nabla_2\,|\mathbf{r}_1-\mathbf{r}_2|^{-1} - \mathbf{R}_v^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon^{-1})]\cdot\boldsymbol{\mu}(2). \quad (5.6)\end{aligned}$$

The term involving the reaction field tensor may be evaluated. The reaction field for a spherical cavity of radius $A$ in a dielectric continuim of dielectric constant $\epsilon$ is given by

$$\begin{aligned}\mathbf{R}_v^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon) = {}& A^{-1}\nabla_1\nabla_2\\ &\times\sum_{L=1}^{\infty}\frac{(\epsilon-1)(L+1)}{L+\epsilon(L+1)}\left(\frac{r_1r_2}{A^2}\right)^L P_L(\cos\theta_{12}) \quad (5.7)\end{aligned}$$

[see Eq. (A13) in the Appendix of Ref. 1]. It follows that

$$\begin{aligned}\mathbf{R}_v^*(\mathbf{r}_1, \mathbf{r}_2; \epsilon^{-1}) = {}& -\left(\frac{\epsilon-1}{A}\right)\nabla_1\nabla_2\\ &\times\sum_{L=1}^{\infty}\frac{L+1}{L+1+\epsilon L}\left(\frac{r_1r_2}{A^2}\right)^L P_L(\cos\theta_{12}). \quad (5.8)\end{aligned}$$

When this expression is substituted into Eq. (5.6) we obtain exact agreement with the asymptotic potential of mean force Eq. (5.2) obtained by Wertheim for the MSM in the case of a finite spherical sample geometry.

## VI. THERMODYNAMICS OF THE MSM DIPOLAR FLUID

In the second article of our series on the structure of dipolar fluids[3] we presented a formula that permits calculation of the excess free energy of the dipolar system once the two particle correlation function is known. The formula is obtained by formally scaling the dipole moment by a parameter $\lambda^{1/2}$, so that each molecule has a dipole moment equal to $\lambda^{1/2}\mu$, and then considering the free energy of the system $A(\lambda)$ as a function of $\lambda$. If $\lambda=1$ the system is the dipolar fluid of interest; if $\lambda=0$ the system is a reference system where the molecules interact exclusively by the short range potential. The general formula we obtained is

$$A(1)-A(0)=-\frac{1}{2}\int_0^1 d\lambda \int_v d(1)d(2)$$

$$\times\left(\frac{\rho}{\Omega}\right)^2 h(1,2;\lambda)\boldsymbol{\mu}(1)\cdot\mathbf{T}(1,2)\cdot\boldsymbol{\mu}(2), \quad (6.1)$$

where $h(1,2;\lambda)$ is the two particle distribution function for the polar system where the molecules have dipole moment $\lambda^{1/2}\mu$. The reader is referred to Ref. 3 for details of the derivation and related discussion.

Wertheim's calculation of $h(1,2)$ for the MSM dipolar fluid provides a new and important approximation for this excess free energy. It turns out that the answer is remarkably simple. By closely following Wertheim's argument for an infinite system with $\lambda=1$, it is an easy matter to show that

$$h(1,2;\lambda)=h_s(r)+h_\Delta(r;\lambda)\Delta(1,2)+h_D(r;\lambda)D(1,2), \quad (6.2)$$

where $h_\Delta(r;\lambda)$ and $h_D(r;\lambda)$ have the same functional form as in Eqs. (3.6) and (3.12)–(3.13), respectively, except that $\kappa$ is replaced by a function of $\lambda$, $K(\lambda)$. The function $K(\lambda)$ is determined by an equation similar to Eq. (3.7),

$$\lambda y=(4\pi/9)\beta\rho\lambda\mu^2=\tfrac{1}{3}\{q[2K(\lambda)\eta]-q[-K(\lambda)\eta]\}, \quad (6.3)$$

where $\eta$ is given by Eq. (3.10) and the functional form of $q(x)$ by Eq. (3.11).

If Eq. (6.2) for $h$ is substituted into the expression for the free energy, Eq. (5.1), the resulting integrals can be performed. The singularity in $\mathbf{T}$ does not contribute in any of the three resulting terms because $h_\Delta$, and $h_D$ all vanish for $r<R^{(2)}$, and the term involving $h_s$ does not contribute since $h_s(r)=-1$ if $r<R$. The term involving $h_\Delta$ vanishes after integration over orientations because $\mathrm{Tr}[\mathbf{T}]=0$. After integration over angles the term involving $h_D$ may be expressed as

$$A(1)-A(0)=-\tfrac{1}{2}V\tfrac{1}{3}(2\rho^2\mu^2)\int_0^1 d\lambda\int d\mathbf{r}h_D(r;\lambda)r^{-3} \quad (6.4)$$

$$=-\tfrac{4}{3}\pi\rho^2\mu^2V\int_0^1 d\lambda\int_R^\infty dr h_D(r;\lambda)r^{-1}, \quad (6.5)$$

where we have used the fact that $h_D$ vanishes for $r<R$. Wertheim has shown that

$$\int_R^\infty dr h_D(r,\lambda)r^{-1}=K(\lambda) \quad (6.6)$$

[see Eq. (36) of Ref. 2], so that the final answer for the excess free energy of the MSM dipolar fluid is given by the simple expression.

$$\frac{A(1)-A(0)}{V}=-\tfrac{4}{3}\pi\rho^2\mu^2\int_0^1 d\lambda K(\lambda). \quad (6.7)$$

For fixed $\rho$ and $\beta$ the function $K(\lambda)$ is found by solving the equation

$$\lambda y=\tfrac{1}{3}\{[1+4K(\lambda)\eta]^2/[1-2K(\lambda)\eta]^4$$

$$-[1-2K(\lambda)\eta]^2/[1+K(\lambda)\eta]^4\}. \quad (6.8)$$

In Eq. (6.7), $A(0)$ is to be interpreted as the Helmholtz free energy of a hard sphere fluid in the Percus–Yevick approximation.

We expect that the MSM expression for the excess Helmholtz free energy, Eqs. (5.7)–(5.8), will prove quite successful in predicting the thermodynamic properties of highly polar fluids. Furthermore, the MSM expression may be more successful than the Onsager model expression for the excess free energy,[2] because the MSM takes into account short-range forces in a more realistic manner. We intend to compare the MSM predictions for the dielectric constant and the free energy (as well as the Onsager model predictions) with experiment in the near future.

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