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Molecular theory of orientationally ordered liquids: Exact formal expressions and the application of integral-equation methods with results for ferrofluids

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The purpose of this paper is to describe a number of theoretical results for fluids consisting of orientationally ordered particles. The model considered assumes perfect orientational order, with all molecules fully aligned in a particular direction with respect to a laboratory fixed frame of reference. However, rotations about the fixed axis are permitted and hence the present theory can be applied to particles which are not axially symmetric. Physically, such a model can represent liquid crystals in a dense nematic phase or fluids of particles aligned by strong electric or magnetic fields. A general formulation is given which allows the hypernetted-chain, Percus-Yevick, and closely related integral-equation approximations to be solved for orientationally ordered systems. For anisotropic fluids it is interesting to analyze the compressibility and pressure tensors and this is done in some detail for particles interacting with both short- and long-range (i.e., dipolar) potentials. The compressibility equation is used to demonstrate microscopically the physical requirement that these tensors be isotropic in a fluid. Also, the conditions placed upon the pair distribution function $g(12)$ by isotropy of the pressure tensor were determined by examining the virial equation of state. For the dipolar case explicit expressions are derived relating the elements of the dielectric tensor to $g(12)$ for an infinite system. Finally, numerical results are presented and discussed for ferrofluids and for another model defined by a closely related but short-range potential.

I. INTRODUCTION

The purpose of this paper is to describe some general theoretical techniques which can be applied to liquids of orientationally ordered particles. These include liquid crystals in the nematic phase or fluids of molecules orientationally ordered by strong electric or magnetic fields. Despite the physical interest of such systems there has been relatively little attempt to apply theories which have been quite successful for isotropic fluids to ordered liquids of this type. Notable exceptions have been the solution of the Percus-Yevick (PY) approximation given by Lebowitz and Perram[1] for a fluid of hard parallel ellipsoids, the solution of the mean spherical approximation (MSA) for charged parallel ellipsoids by Dhont,[2] and the application of the MSA and the hypernetted-chain approximation (HNC) to ferrofluids as described by Hayter and Pynn[3] and Martin *et al.*,[4] respectively. In this paper we extend and generalize this earlier work, enlarging both the class of models which can be considered and the theories which can be applied.

Following previous work,[1–6] we assume a somewhat simplified model in which the orientational order is "perfect." That is, all molecules are constrained to be aligned in a particular direction defined in a laboratory fixed reference frame and orientational fluctuations with respect to this direction are not permitted. However, we do consider the case of nonaxially symmetric particles allowing the molecules to rotate about the fixed axis. It should be emphasized that although in the present model the particles are orientationally fixed the fact that they are spatially free to move ensures that the physical behavior of such systems is by no means simple. For example, Monte Carlo calculations[6] have recently shown that a fluid of hard parallel spherocylinders can undergo a nematic-smectic phase transition.

In the present work we use the language and methods often employed in liquid-state theory.[7,8] It is shown that if the pair correlation function, etc. is expanded in an appropriate angle-dependent basis set then the HNC and PY integral-equation theories can be solved for orientationally ordered systems in a manner similar to that previously applied in the solution of these theories for isotropic fluids of nonspherical particles.[3,4,9–14] It is also found that this formulation allows interesting and convenient exact formal expressions to be derived for the dielectric and pressure tensors. Finally, the properties of ferrofluids are discussed in some detail and explicit HNC and PY results are given.

II. GENERAL THEORY

In this section we describe how the integral-equation theories can be solved for the present model, and derive exact expressions for the dielectric and pressure tensors. The approach followed is analogous in spirit to those which have been applied in theoretical treatments of isotropic fluids of nonspherical particles.[11–14] That is, the pair correlation and related functions are expanded in an appropriate angle-dependent basis set constructed such as to take advantage of all symmetry requirements of the orientationally ordered system.

A. Expansion of the pair correlation function

For the orientationally ordered but translationally invariant fluids we consider the pair correlation function

$$h(12)=h(\mathbf{r}_{12},\chi_1,\chi_2)\ , \tag{1}$$

where the vector $\mathbf{r}_{12}=\mathbf{r}_2-\mathbf{r}_1$ and the angles χ_1 and χ_2 describe rotation about the orientationally fixed molecular axis which we choose to be parallel to the z axis of the reference frame. For the present model it is convenient to expand $h(12)$ on a complete angular basis set to obtain

$$h(12)=\sum_{m,n=-\infty}^{+\infty}\sum_{l=0}^{\infty}\sum_{\lambda=-l}^{l}h^{mnl\lambda}(r_{12})\times e^{im\chi_1}e^{in\chi_2}Y_l^{\lambda}(\boldsymbol{\Omega}_{12})\ , \tag{2}$$

where $\boldsymbol{\Omega}_{12}=(\theta_{12},\varphi_{12})$ describes the orientation of the vector $\mathbf{r}_{12}$ and $Y_l^{\lambda}(\boldsymbol{\Omega})$ denotes the usual spherical harmonic.[15] The number of projections in (2) can be reduced by requiring that $h(12)$ must be invariant through an arbitrary rotation of the reference frame about the z axis (i.e., through the operations of the C_∞ group). Following Blum and Torruella[9] we project $h(12)$ onto the totally symmetric representation of C_∞,

$$\hat{h}(12)=\frac{\int dR_\varphi R_\varphi h(12)}{\int dR_\varphi}\ , \tag{3}$$

where R_φ denotes the representation of a rotation φ about the z axis and the measure dR_φ is equal to $d\varphi$ with $\varphi\in[0,2\pi)$. The action of R_φ on the angular functions is

$$R_\varphi e^{im\chi_1}e^{in\chi_2}Y_l^{\lambda}(\boldsymbol{\Omega}_{12})=e^{i(m+n+\lambda)\varphi}e^{im\chi_1}e^{in\chi_2}Y_l^{\lambda}(\boldsymbol{\Omega}_{12})\ , \tag{4}$$

so that the symmetrized $\hat{h}(12)$ [which henceforth we will identify with $h(12)$] can be written as

$$h(12)=\sum_{m,n,l}h^{mnl}(r_{12})\psi^{mnl}(1,2)\ , \tag{5a}$$

where

$$\psi^{mnl}(1,2)=f^{mnl}e^{im\chi_1}e^{in\chi_2}Y_l^{-(m+n)}(\boldsymbol{\Omega}_{12})\ , \tag{5b}$$

and f^{mnl} is an arbitrary, nonzero, normalization constant. We emphasize that, by construction, the complete angular basis set (5b) is appropriate only for the expansion of pair correlation functions of phases having perfect orientational order and invariant under the symmetry operation C_∞ (e.g., ferrofluids). These include, as a particular case, fully aligned nematics of $D_{\infty h}$ symmetry.

It is possible to write two additional symmetry requirements (i.e., independent of the details of the molecular model) which the $h^{mnl}(r_{12})$ projections must obey. The fact that $h(12)$ is real requires that

$$h^{mnl}(r_{12})=(-1)^{m+n}h^{-m-nl*}(r_{12})\ , \tag{6a}$$

where the asterisk denotes the complex conjugate. Also, since $h(12)$ must be invariant to the exchange of labels of identical particles, the condition

$$h^{mnl}(r_{12})=(-1)^{l}h^{nml}(r_{12}) \tag{6b}$$

must hold. Molecular symmetry will further reduce the number of projections in (5). For instance, for cylindrically symmetric molecules one has $m=n=0$, l even.

B. Integral-equation theories: The HNC approximation

Integral-equation theories consist of the Ornstein-Zernike (OZ) equation supplemented with an appropriate closure approximation.[8–10] For the present model the OZ equation can be written in the form

$$h(12)-c(12)=\frac{\rho}{2\pi}\int h(13)c(32)d(3)\ , \tag{7}$$

where $c(12)$ is the direct correlation function, ρ is the number density, and $d(3)=d\chi_3 d\mathbf{r}_3$. In general, for isotropic fluids the HNC approximation has proven to be the most accurate integral-equation theory. The HNC closure is defined by the equation

$$c(12)=h(12)-\ln g(12)-\beta u(12)\ , \tag{8}$$

where $g(12)=h(12)+1$, $u(12)$ is the pair interaction, and $\beta=1/k_BT$. In this paper we will be mainly concerned with the HNC theory but we note that using the present techniques the PY equations can be easily solved along the lines described in Refs. 12 and 14. Also, of course, the solution of the MSA follows in a near trivial manner.

As in the case of isotropic fluids, the reduction and solution of Eqs. (7) and (8) is based upon expanding $h(12)$, $c(12)$, and $u(12)$ in an appropriate basis set. For the present model these expansions are defined by Eqs. (5). Since the final expressions obtained are somewhat simpler if

$$f^{mnl}=[4\pi/(2l+1)]^{1/2}\ , \tag{9}$$

all following equations are written assuming this particular choice. We also remark that if f^{mnl} is defined by Eq. (9), then for particles which are cylindrically symmetrical about the oriented axis the $\psi^{mnl}(12)$ reduce to Legendre polynomials consistent with the expressions employed by previous authors.[3–5]

1. *Reduction of the OZ equation*

Following the original method of Blum and Torruella[9] for isotropic systems, Eq. (7) is Fourier transformed to give

$$\tilde{h}(\mathbf{k},\chi_1,\chi_2)-\tilde{c}(\mathbf{k},\chi_1,\chi_2)=\frac{\rho}{2\pi}\int_0^{2\pi}\tilde{h}(\mathbf{k},\chi_1,\chi_3)\tilde{c}(\mathbf{k},\chi_3,\chi_2)d\chi_3\ , \tag{10a}$$

where

$$\tilde{h}(\mathbf{k},\chi_1,\chi_2)=\int h(\mathbf{r},\chi_1,\chi_2)e^{i\mathbf{k}\cdot\mathbf{r}}d\mathbf{r} \tag{10b}$$

and $\tilde{c}(\mathbf{k},\chi_1,\chi_2)$ is analogously defined. The Fourier transforms $\tilde{h}(\mathbf{k},\chi_1,\chi_2)$ and $\tilde{c}(\mathbf{k},\chi_1,\chi_2)$ are then expanded in the form[9]

$$\tilde{h}(\mathbf{k},\chi_1,\chi_2)=\sum_{m,n,l}\tilde{h}^{mnl}(k)\psi^{mnl}(\chi_1,\chi_2,\mathbf{\Omega}_{\mathbf{k}})\ , \tag{11a}$$

where

$$\tilde{h}^{mnl}(k)=4\pi i^l\int_0^\infty r^2 j_l(kr)h^{mnl}(r)dr\ , \tag{11b}$$

with $j_l(kr)$ denoting the usual spherical Bessel functions. The $\psi^{mnl}(\chi_1,\chi_2,\mathbf{\Omega}_{\mathbf{k}})$ is defined as in Eq. (5b) with $\mathbf{\Omega}_{\mathbf{k}}$ now describing the orientation of the vector **k**.

The procedure now followed is to substitute the $\tilde{h}(12)$ and $\tilde{c}(12)$ expansions into Eq. (10a) and simplify. This requires the evaluation of convolutions of the type

$$\psi^{m_1n_1l_1}(13)\times\psi^{m_2n_2l_2}(32)=\frac{1}{2\pi}\int_0^{2\pi}\psi^{m_1n_1l_1}(\chi_1,\chi_3,\mathbf{\Omega})\times\psi^{m_2n_2l_2}(\chi_3,\chi_2,\mathbf{\Omega})d\chi_3\ , \tag{12}$$

which occur on the left-hand side of Eq. (10a) after substitution for $\tilde{h}(12)$ and $\tilde{c}(12)$. If we insert the definition (5b) for $\psi^{mnl}(12)$ [assuming Eq. (9)] into Eq. (12) the integration over χ_3 can be easily performed to yield

$$\psi^{m_1n_1l_1}(13)\times\psi^{m_2n_2l_2}(32)=\frac{4\pi}{[(2l_1+1)(2l_2+1)]^{1/2}}\delta_{n_1,-m_2}e^{im_1\chi_1}e^{in_1\chi_2}\times Y_{l_1}^{-(m_1+n_1)}(\mathbf{\Omega})Y_{l_2}^{-(m_2+n_2)}(\mathbf{\Omega})\ . \tag{13}$$

Applying the product rule for spherical harmonics[15] Eq. (13) becomes

$$\psi^{m_1n_1l_1}(13)\times\psi^{m_2n_2l_2}(32)=\delta_{n_1,-m_2}\sum_l(2l+1)\begin{pmatrix}l_1 & l_2 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1 & l_2 & l\\ m_1+n_1 & n_2-n_1 & -(m_1+n_2)\end{pmatrix}(-1)^{m_1+n_2}\psi^{m_1n_2l}(12)\ , \tag{14}$$

where the large parentheses indicate the usual 3-j symbol.[15] In deriving Eq. (14) we have used the standard properties of the 3-j symbols noting in particular that l_1+l_2+l must be even.

Using Eq. (14) the OZ relationship (10a) immediately reduces to a set of coupled algebraic equations relating the $\tilde{h}^{mnl}(k)$ and $\tilde{c}^{mnl}(k)$ coefficients. These equations are defined by the expression

$$\tilde{h}^{mnl}(k)-\tilde{c}^{mnl}(k)=(2l+1)(-1)^{m+n}\rho\sum_{l_1,l_2,p}\begin{pmatrix}l_1 & l_2 & l\\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix}l_1 & l_2 & l\\ m+p & n-p & -(m+n)\end{pmatrix}\tilde{h}^{mpl_1}(k)\tilde{c}^{-pnl_2}(k)\ . \tag{15}$$

We note that for cylindrically symmetrical particles $h^{mnl}(r)\equiv h^{00l}(r)$, and Eq. (15) reduces to the result given by Hayter and Pynn[3] and Martin *et al.*[4] for ferrofluids.

For reasons which will become clear in the later development of this paper it is convenient to introduce the functions

$$H^{mn}(\mathbf{k})=\sum_l f^{mnl}\tilde{h}^{mnl}(k)Y_l^{-(m+n)}(\mathbf{\Omega}_{\mathbf{k}})\ . \tag{16}$$

In terms of these functions which depend both on the magnitude and direction of **k** we have

$$\tilde{h}(\mathbf{k},\chi_1,\chi_2)=\sum_{m,n}H^{mn}(\mathbf{k})e^{im\chi_1}e^{in\chi_2}\ , \tag{17}$$

and the OZ, Eq. (10), takes the alternative form

$$H^{mn}(\mathbf{k})=C^{mn}(\mathbf{k})+\rho\sum_p H^{mp}(\mathbf{k})C^{-pn}(\mathbf{k})\ , \tag{18}$$

where $C^{mn}(\mathbf{k})$ is defined similarly to (16).

2. *The HNC closure*

Following the arguments given in Ref. 11 we rewrite Eq. (8) in the form

$$c(12)=\int_r^\infty h(12)\frac{\partial w(12)}{\partial r'}dr'-\beta u(12)\ , \tag{19a}$$

where

$$w(12)=-\eta(12)+\beta u(12)\ , \tag{19b}$$

$$\eta(12)=h(12)-c(12)\ . \tag{19c}$$

In order to simplify Eq. (19a) we expand $h(12)$, $w(12)$, and $u(12)$ in $\psi^{mnl}(12)$ and apply the product rule

$$\psi^{m_1n_1l_1}(12)\psi^{m_2n_2l_2}(12)$$
$$=\sum_l (2l+1)\begin{bmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} l_1 & l_2 & l \\ -(m_1+n_1) & -(m_2+n_2) & (m_1+n_1+m_2+n_2) \end{bmatrix}(-1)^{m_1+n_1+m_2+n_2}\psi^{(m_1+m_2)(n_1+n_2)l} \tag{20}$$

which can be derived with the aid of the product rule for spherical harmonics.[15] Using Eq. (20) it is easy to show that Eq. (19) leads to the result

$$c^{mnl}(r)=(-1)^{m+n}(2l+1)\sum_{m_1,n_1,l_1,l_2}\begin{bmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{bmatrix}\begin{bmatrix} l_1 & l_2 & l \\ -(m_1+n_1) & (m_1+n_1-m-n) & (m+n) \end{bmatrix}$$
$$\times\int_r^\infty h^{m_1n_1l_1}(r')\frac{\partial w^{(m-m_1)(n-n_1)l_2}(r')}{\partial r'}dr'-\beta u^{mnl}(r) \ . \tag{21}$$

Equation (21) combined with Eq. (15) allows the HNC theory to be solved for orientationally ordered fluids. (An alternative method would be to use the procedure described in Ref. 16.)

We note that Eqs. (15) and (21) can be applied directly for models where the pair potential is a continuous function of the angles $(\chi_1,\chi_2,\mathbf{\Omega}_{12})$. This is the case for the ferrofluid discussed below. (See also Refs. 3 and 4.) For hard particles where this is not the case the discontinuous behavior can be handled as described in Ref. 14.

Finally, it is useful to point out that the electrostatic multipole expansion describing the interaction between orientationally ordered particles can be readily expressed in terms of the $\psi^{mnl}(12)$. Beginning with the usual general expansion,[9,10] it is not difficult to show that for a pair of orientationally ordered particles the electrostatic interaction $u^{\mathrm{el}}(\chi_1,\chi_2,\mathbf{\Omega}_{12})$ can be written in the form

$$u^{\mathrm{el}}(\chi_1,\chi_2,\mathbf{\Omega}_{12})=\sum_{m,n,l} u^{mnl;\mathrm{el}}(r)\psi^{mnl*}(12) \ , \tag{22a}$$

where

$$u^{mnl;\mathrm{el}}(r)=\sum_{j=0}^{|m|}(-1)^j\left[\frac{(2l+1)!}{(2j)!(2l-2j)!}\right]^{1/2}\begin{bmatrix} j & (l-j) & l \\ m & n & (-m-n) \end{bmatrix}\frac{\bar{Q}_j^m(1)\bar{Q}_{l-j}^n(2)}{r^{l+1}} \ . \tag{22b}$$

In Eq. (22b) the $\bar{Q}_j^m$ represent multipole moments in spherical tensor notation. These are defined by[10,17]

$$\bar{Q}_j^m=[4\pi/(2j+1)]^{1/2}\sum_i e_i(r_i)^jY_j^m(\theta_i,\varphi_i) \ , \tag{23}$$

where e_i is a charge located at $\mathbf{r}_i\equiv(r_i,\theta_i,\varphi_i)$ in the molecular frame.

C. Thermodynamic Properties

In this section we derive expressions for some thermodynamic properties (internal energy, pressure, compressibility) in terms of the projections h^{mnl} of the pair correlation function $h(12)$ on the basis set ψ^{mnl} [cf. Eq. (5)]. The internal energy is given by[8]

$$U=\frac{1}{2}\frac{\rho}{(2\pi)^2}\int d\mathbf{r}_{12}d\chi_1 d\chi_2 g(12)u(12) \ , \tag{24}$$

where

$$g(12)=h(12)+1 \ . \tag{25}$$

Expanding g and u in a way analogous to Eq. (5) and using the orthogonality relationship between the ψ^{mnl},

$$\int_0^{2\pi}d\chi_1\int_0^{2\pi}d\chi_2\int_0^{\pi}\sin\theta_{12}d\theta_{12}\int_0^{2\pi}d\varphi_{12}\psi^{m_1n_1l_1}(12)\psi^{mnl*}(12)=(2\pi)^2(f^{mnl})^2\delta_{mm_1}\delta_{nn_1}\delta_{ll_1} \ , \tag{26}$$

together with the choice (9) for the f^{mnl}, Eq. (24) is readily expressed as

$$U=\tfrac{1}{2}\rho\sum_{m,n,l}\frac{1}{2l+1}\int d\mathbf{r}g^{mnl*}(r)u^{mnl}(r) \ . \tag{27}$$

Analogous expressions for the pressure tensor and compressibility are somewhat less straightforward to derive. Particular care is necessary for the ferrofluid case due to the long-range nature of the dipolar potential. For this reason we shall consider separately the cases of short-range potentials (i.e., decaying faster than $1/r^3$) and the dipolar potential which decays as $1/r^3$.

1. Short-range potentials

a. Pressure tensor. Applying the virial theorem we define the pressure tensor $\overleftrightarrow{\pi}$ according to the equation

$$\frac{\beta\overleftrightarrow{\pi}}{\rho}=\overleftrightarrow{U}-\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}\ , \tag{28a}$$

where

$$\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}=\frac{\beta}{2N}\left\langle \sum_{\substack{i,j\\ i\neq j}} \mathbf{r}_{ij}\nabla u(\mathbf{r}_{ij},\chi_1,\chi_2)\right\rangle\ , \tag{28b}$$

$\overleftrightarrow{U}$ is the unit tensor, N is the number of particles, and the angular brackets denote an average value. Equation (28b) can be written in terms of the pair distribution function $g(\mathbf{r},\chi_1,\chi_2)$ as follows:

$$\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}=\frac{\beta\rho}{2}\int_0^{2\pi}\frac{d\chi_1}{2\pi}\int_0^{2\pi}\frac{d\chi_2}{2\pi}\int d\mathbf{r}\, g(\mathbf{r},\chi_1,\chi_2)\mathbf{r}\nabla \times u(\mathbf{r},\chi_1,\chi_2)\ . \tag{29}$$

Since $g\rightarrow 1$ as $r\rightarrow\infty$ and u decays faster than $1/r^3$, the integral in (29) is absolutely convergent and an unambiguous definition of the pressure tensor is obtained. (This is, however, not the case for a ferrofluid where u decays as $1/r^3$ as $r\rightarrow\infty$, see below.) Due to the symmetry of the system, $\beta\Delta\overleftrightarrow{\pi}/\rho$ can, *a priori*, be expressed in the form

$$\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}=\begin{bmatrix} A_\perp & 0 & 0\\ 0 & A_\perp & 0\\ 0 & 0 & A_\parallel \end{bmatrix}\ , \tag{30}$$

where $A_\parallel$ and $A_\perp$ indicate the elements of the tensor, respectively, parallel and perpendicular to the axis along which the particles are aligned (i.e., the z axis). However, the observation that the thermodynamic properties, in particular, the free energy, cannot depend upon the shape of the sample suggests that $A_\parallel$ and $A_\perp$ should be equal. This statement will indeed be proved in the next section under the commonly made assumption that $c(12)\sim-\beta u(12)$ as $r\rightarrow\infty$.

The evaluation of the elements $A_\parallel$ and $A_\perp$ in terms of g^{mnl} and u^{mnl} is rather complicated and the details are given in Appendix A. Essentially it is possible to derive the relationships

$$2A_\perp+A_\parallel=\mathrm{Tr}\frac{\beta\Delta\overleftrightarrow{\pi}}{\rho} =\frac{\beta\rho}{2}\sum_{m,n,l} f^{mnl^2}\int_0^\infty dr\, r^3 g^{mnl*}(r)\frac{\partial}{\partial r}u^{mnl}(r)\ , \tag{31a}$$

and

$$A_\parallel-A_\perp=\frac{\beta\rho}{4}\sqrt{30}\sum_{m,n,l,l',j} f^{mnl}f^{mnl'}(-1)^{l+l'+m+n} \times\begin{bmatrix} l & 2 & l'\\ m+n & 0 & -m-n\end{bmatrix}\begin{Bmatrix}1 & 1 & 2\\ l' & l & j\end{Bmatrix}\begin{bmatrix} l & 1 & j\\ 0 & 0 & 0\end{bmatrix}\sqrt{(2l+1)(2j+1)} \times\int_0^\infty dr\, r^3\left[\delta_{j,l'+1}\sqrt{l'+1}\left[\frac{\partial}{\partial r}-\frac{l'}{r}\right]u^{mnl'}(r)-\delta_{j,l'-1}\sqrt{l'}\left[\frac{\partial}{\partial r}+\frac{l'+1}{r}\right]u^{mnl'}(r)\right]g^{mnl*}(r)\ . \tag{31b}$$

From this last expression it is obvious that the requirement $A_\parallel=A_\perp$ imposes nontrivial conditions upon the $g^{mnl}(r)$ projections.

It is interesting to consider the explicit expression obtained for a pair potential of the form

$$u(12)=u_{\mathrm{HS}}(r_{12})+u_{\mathrm{aniso}}(r_{12},\theta_{12})\ , \tag{32a}$$

where

$$u_{\mathrm{HS}}(r)=\begin{cases}\infty, & r<d\\ 0, & r>d\end{cases} \tag{32b}$$

$$u_{\mathrm{aniso}}(r,\theta)=-\frac{a}{r^n}P_2(\cos\theta)\ , \tag{32c}$$

d is the hard-sphere (HS) diameter, θ_{12} is the polar angle describing the orientation of the vector $\mathbf{r}_{12}$, and $P_2(\cos\theta)$ is the usual second-order Legendre polynomial. This model does not have the symmetry required to describe the nematic phase (i.e., it is not invariant under symmetry with respect to the xOy plane). However, if $n=3$ and $a=2\mu^2$, where μ is the dipole moment, the potential (32) defines the ferrofluid model discussed below. More appropriate models for a nematic system would be either a potential of the form

$$u_{\mathrm{aniso}}(r,\theta)=-\frac{a}{r^n}P_4(\cos\theta)\ , \tag{33}$$

where P_4 is the fourth order Legendre polynomial or an equal mixture of two species of molecules interacting by

$$u^{\alpha\beta}_{\mathrm{aniso}}(r,\theta)=-\alpha\beta a\frac{P_2(\cos\theta)}{r^n}\quad(\alpha,\beta=\pm 1)\ . \tag{34}$$

Since $u(12)$ given by (32) does not depend on χ_1 and χ_2, we have $m=n=0$ and with some effort we can derive the explicit expressions, valid for $n>3$,

$$\tfrac{1}{3}(2A_{\perp}+A_{\parallel})=-\frac{2\pi}{3}\rho d^3 g^{000}(d)+\frac{2\pi}{15}\rho\beta a n\int_0^{\infty} dr\frac{g^{002}(r)}{r^{n-2}}\ , \tag{35a}$$

$$\begin{aligned}A_{\parallel}={}&-\frac{2\pi}{3}\rho d^3 g^{000}(d)-\frac{4\pi\rho d^3}{15}g^{002}(d)\\&+\frac{4\pi}{15}\rho\beta a(n-3)\int_0^{\infty} dr\frac{g^{000}(r)}{r^{n-2}}\\&+\frac{2\pi}{105}\rho\beta a(11n-6)\int_0^{\infty} dr\frac{g^{002}}{r^{n-2}}\\&+\frac{8\pi}{105}\rho\beta a(n+2)\int_0^{\infty} dr\frac{g^{004}}{r^{n-2}}\ .\end{aligned} \tag{35b}$$

The first term in Eq. (35a) and the first two terms in Eq. (35b) result from the hard-sphere part of the potential. The remaining terms in both equations come from the anisotropic part of the interaction. We stress again that Eq. (35b) is not valid when $n=3$. In particular, it would be simplistic to assume that the $n-3$ factor would kill the logarithmically divergent integral in the third term of Eq. (35b).

The isotropy of the pressure tensor can easily be demonstrated in the limit $\rho\to 0, a\to 0$. As $\rho\to 0$ we can write

$$\begin{aligned}g(12)&=e^{-\beta u(12)}\\&=e^{-\beta u_{\mathrm{HS}}(r_{12})}e^{-\beta u_{\mathrm{aniso}}(r_{12},\theta_{12})}\ .\end{aligned} \tag{36}$$

Expanding $e^{-\beta u_{\mathrm{aniso}}(r_{12},\theta_{12})}$ and keeping only the term linear in a leads immediately to the expressions

$$g^{000}(r)=\begin{cases}0, & r<d\\ 1, & r\geq d\end{cases} \tag{37a}$$

$$g^{002}(r)=\begin{cases}0, & r<d\\ \dfrac{\beta a}{r^n} & r\geq d\ .\end{cases} \tag{37b}$$

Also, since the $\psi^{mnl}(12)$ are orthogonal, it is easy to deduce that the term linear in a does not contribute to the $g^{00l}(r)$ for $l>2$.

Substituting Eqs. (37) into Eqs. (35) one obtains

$$\tfrac{1}{3}(2A_{\perp}+A_{\parallel})=-\frac{2\pi}{3}\rho d^3+O(a^2)\ , \tag{38a}$$

$$\begin{aligned}A_{\parallel}={}&-\frac{2\pi}{3}\rho d^3-\frac{4\pi\rho}{15}\beta\frac{a}{d^{n-3}}\\&+\frac{4\pi\rho}{15}\beta a(n-3)\int_d^{\infty}\frac{1}{r^{n-2}}dr+O(a^2)\ .\end{aligned} \tag{38b}$$

For $n>3$ the integral in Eq. (38b) can be evaluated and the second and third terms cancel exactly leading to

$$A_{\parallel}=A_{\perp}=-\frac{2\pi}{3}\rho d^3\ , \tag{39}$$

which is just the result one would find for an isotropic system. This illustrates that as discussed above one does obtain $\pi_{\parallel}=\pi_{\perp}=\frac{1}{3}\mathrm{Tr}\overleftrightarrow{\pi}$ for systems with short-range potentials. However, we note that even to linear order in a this comes about through a nontrivial cancellation of terms dependent upon a.

b. Compressibility. The isothermal compressibility is, *a priori*, a tensor defined by

$$\overleftrightarrow{\chi}_T^{-1}=\rho\left[\frac{\partial\overleftrightarrow{\pi}}{\partial\rho}\right]_T\ , \tag{40}$$

where $\overleftrightarrow{\pi}$ is the pressure tensor introduced in Sec. II C 1 a. To evaluate $\overleftrightarrow{\pi}$ we make use of the equation[18]

$$\nabla\cdot\overleftrightarrow{\pi}+\rho\nabla\Phi=\mathbf{0}\ , \tag{41}$$

which expresses hydrostatic equilibrium in an external potential Φ. Equation (41) is an exact relationship provided the potential u is short ranged and can be derived from the Bogoliubov-Born-Green-Yvon hierarchy. [In Sec. II C 2 b we shall show how Eq. (41) must be modified when the potential is long ranged.] For a small disturbance

$$\delta\Phi(\mathbf{r})=\delta\Phi_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}\ . \tag{42}$$

In Fourier space Eq. (41) can be written to linear order in $\delta\Phi_{\mathbf{k}}$ to give

$$\hat{\mathbf{k}}\cdot\delta\overleftrightarrow{\pi}_{\mathbf{k}}+\rho\hat{\mathbf{k}}\delta\Phi_{\mathbf{k}}=0\ , \tag{43}$$

where $\hat{\mathbf{k}}=\mathbf{k}/k$. The density variation $\delta\rho$ induced by $\delta\Phi$ is related to the latter by

$$-\beta\delta\Phi_{\mathbf{k}}=\frac{1}{\rho}\delta\rho_{\mathbf{k}}-\int\frac{d\chi_1}{2\pi}\int\frac{d\chi_2}{2\pi}\tilde{c}(\mathbf{k},\chi_1,\chi_2)\delta\rho_{\mathbf{k}}\ , \tag{44}$$

which follows from the definition of the direct correlation function.[19] Using the notation introduced in Sec. II B 1, Eq. (44) can be written in the form

$$-\beta\delta\Phi_{\mathbf{k}}=\frac{1}{\rho}\delta\rho_{\mathbf{k}}(1-\rho C^{00}(\mathbf{k}))\ . \tag{45}$$

From this expression and Eq. (43) it follows that

$$\hat{\mathbf{k}}\cdot\delta\overleftrightarrow{\pi}_{\mathbf{k}}=\frac{1}{\beta}\delta\rho_{\mathbf{k}}(1-\rho C^{00}(\mathbf{k}))\hat{\mathbf{k}}\ . \tag{46}$$

Consider now the $\mathbf{k}\to 0$ limit of Eq. (46). In this limit we must have

$$\delta\overleftrightarrow{\pi}_{\mathbf{k}}=\frac{\delta\overleftrightarrow{\pi}}{\delta\rho}\delta\rho_{\mathbf{k}}\ . \tag{47}$$

Also, assuming that $c(12)$ behaves asymptotically as $-\beta u(12)$, all Hankel transforms $\tilde{c}^{\,mnl}(k)$ with $l\neq 0$ vanish in the limit $k\to 0$ [for $u(12)$ short ranged] and hence

$$\lim_{\mathbf{k}\to 0}C^{00}(\mathbf{k})=\tilde{c}^{\,000}(0)\ . \tag{48}$$

Comparing Eqs. (46) and (47) and using Eq. (48) we conclude that

$$\left[\frac{\delta\overleftrightarrow{\pi}}{\delta\rho}\right]_T=\frac{1}{\rho}\overleftrightarrow{\chi}_T^{-1}=\frac{1}{\beta}(1-\rho\tilde{c}^{\,000}(0))\overleftrightarrow{U}\ . \tag{49}$$

Thus the compressibility tensor is isotropic and the isotropy of $\overleftrightarrow{\pi}$ follows from integration over ρ.

Using Eq. (18) an alternative expression for $\delta\overleftrightarrow{\pi}/\delta\rho$ can be derived in terms of $H^{00}(\mathbf{k})$. By observing that

$$\lim_{\mathbf{k}\to 0} C^{0m}(\mathbf{k})=\tilde{c}^{\,0m0}(0)=\delta_{m,0}\tilde{c}^{\,000}(0)\ , \qquad (50)$$

one easily finds that

$$\frac{\delta\overleftrightarrow{\pi}}{\delta\rho}=\frac{1}{\beta(1+\rho H^{00}(0))}\overleftrightarrow{U}\ . \qquad (51)$$

2. *Long-range potentials (oriented dipolar fluids)*

In this section we consider the case of a system of molecules ordered along the z axis interacting through a potential of the form

$$u(12)=u_s(12)+u_{DD}(12)\ , \qquad (52)$$

where u_s denotes a short-range potential (spherical or anisotropic) and u_{DD} is the usual dipole-dipole interaction whose radial dependence is $1/r_{12}^3$. We assume that the dipole moment of each molecule is of the form

$$\boldsymbol{\mu}_i=u_{\parallel}\hat{\mathbf{z}}+\mu_{\perp}(\cos\gamma_i\hat{\mathbf{x}}+\sin\gamma_i\hat{\mathbf{y}}) \qquad (53)$$

where $\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}$ are unit vectors along the $0x,0y,0z$ directions of the reference frame. The component parallel to the z axis is fixed whereas the perpendicular frame component can rotate freely around the z axis.

Due to the long-range nature of the dipole-dipole interaction, the expressions given in Sec. II C 1 for the pressure tensor and compressibility do not apply to the present case, and the correct equations are derived here. In addition, the dipolar system has dielectric properties which we shall characterize. In view of the fact that for the orientationally ordered dipolar fluid electrostriction is linear in the electric field (contrary to isotropic system where it is quadratic) it is not surprising that the dielectric constant turns out to be closely related to the isothermal compressibility. Therefore, for clarity of presentation we will first discuss the dielectric results.

a. Dielectric tensor of an oriented polar fluid. We consider an infinite system (i.e., without boundaries) having a net polarization

$$\mathbf{P}=\rho\mu_{\parallel}\hat{\mathbf{z}}\ . \qquad (54)$$

The dielectric tensor $\overleftrightarrow{\epsilon}$ is defined by

$$4\pi\delta\mathbf{P}(\mathbf{r})=\int d\mathbf{r}'[\overleftrightarrow{\epsilon}(\mathbf{r},\mathbf{r}')-\overleftrightarrow{U}\delta(\mathbf{r}-\mathbf{r}')]\cdot\delta\mathbf{E}(\mathbf{r}')\ , \qquad (55)$$

where $\delta\mathbf{P}$ and $\delta\mathbf{E}$ are the variations of the polarization and Maxwell field induced by a variation of the external field $\delta\mathcal{E}$. It is convenient to write (55) in the condensed form

$$4\pi\delta\mathbf{P}=(\overleftrightarrow{\epsilon}-\overleftrightarrow{1})\cdot\delta\mathbf{E}\ , \qquad (56)$$

where the dot denotes both convolution over space and tensor contraction. In fact, as we are interested mainly in the long wavelength limit (i.e., $\mathbf{k}\to 0$) of $\overleftrightarrow{\epsilon}$, we will assume that $\overleftrightarrow{\epsilon}$ is a local quantity and therefore expressible in the form

$$\overleftrightarrow{\epsilon}(\mathbf{r},\mathbf{r}')=\overleftrightarrow{\epsilon}\delta(\mathbf{r}-\mathbf{r}')\ . \qquad (57)$$

Furthermore, for the present problem symmetry requires that $\overleftrightarrow{\epsilon}$ be of the form

$$\epsilon=\begin{bmatrix}\epsilon_{\perp} & 0 & 0\\ 0 & \epsilon_{\perp} & 0\\ 0 & 0 & \epsilon_{\parallel}\end{bmatrix}\ . \qquad (58)$$

In order to find an expression of $\overleftrightarrow{\epsilon}$ in terms of the pair correlation function $h(12)$ it seems natural to apply linear response theory which relates $\delta\mathbf{P}$ to $\delta\mathcal{E}$ through the susceptibility tensor $\overleftrightarrow{\chi}$ according to the equation

$$4\pi\delta\mathbf{P}=\overleftrightarrow{\chi}\cdot\delta\mathcal{E}\ . \qquad (59)$$

Moreover, the Maxwell field $\delta\mathbf{E}$ and the external field $\delta\mathcal{E}$ satisfy the equation[20]

$$\delta\mathbf{E}=\delta\mathcal{E}+4\pi\overleftrightarrow{G}_0\cdot\delta\mathbf{P}\ , \qquad (60)$$

where $\overleftrightarrow{G}_0$ is the free-field Green's function

$$\overleftrightarrow{G}_0(\mathbf{r},\mathbf{r}')=\frac{1}{4\pi}\nabla\nabla\frac{1}{|\mathbf{r}-\mathbf{r}'|}\ . \qquad (61)$$

Eliminating $\delta\mathbf{E}$ from (56) and (60) and comparing with Eq. (59) yields a relationship between the susceptibility and dielectric tensors which can be expressed in the form

$$\overleftrightarrow{\chi}=\overleftrightarrow{\epsilon}-\overleftrightarrow{1}+(\overleftrightarrow{\epsilon}-\overleftrightarrow{1})\cdot\overleftrightarrow{G}\cdot(\overleftrightarrow{\epsilon}-1)\ , \qquad (62)$$

where, following Fulton,[20] we have introduced the Green's function

$$\overleftrightarrow{G}=\overleftrightarrow{G}_0\cdot[\overleftrightarrow{1}-(\overleftrightarrow{\epsilon}-\overleftrightarrow{1})\cdot\overleftrightarrow{G}_0]^{-1}\ . \qquad (63)$$

We recall that the dots denote both tensor contraction and convolution in space. In particular, the inverse in Eq. (63) is defined with respect to these operations.

It is important to note that $\overleftrightarrow{G}$ and $\overleftrightarrow{\chi}$ depend on the geometry of the sample, whereas $\overleftrightarrow{\epsilon}$ and $\overleftrightarrow{G}_0$ do not. Here, we shall limit ourselves to an infinite system without surfaces which is also the situation considered in integral equation theories. In this case Eq. (62) is easily Fourier transformed to yield

$$\overleftrightarrow{\chi}(k)=(\overleftrightarrow{\epsilon}-\overleftrightarrow{U})+(\overleftrightarrow{\epsilon}-\overleftrightarrow{U})\cdot\overleftrightarrow{G}(\mathbf{k})\cdot(\overleftrightarrow{\epsilon}-\overleftrightarrow{U})\ , \qquad (64)$$

where it should be clear that the dots now denote tensor contraction only. Also as $\overleftrightarrow{\epsilon}$ has been assumed local, it is understood that we will ultimately take the $\mathbf{k}\to 0$ limit of this equation.

The Green's function G for an infinite system can either be evaluated directly from Eqs. (61) and (63) using Fourier transform techniques or one can simply remark that[20]

$$\overleftrightarrow{G}(\mathbf{r},\mathbf{r}')=\frac{1}{4\pi}\nabla\nabla\Phi(\mathbf{r},\mathbf{r}')\ , \qquad (65)$$

where $\Phi(\mathbf{r},\mathbf{r}')$ is the electrical potential created at $\mathbf{r}$ by a unit charge located at $\mathbf{r}'$ in the presence of the infinite dielectric medium. The explicit expression obtained is (see, e.g., Ref. 21)

$$\Phi(\mathbf{r}-\mathbf{r}')=\frac{1}{\sqrt{\epsilon_\perp^2\epsilon_\parallel}}\frac{1}{\left[\frac{(x-x')^2}{\epsilon_\perp}+\frac{(y-y')^2}{\epsilon_\perp}+\frac{(z-z')^2}{\epsilon_\parallel}\right]^{1/2}} . \tag{66}$$

Fourier transformation of (65) then gives

$$\overleftrightarrow{G}(\mathbf{k})=-\frac{\hat{\mathbf{k}}\hat{\mathbf{k}}}{\epsilon_\perp+(\epsilon_\parallel-\epsilon_\perp)(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})^2} , \tag{67}$$

where $\hat{\mathbf{k}}$ is a unit vector in the direction of $\mathbf{k}$.

Our next task is to express χ in terms of h (12). From linear response theory we have

$$\overleftrightarrow{\chi}(\mathbf{r},\mathbf{r}')=4\pi\beta[\langle\hat{\mathbf{P}}(\mathbf{r})\hat{\mathbf{P}}(\mathbf{r}')\rangle-\langle\hat{\mathbf{P}}(\mathbf{r})\rangle\langle\hat{\mathbf{P}}(\mathbf{r}')\rangle] , \tag{68}$$

where $\langle\cdots\rangle$ denotes an equilibrium average and $\hat{\mathbf{P}}$ is the microscopic polarization defined by

$$\hat{\mathbf{P}}(\mathbf{r})=\sum_i\boldsymbol{\mu}_i\delta(\mathbf{r}-\mathbf{r}_i) . \tag{69}$$

Substituting (69) into (68) and recalling that the average polarization of our system is nonzero and given by

$$\langle\hat{\mathbf{P}}(\mathbf{r})\rangle=\rho\mu_\parallel\hat{\mathbf{z}} , \tag{70}$$

one obtains

$$\overleftrightarrow{\chi}(\mathbf{r},\mathbf{r}')=4\pi\beta\int d\chi\, d\chi'\boldsymbol{\mu}(\chi)\boldsymbol{\mu}(\chi')\times\left[\frac{\rho}{2\pi}\delta(\mathbf{r}-\mathbf{r}')\delta(\chi-\chi')+\left[\frac{\rho}{2\pi}\right]^2 h(|\mathbf{r}-\mathbf{r}'|,\chi,\chi')\right] , \tag{71}$$

and by Fourier transform

$$\overleftrightarrow{\chi}(\mathbf{k})=9y_\parallel\hat{\mathbf{z}}\hat{\mathbf{z}}+9y_\perp\tfrac{1}{2}(\hat{\mathbf{x}}\hat{\mathbf{x}}+\hat{\mathbf{y}}\hat{\mathbf{y}})+4\pi\beta\left[\frac{\rho}{2\pi}\right]^2\int d\chi_1 d\chi_2\tilde{h}(\mathbf{k},\chi_1\chi_2)\boldsymbol{\mu}(\chi_1)\boldsymbol{\mu}(\chi_2) , \tag{72}$$

with

$$y_\parallel=\frac{4\pi\beta\rho\mu_\parallel^2}{9} , \tag{73a}$$

$$y_\perp=\frac{4\pi\beta\rho\mu_\perp^2}{9} . \tag{73b}$$

Combining (64), (67), and (72) we arrive at the fundamental relationship

$$(\overleftrightarrow{\epsilon}-\overleftrightarrow{U})-(\overleftrightarrow{\epsilon}-\overleftrightarrow{U})\cdot\frac{\hat{\mathbf{k}}\hat{\mathbf{k}}}{\epsilon_\perp\left[1+\frac{\epsilon_\parallel-\epsilon_\perp}{\epsilon_\perp}(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})^2\right]}\cdot(\overleftrightarrow{\epsilon}-\overleftrightarrow{U})=9y_\perp\tfrac{1}{2}(\hat{\mathbf{x}}\hat{\mathbf{x}}+\hat{\mathbf{y}}\hat{\mathbf{y}})+9y_\parallel\hat{\mathbf{z}}\hat{\mathbf{z}}+4\pi\beta\rho^2\int\frac{d\chi_1}{2\pi}\int\frac{d\chi_2}{2\pi}\tilde{h}(\mathbf{k},\chi_1\chi_2)\boldsymbol{\mu}(\chi_1)\boldsymbol{\mu}(\chi_2) . \tag{74}$$

Equation (74) enables us to express $\epsilon_\parallel$ and $\epsilon_\perp$ in terms of the pair correlation function. This is most easily achieved by calculating the trace and the $\hat{\mathbf{z}}\cdot\hat{\mathbf{z}}$ component of Eq. (74). For the trace, taking the zero wave-vector limit, one finds

$$\epsilon_\perp-1+\left[\frac{\epsilon_\perp-1}{\epsilon_\perp}+\epsilon_\parallel-1\right]\frac{1}{1+\frac{\epsilon_\parallel-\epsilon_\perp}{\epsilon_\perp}(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})^2}$$

$$=9y+4\pi\beta\rho^2\int\frac{d\chi_1}{2\pi}\int\frac{d\chi_2}{2\pi}\lim_{\mathbf{k}\to 0}\tilde{h}(\mathbf{k},\chi_1\chi_2)\boldsymbol{\mu}(\chi_1)\cdot\boldsymbol{\mu}(\chi_2) \tag{75a}$$

$$=9y+9y_\parallel\rho\sum_l\tilde{h}^{00l}(0)P_l(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})+9y_\perp\rho\sum_l\tfrac{1}{2}[\tilde{h}^{1-1l}(0)+\tilde{h}^{-11l}(0)]P_l(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}) \tag{75b}$$

$$=9y_\parallel[1+\rho\lim_{\mathbf{k}\to 0}H^{00}(\mathbf{k})]+9y_\perp[1+\rho\lim_{\mathbf{k}\to 0}H^{1-1}(\mathbf{k})] , \tag{75c}$$

where $y=y_\parallel+y_\perp$. In deriving Eq. (75b) the Fourier transform of the pair correlation function has been expanded on the ψ^{mnl} according to (11a). By virtue of (6b) only even values of l will contribute to the sum. The last equation reexpresses the result in terms of the correlation functions defined by Eq. (16). The limits of $H^{00}(\mathbf{k})$ and $H^{1-1}(\mathbf{k})$ as $\mathbf{k}\to 0$ depend on the orientation of $\mathbf{k}$. For example, if in Eq. (75b) we assume that $\hat{\mathbf{k}}$ is parallel to $\hat{\mathbf{z}}$ (i.e., $\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}=1$) then

$$2\epsilon_\perp-1-\frac{1}{\epsilon_\parallel}=9y_\parallel(1+\rho H_\parallel^{00}(0))+9y_\perp(1+\rho H_\parallel^{1-1}(0)) , \tag{76}$$

where the obvious notation

$$H_\parallel^{mn}(0)=\lim_{\substack{\mathbf{k}\to 0\\ \hat{\mathbf{k}}\parallel\hat{\mathbf{z}}}}H^{mn}(\mathbf{k}) \tag{77}$$

has been used.

The $\hat{\mathbf{z}}\cdot\hat{\mathbf{z}}$ component of the tensorial Eq. (74) is

$$\frac{\epsilon_\parallel-1}{\epsilon_\parallel-\epsilon_\perp}\left[-(\epsilon_\perp-1)+\frac{\epsilon_\parallel-1}{1+\dfrac{\epsilon_\parallel-\epsilon_\perp}{\epsilon_\perp}(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})^2}\right] =9y_\parallel\left[1+\rho\lim_{\mathbf{k}\to 0}H^{00}(\mathbf{k})\right] . \quad (78)$$

For the particular choice $\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}=1$, Eq. (78) reduces to

$$1-\frac{1}{\epsilon_\parallel}=9y_\parallel(1+\rho H_\parallel^{00}(0)) . \quad (79a)$$

Substituting (79a) into (76) then yields

$$\epsilon_\perp-1=\tfrac{9}{2}y_\perp(1+\rho H_\parallel^{1-1}(0)) . \quad (79b)$$

Further relationships can be found by assuming $\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}=0$ (i.e., $\hat{\mathbf{k}}\perp\hat{\mathbf{z}}$) in Eqs. (75) and (78). One obtains

$$\epsilon_\parallel-1=9y_\parallel(1+\rho H_\perp^{00}(0)) , \quad (79c)$$

$$\frac{(\epsilon_\perp-1)(\epsilon_\perp+1)}{\epsilon_\perp}=9y_\perp(1+\rho H_\perp^{1-1}(0)) , \quad (79d)$$

with

$$H_\perp^{mn}(0)=\lim_{\substack{\mathbf{k}\to 0\\ \hat{\mathbf{k}}\perp\hat{\mathbf{z}}}}H^{mn}(\mathbf{k}) . \quad (80)$$

From Eqs. (79a) and (79c) it is clear that $H_\parallel^{00}(0)$ and $H_\perp^{00}(0)$ are not independent and satisfy the equation

$$\frac{1+\rho H_\parallel^{00}(0)}{1+\rho H_\perp^{00}(0)}=1-9y_\parallel(1+\rho H_\parallel^{00}(0)) \quad (81a)$$

$$=[1+9y_\parallel(1+\rho H_\perp^{00}(0))]^{-1} . \quad (81b)$$

A similar relationship holds between $H_\parallel^{1-1}(0)$ and $H_\perp^{1-1}(0)$. In Appendix B a more direct proof of Eq. (81) is given by considering the $\mathbf{k}\to 0$ limit of the OZ equation.

We have not yet fully exploited the information contained in Eqs. (75). Further interesting relationships can be extracted by expanding the function

$$f(u)=\frac{1}{1+\dfrac{\epsilon_\parallel-\epsilon_\perp}{\epsilon_\perp}u^2} , \quad (82)$$

where $u=\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}$, on the basis set of Legendre polynomials according to the equation

$$f(u)=\frac{1}{\delta}\sum_{l\ \mathrm{even}}(2l+1)Q_l\left[\frac{1}{\delta}\right]P_l(u) , \quad (83)$$

where Q_l is the Legendre function of the second kind[22] and

$$\delta=\begin{cases}\sqrt{(\epsilon_\perp-\epsilon_\parallel)/\epsilon_\perp} & \text{if } \epsilon_\perp>\epsilon_\parallel ,\\ i\sqrt{(\epsilon_\parallel-\epsilon_\perp)/\epsilon_\perp} & \text{if } \epsilon_\perp<\epsilon_\parallel .\end{cases} \quad (84)$$

For the conditions considered in this paper, specifically $|\mathbf{u}|\le 1$, the series in Eq. (83) will be convergent.[22]

Now by identifying the coefficients of equal Legendre polynomials in Eq. (75b) we can derive the $\mathbf{k}=0$ values of the functions $\tilde{h}^{00l}$ and $\tilde{h}^{1-1l}$ $(l>0)$. Explicitly we obtain

$$9y_\parallel\rho h^{00l}(0)=\frac{(\epsilon_\parallel-1)^2}{\epsilon_\parallel-\epsilon_\perp}\frac{1}{\delta}Q_l\left[\frac{1}{\delta}\right](2l+1) , \quad (85a)$$

$$9y_\perp\rho h^{1-1l}(0)=\left[\epsilon_\parallel-\frac{1}{\epsilon_\perp}-\frac{\epsilon_\parallel-1}{\epsilon_\parallel-\epsilon_\perp}\right]\frac{1}{\delta}Q_l\left[\frac{1}{\delta}\right](2l+1) . \quad (85b)$$

These results are compatible with a $1/r^3$ decay of the functions $h^{00l}(r)$ and $h^{1-1l}(r)$ $(l>0)$ at long range.

b. Pressure tensor. As indicated earlier in Sec. II C 1 b the balance equation (41) satisfied by the pressure tensor has to be modified in the presence of the long-range dipolar interactions. For this case the appropriate expression has been given by Suttorp and De Groot.[23] It reads

$$\nabla\cdot\overleftrightarrow{\pi}=(\nabla\mathbf{E})\cdot\mathbf{P} , \quad (86)$$

where $\mathbf{P}$ is the polarization of the system [cf. Eq. (54)] and $\mathbf{E}$ the Maxwell field. Following Suttorp and De Groot[23] we identify four terms in the pressure tensor

$$\frac{\beta}{\rho}\overleftrightarrow{\pi}=\overleftrightarrow{U}-\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}_s-\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}_L^{(1)}-\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}_L^{(2)} . \quad (87)$$

The first term in (87) is the ideal-gas term. The second term is the contribution from the short-range part of the potential u_s. Its explicit form is as previously given in Eqs. (30) and (31) with u replaced by u_s. The last two terms are the contributions to the pressure tensor from the dipolar forces and are given by

$$\frac{\beta\Delta\overleftrightarrow{\pi}_L^{(1)}}{\rho}=-\tfrac{1}{2}\beta\rho\mathcal{P}\int\frac{d\chi_1}{2\pi}\int\frac{d\chi_2}{2\pi}\times\int d\mathbf{r}\,h(\mathbf{r},\chi_1,\chi_2)\mathbf{r}\nabla u_{DD}(\mathbf{r}) , \quad (88)$$

$$\frac{\beta\Delta\overleftrightarrow{\pi}_L^{(2)}}{\rho}=4\pi(\tfrac{1}{5}\mathbf{P}\mathbf{P}+\tfrac{1}{10}\mathbf{P}^2\overleftrightarrow{U})\frac{\beta}{\rho} . \quad (89)$$

In (88) the symbol $\mathcal{P}$ indicates that the principal value of the integral has to be taken (i.e., integration is performed for $|\mathbf{r}|>\epsilon$ and the limit $\epsilon\to 0$ is taken subsequently). This ensures convergence of the integral at small r where the integrand diverges as $1/r$ (for finite ϵ the divergence of the integral is killed by the angular integration). At long range $h(\mathbf{r},\chi_1,\chi_2)$ vanishes (the results of Sec. II C 2 a suggest that h decays as $1/r^3$) so that the integral is absolutely convergent for $r\to\infty$. Finally, we remark that as $\mathbf{P}\neq 0$ the last term $\beta\Delta\overleftrightarrow{\pi}_L^{(2)}/\rho$ contains an anisotropic part. However, as shown in Ref. 23, this anisotropic part is exactly cancelled by a similar term in $\beta\Delta\overleftrightarrow{\pi}_L^{(1)}/\rho$ so that the total pressure tensor $\overleftrightarrow{\pi}$ as defined in (87) is in fact isotropic. A further proof of this result will be given below.

We conclude this section by giving explicit expressions of the pressure tensor for the model potential defined by

Eq. (32) where we assume $n=3$, $a=2\mu_{\parallel}^2$, and $\mu_{\perp}=0$. If we define

$$\frac{\beta\Delta\overleftrightarrow{\pi}_s}{\rho}=\begin{bmatrix} A_{s\perp} & 0 & 0 \\ 0 & A_{s\perp} & 0 \\ 0 & 0 & A_{s\parallel} \end{bmatrix}, \tag{90a}$$

$$\frac{\beta\Delta\overleftrightarrow{\pi}_L^{(1)}}{\rho}=\begin{bmatrix} A_{L\perp}^{(1)} & 0 & 0 \\ 0 & A_{L\perp}^{(1)} & 0 \\ 0 & 0 & A_{L\parallel}^{(1)} \end{bmatrix}, \tag{90b}$$

$$\frac{\beta\Delta\overleftrightarrow{\pi}_L^{(2)}}{\rho}=\begin{bmatrix} A_{L\perp}^{(2)} & 0 & 0 \\ 0 & A_{L\perp}^{(2)} & 0 \\ 0 & 0 & A_{L\parallel}^{(2)} \end{bmatrix}, \tag{90c}$$

then

$$A_{s\parallel}=-\frac{2\pi}{3}\rho d^3 g^{000}(d)-\frac{4\pi}{15}\rho d^3 h^{002}(d)\ , \tag{91a}$$

$$A_{s\perp}=-\frac{2\pi}{3}\rho d^3 g^{000}(d)+\frac{2\pi}{15}\rho d^3 h^{002}(d)\ , \tag{91b}$$

$$\begin{aligned} A_{L\parallel}^{(1)}=&\frac{4\pi}{15}\rho\beta a(n-3)\int_0^\infty dr\frac{h^{000}(r)}{r^{n-2}} \\ &+\frac{2\pi}{105}\rho\beta a(11n-6)\int_0^\infty dr\frac{h^{002}(r)}{r^{n-2}} \\ &+\frac{8\pi}{105}\rho\beta a(n+2)\int_0^\infty dr\frac{h^{004}(r)}{r^{n-2}}\ , \end{aligned} \tag{91c}$$

$$\tfrac{1}{3}(2A_{L\perp}^{(1)}+A_{L\parallel}^{(1)})=\frac{2\pi}{15}\rho\beta a n\int_0^\infty dr\frac{h^{002}(r)}{r^{n-2}}\ , \tag{91d}$$

$$A_{L\perp}^{(2)}=\frac{\pi}{5}\rho\beta a\ , \tag{91e}$$

and

$$A_{L\parallel}^{(2)}=\frac{3\pi}{5}\rho\beta a\ . \tag{91f}$$

In Eq. (91c) the $n-3$ term has been purposely retained in order to show how it differs from the corresponding term in Eq. (35). We observe that now in the integral in question $g^{000}(r)$ [Eq. (35)] has been replaced by the short-range function $h^{000}(r)=g^{000}(r)-1$. This ensures convergence of the integral and hence that the term proportional to $n-3$ vanishes. This contrasts with the situation in Eq. (35) where for dipolar systems we have $n-3$ multiplying a divergent integral and the product cannot be assigned a well-defined value.

Finally, as in Sec. II C 1 a we can evaluate the low ρ, small a limit of the pressure tensor (87) for the dipolar potential. One easily finds

$$\frac{\beta\pi_\parallel}{\rho}=\frac{\beta\pi_\perp}{\rho}=1+\frac{2\pi}{3}\rho d^3-\frac{\pi}{3}\rho\beta a\ . \tag{92}$$

Thus the isotropy of the pressure is confirmed in this limit.

c. Electrostriction. In a system of aligned dipoles electrostriction (i.e., the density variation induced by an applied electric field) is linear in this field (contrary to an isotropic dipolar system for which it is quadratic). This is easily seen by projecting Eq. (59) onto the z axis to obtain

$$4\pi\delta\mathbf{P}\cdot\hat{\mathbf{z}}=\hat{\mathbf{z}}\cdot\overleftrightarrow{\chi}\cdot\delta\mathcal{E}\ , \tag{93}$$

and recalling that

$$\delta\mathbf{P}\cdot\hat{\mathbf{z}}=\mu_\parallel\delta\rho\ . \tag{94}$$

By combining Eqs. (93) and (94) we obtain

$$\delta\rho=\frac{1}{4\pi\mu_\parallel}\hat{\mathbf{z}}\cdot\overleftrightarrow{\chi}\cdot\delta\mathcal{E}\ . \tag{95}$$

Alternatively, we can use (56) to derive the density response to the variation of the Maxwell field induced by $\delta\mathcal{E}$. This yields

$$\delta\rho=\frac{1}{4\pi\mu_\parallel}\hat{\mathbf{z}}\cdot(\overleftrightarrow{\epsilon}-\overleftrightarrow{1})\cdot\delta\mathbf{E}\ . \tag{96}$$

Thus for a variation of the form $\delta\mathbf{E}=\delta\mathbf{E}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$ we have, in the limit $k\to 0$

$$\delta\rho_k=\frac{1}{4\pi\mu_\parallel}(\epsilon_\parallel-1)(\delta\mathbf{E}_{\mathbf{k}}\cdot\hat{\mathbf{z}})\ . \tag{97}$$

d. Compressibility and isotropy of the pressure tensor. Consider a variation $\delta\rho=\delta\rho_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$ of the density of the system. It induces variations $\delta\overleftrightarrow{\pi}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$ and $\delta\mathbf{E}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}$ of the pressure tensor and Maxwell field, which, by virtue of the balance equation (86) and Eq. (54) for $\mathbf{P}$ are related, to linear order, by

$$\hat{\mathbf{k}}\cdot\delta\overleftrightarrow{\pi}_{\mathbf{k}}\simeq(\hat{\mathbf{k}}\delta\mathbf{E}_k)\cdot\rho\mu_\parallel\hat{\mathbf{z}}\ . \tag{98}$$

In the $\mathbf{k}\to 0$ limit we have

$$\delta\overleftrightarrow{\pi}_{\mathbf{k}}=\frac{\delta\overleftrightarrow{\pi}}{\delta\rho}\delta\rho_{\mathbf{k}}\ . \tag{99}$$

From (98) and (97) it then follows that

$$\hat{\mathbf{k}}\cdot\frac{\delta\overleftrightarrow{\pi}}{\delta\rho}=\frac{9y_\parallel}{\beta}\frac{1}{\epsilon_\parallel-1}\hat{\mathbf{k}}\ , \tag{100}$$

which shows that $\delta\overleftrightarrow{\pi}/\delta\rho$ is isotropic and

$$\frac{\delta\pi_\parallel}{\delta\rho}=\frac{\delta\pi_\perp}{\delta\rho}=\frac{9y_\parallel}{\beta(\epsilon_\parallel-1)}\ . \tag{101}$$

The compressibility is given by

$$\chi_T=\frac{1}{\rho\dfrac{\delta\pi_\parallel}{\delta\rho}}=\frac{\beta(\epsilon_\parallel-1)}{9\rho y_\parallel}\ , \tag{102}$$

which by means of (79c) and (79a) can also be expressed as

$$\chi_T=\frac{\beta}{\rho}(1+\rho H_\perp^{00}(0))=\frac{\beta}{\rho}\epsilon_\parallel(1+\rho H_\parallel^{00}(0))\ . \tag{103}$$

Again the isotropy of $\overleftrightarrow{\pi}$ results from that of $\delta\overleftrightarrow{\pi}/\delta\rho$ by integration over density.

III. NUMERICAL RESULTS

Calculations have been carried out for the potential defined by Eqs. (32) with $n=3$ and 6. The $n=3$ case corresponds to a ferrofluid with the dipole moment given by $\mu=\sqrt{a/2}$. The $n=6$ case does not model any particular physical system, but in view of the discussion given in Sec. II C it is of theoretical interest to investigate how changing the range of the anisotropic interaction influences the results obtained. For the models considered a thermodynamic state is conveniently characterized by the reduced density $\rho^*=\rho d^3$ and the dimensionless parameter $a^*=a/k_BTd^n$ which determines the strength of the anisotropic interaction.

At low density the calculations were performed using the HNC closure and at high density the reference HNC (RHNC) approximation[24,11] was employed. The RHNC equation is a simple variant of the HNC closure which ensures that the hard-sphere (i.e., reference) part of the pair potential is treated "exactly" instead of at the HNC level which is not particularly accurate for strongly repulsive potentials at high density. For purposes of comparison a few calculations for the $n=6$ case were also carried out using the reference PY (RPY) closure. Both the RHNC and RPY theories require the "exact" hard-sphere radial distribution function and in the present calculations this was provided by the Verlet-Weis[25] fit to the Monte Carlo data.

The integral equation theories were solved numerically as described in Refs. 11 and 12. A grid width $\Delta r=0.02d$ was used and the Fourier transforms were performed using fast Fourier transform techniques with 512 grid points. In all calculations terms in the correlation function expansions [cf. Eq. (5a)] were retained up to $l=10$. For the values of a^* considered here this was sufficient to ensure convergence.

A. Thermodynamic Properties

The thermodynamic properties for $n=3$, $\rho^*=0.2$ and 0.6, and for $n=6$, $\rho^*=0.6$ are summarized in Table I. We note that the average internal energies per particle for these fluids are generally rather small in magnitude. For example, for the ferrofluid (i.e., fully aligned dipoles) at $\rho^*=0.6$ the average energies are about *five times* smaller in magnitude than the corresponding values for orientationally disordered dipolar fluids at the same density and a^*.[26,11] At the lower density $\rho^*=0.2$ the energies of the ordered and disordered systems are of comparable magnitude.

The compressibility factors $Z_{\rm av}$ have been calculated using the equations

$$Z_{\rm av}=\frac{\beta}{\rho}\mathrm{Tr}\overleftrightarrow{\pi}$$

$$=1+\frac{2\pi}{3}\rho d^3 g^{000}(d)+2\beta U \qquad (104a)$$

for $n=6$ [cf. Eq. (35a)], and

$$Z_{\rm av}=1+\frac{2\pi}{3}\rho d^3 g^{000}(d)+\beta U-\tfrac{1}{3}\pi\rho\beta a \qquad (104b)$$

for $n=3$ [cf. Eqs. (90) and (91)]. The last term occurring in Eq. (104b) is a consequence of the polarization of the ferrofluid and is not present in the $Z_{\rm av}$ expression for orientationally disordered dipolar systems. It can be seen from Table I that the behavior of $Z_{\rm av}$ as a function of a^* is quite different for the $n=3$ and 6 cases. For the ferrofluid $Z_{\rm av}$ decreases in a near linear fashion with increasing a^*. This behavior is largely due to the presence of the last term in Eq. (104b). For $n=6$ $Z_{\rm av}$ has only a very weak dependence on a^* remaining practically constant at the hard-sphere result for the range of a^* values

TABLE I. A summary of the thermodynamic properties for the models defined by Eqs. (32).

a^*	Closure	$\beta U/N$	$Z_{\rm av}$	$Z_\parallel$	$Z_\perp$	$\frac{\rho}{\beta}\chi_T$	$\epsilon_\parallel$
			$n=3$, $\rho^*=0.2$				
0.5	HNC	−0.0108	1.460	1.460	1.460	0.493	1.31
1.0	HNC	−0.0436	1.351	1.351	1.350	0.550	1.69
2.0	HNC	−0.181	1.125	1.126	1.125	0.710	2.79
3.0	HNC	−0.436	0.897	0.897	0.896	0.975	4.69
			$n=3$, $\rho^*=0.6$				
0.5	RHNC	−0.0063	3.98	3.94	4.00	0.093	1.175
1.0	RHNC	−0.025	3.67	3.60	3.70	0.098	1.37
1.5	RHNC	−0.056	3.37	3.27	3.43	0.104	1.59
2.5	RHNC	−0.152	2.82	2.65	2.90	0.118	2.11
4.0	RHNC	−0.386	2.05	1.79	2.18	0.144	3.18
			$n=6$, $\rho^*=0.6$				
0.5	RHNC	−0.0088	4.28	4.24	4.30	0.088	
	RPY	−0.013	4.29	4.33	4.27	0.088	
1.0	RHNC	−0.035	4.28	4.20	4.32	0.088	
	RPY	−0.051	4.31	4.40	4.26	0.087	
2.0	RHNC	−0.143	4.30	4.13	4.39	0.088	
3.0	RHNC	−0.330	4.33	4.10	4.45	0.087	
4.0	RHNC	−0.606	4.40	4.10	4.55	0.087	

considered. It is not obvious why this is so but it appears to be true for both RHNC and RPY theories.

Also included in the table are the perpendicular and parallel compressibility factors given by

$$Z_{\parallel}=\frac{\beta}{\rho}\pi_{\parallel}\ , \tag{105a}$$

$$Z_{\perp}=\frac{\beta}{\rho}\pi_{\perp}\ , \tag{105b}$$

where $\pi_{\parallel}$ and $\pi_{\perp}$ are calculated using the expressions derived in Sec. II C. Again we emphasize that for these fluids one must have $Z_{\parallel}=Z_{\perp}=Z_{\text{av}}$. It is obvious from Table I that the *approximate* integral equation theories *do not satisfy* this exact condition at high density. It is important to note that we are convinced that the discrepancies between $Z_{\parallel}$ and $Z_{\perp}$ are due to the closure approximations themselves, and not to the basis set truncation or numerical inaccuracies. We remark that for the RHNC closures at $\rho=0.6$ and $n=6$ the error is such that $Z_{\perp}>Z_{\parallel}$ whereas the reverse is true for the RPY approximation.

For the ferrofluid it is interesting to examine the dielectric tensor. For the present model $\epsilon_{\perp}=1$ and $\epsilon_{\parallel}$ can be calculated either from (79c) or (79a). When expressed in terms of the structure factor defined by

$$S(\mathbf{k})=1+\rho H^{00}(\mathbf{k})\ , \tag{106a}$$

$$=1+\rho\sum_{l}\tilde{h}^{00l}(k)P_l(\cos\theta)\ , \tag{106b}$$

$$=\left[1-\rho\sum_{l}\tilde{c}^{\,00l}(k)P_l(\cos\theta)\right]^{-1}\ , \tag{106c}$$

these relationships can be expressed in the form

$$\epsilon_{\parallel}-1=9y_{\parallel}S_{\perp}(0)\ , \tag{107a}$$

$$\epsilon_{\parallel}=\frac{S_{\perp}(0)}{S_{\parallel}(0)}\ , \tag{107b}$$

where $S_{\perp}(0)$ and $S_{\parallel}(0)$ are defined as the $k\rightarrow 0$ limit of (106) for $\cos\theta=0$ and 1, respectively. Equation (106c) is obtained by using the expanded form of the OZ relationship and this reexpression for $S(\mathbf{k})$ is the most convenient for calculating $\epsilon_{\parallel}$. In the $k\rightarrow 0$ limit only the terms $\tilde{c}^{\,000}(0)$ and $\tilde{c}^{\,002}(0)=-6y_{\parallel}/\rho$ contribute to Eq. (106c) (cf. Appendix B) leading to the relatively simple results

$$S_{\perp}(0)=\frac{1}{1-\rho\tilde{c}^{\,000}(0)-3y_{\parallel}}\ , \tag{108a}$$

$$S_{\parallel}(0)=\frac{1}{1-\rho\tilde{c}^{\,000}(0)-6y_{\parallel}}\ . \tag{108b}$$

Using Eqs. (108) it is easy to verify that Eqs. (107a) and (107b) will give consistent values of $\epsilon_{\parallel}$ assuming of course that the OZ equation is satisfied. The numerical results obtained for $\epsilon_{\parallel}$ are given in Table I and we note that the values increase more rapidly with a^* at the lower density.

The isothermal compressibilities are also given in Table I. For the ferrofluid Eq. (102) relates χ_T to $\epsilon_{\parallel}$. Specifically we have

$$\chi_T=\frac{\beta}{\rho}\frac{\epsilon_{\parallel}-1}{9y_{\parallel}}=\frac{\beta}{\rho}S_{\perp}(0)\ . \tag{109}$$

For the short-range potential with $n=6$ $\tilde{c}^{\,002}(0)=0$ and the compressibility is given by [cf. Eq. (49)]

$$\chi_T=\frac{\beta}{\rho}\frac{1}{1-\rho\tilde{c}^{\,000}(0)}\ . \tag{110}$$

From Table I we see that for the ferrofluid χ_T increases with a^* whereas for the $n=6$ case χ_T remains essentially constant at the hard-sphere value in accord with the constant pressure. Thus we see that the contribution to $S_{\perp}(0)$ from the long-range dipolar interaction has a large effect upon the thermodynamic properties.

B. Structural Features

For the present model the pair distribution function expansion reduces to the form

$$g(\mathbf{r})=g(r,\theta)=\sum_{l}g^{00l}(r)P_l(\cos\theta)\ . \tag{111}$$

The projections $g^{00l}(r)$ for a ferrofluid at $\rho^*=0.6$ and $a^*=4.0$ are shown in Fig. 1. We note that the magnitude of the projections decreases rapidly with increasing l. As mentioned above $l=10$ was sufficient to ensure the convergence of Eq. (111) for the values of a^* we consider. In practice, a good way to test that the expansions are, in fact, convergent is to check that Eqs. (106b) and (106c)

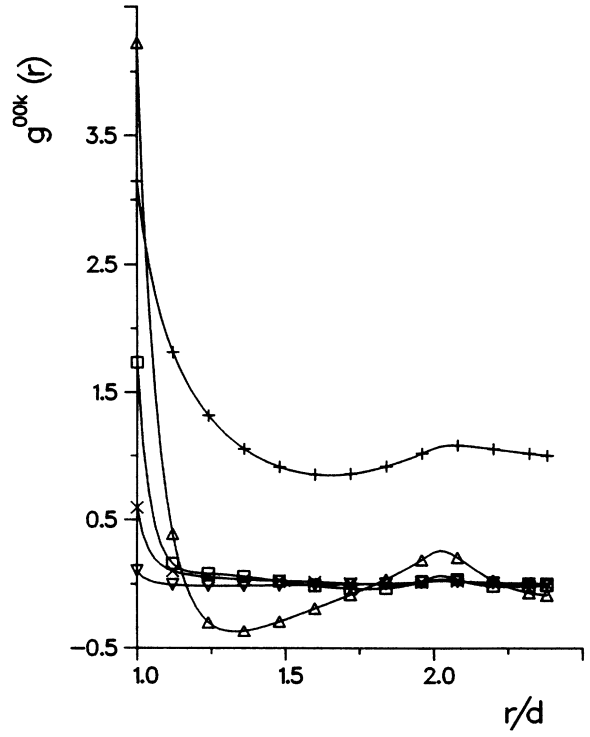

FIG. 1. Projections $g^{00k}(r)$ for the ferrofluid at $\rho^*=0.6$ and $a^*=4.0$. The different values of k are $k=0$ (+), $k=2$ (△), $k=4$ (□); $k=6$ (×), $k=8$ (▽). For $k\geq 10$ the $g^{00k}(r)$ values are too small in magnitude to be seen on the scale used in the figure.

give consistent results for $S(\mathbf{k})$.

The distribution functions $g(r,\theta)$ for $\rho^*=0.6$ and $a^*=4.0$ obtained for the $n=3$ and 6 systems are illustrated in Figs. 2(a) and 2(b), respectively. Curves for selected values of θ ranging from 0° to 90° (i.e., parallel and perpendicular to the z axis) are included in the figures. It is apparent that the orientational dependence of $g(r,\theta)$ is much as we would expect from the symmetry of the dipolar potential. Specifically, near contact $g(r,\theta)$ is greater for $\theta=0°$ [i.e., $g_{\parallel}(r)$] where the dipoles are aligned in attractive configurations, and lowest for $\theta=90°$ [i.e., $g_{\perp}(r)$] where the dipoles interact repulsively. We remark that apart from the fact that the variation with θ near contact is somewhat more extreme for the shorter ranged $n=6$ potential Figs. 2(a) and 2(b) are quite similar.

For the dense ferrofluid the variation of $g_{\parallel}(r)$ and $g_{\perp}(r)$ with a^* is shown in Figs. 3(a) and 3(b), respectively. It is evident from these plots that the tendency to align and form chainlike structures increases rapidly with a^*. The anisotropy developed in the system is quite remarkable with $g_{\parallel}$ being nearly six times larger than $g_{\perp}$ at contact for $a^*=4.0$. Unfortunately, we find, as did Martin *et al.*,[4] that it is not possible with present numerical techniques to obtain converged solutions to the integral equations for the much larger values of a^* (i.e., lower temperatures) of interest for magnetically saturated ferrofluids. It is possible that this problem could be overcome by retaining more terms in the correlation function expansion. However, it is not easy to test this conjecture since the accuracy of the present numerical algorithm used to calculate the Hankel transforms (cf. Ref. 11) would have to be improved in order to include terms for $l>10$.

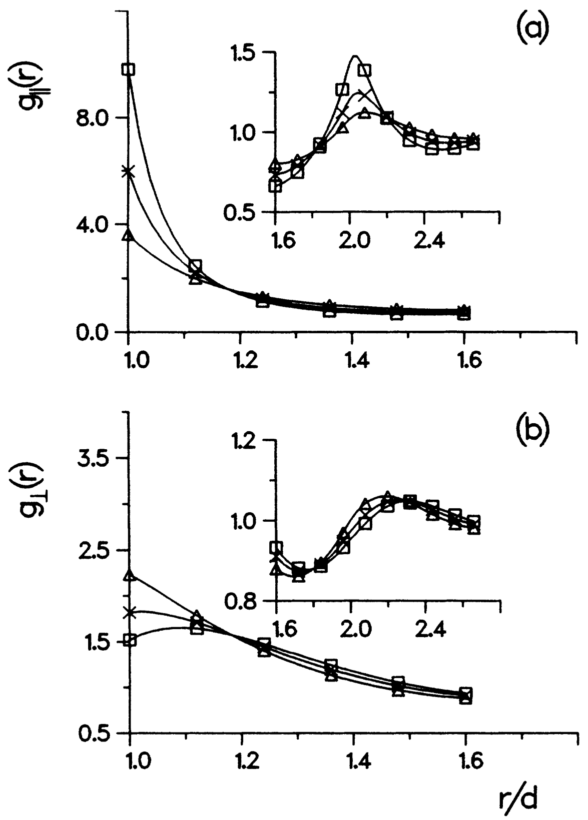

FIG. 3. Dependence of the functions (a) $g_{\parallel}(r)$ and (b) $g_{\perp}(r)$ upon a^* for the ferrofluid at $\rho^*=0.6$. The curves are as follows: $a^*=1.0$ (□), $a^*=2.5$ (×), $a^*=4.0$ (△).

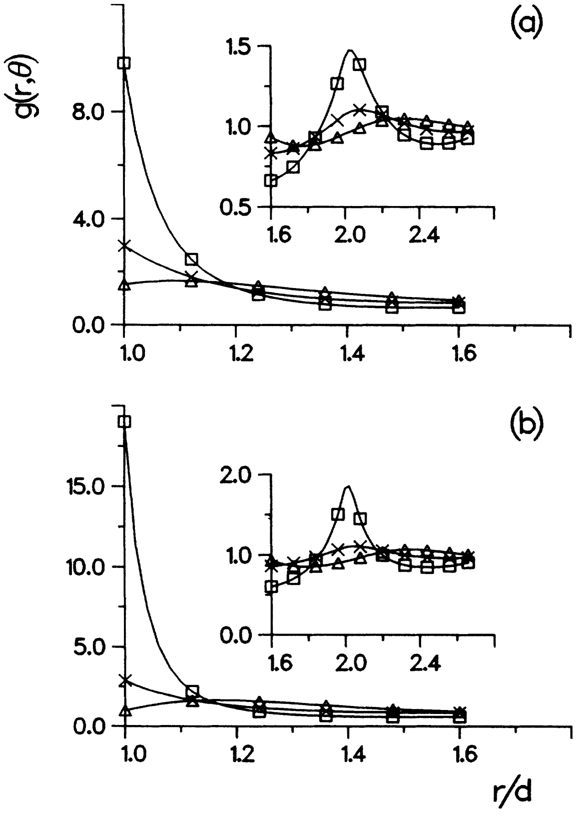

FIG. 2. Distribution function $g(r,\theta)$ for selected orientations at $\rho^*=0.6$ and $a^*=4.0$. The results in (a) are for $n=3$ and those in (b) are for $n=6$. The curves are as follows: $\theta=0°$ (□), $\theta=50°$ (×), $\theta=90°$ (△).

The structure factors $S(k,\theta)$ (for $\rho^*=0.6$, $a^*=4.0$) obtained using Eq. (106c) are plotted in Figs. 4(a) and 4(b). It should be noted that $S(k,\theta)$ is not simply the Fourier transform of $g(r,\theta)$. From Fig. 4 we see that the behavior of $S(k,\theta)$ is qualitatively similar for $n=3$ and 6, but that there is one important difference. For the $n=6$ case, $S(k,\theta)$ becomes independent of θ as $k\rightarrow 0$, whereas for the ferrofluid the $k=0$ values are θ dependent. This difference can be easily understood if we consider Eq. (106c) or (106b). As pointed out above (also see Appendix B) for short-range potentials $\tilde{c}^{\,00l}(0)$ is nonzero only for $l=0$, and hence it is obvious from Eq. (106c) that $S(k,\theta)$ will have no θ dependence at $k=0$. On the other hand, for the dipolar system $\tilde{c}^{\,002}(0)$ is also nonzero and the $l=2$ term therefore contributes to $S(k,\theta)$ [cf. Eqs. (108)] leading to the observed dependence on θ at $k=0$.

The $g(r,\theta)$ and $S(k,\theta)$ results obtained for the

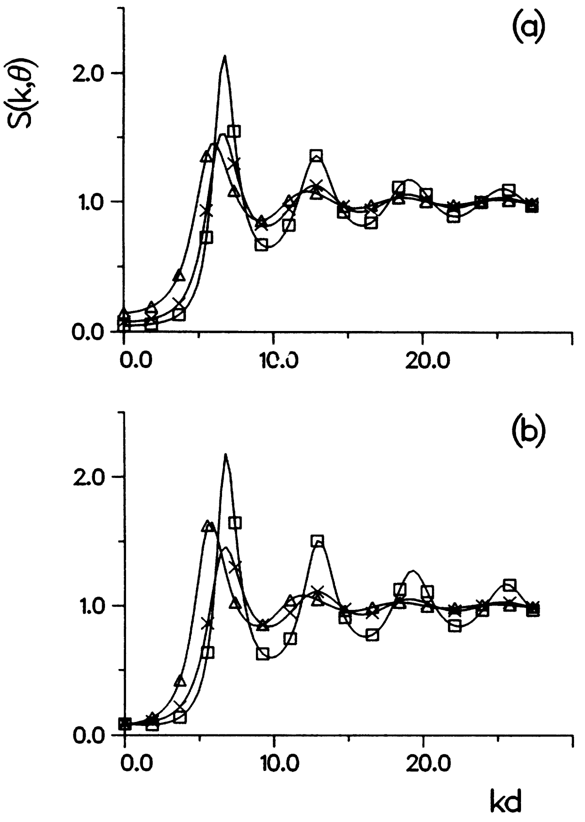

FIG. 4. Structure factor $S(k,\theta)$ for selected orientations at $\rho^*=0.6$ and $a^*=4.0$. The results in (a) are for $n=3$ and these in (b) are for $n=6$. The curves are the same as in Fig. 2.

ferrofluid at low density ($\rho^*=0.2$, $a^*=3.0$) are shown in Figs. 5(a) and 5(b), respectively. These curves indicate the same general tendencies discussed above, but as we would expect the influence of the anisotropic part of the potential appears more strongly at low density. In particular, the dependence of $S(k,\theta)$ upon θ at $k=0$ is very clear in Fig. 5(b).

IV. SUMMARY AND CONCLUSION

The principal purpose of this paper has been to describe a general theoretical framework which can be applied in order to calculate the thermodynamic and structural properties of orientationally ordered fluids. The model considered assumes that the particles are all perfectly aligned with respect to a laboratory fixed direction, but rotation is allowed about the fixed axis. This model can be applied to a number of physically interesting problems including liquid crystals in the nematic phase or dipolar fluids fully ordered by strong electric (or magnetic) fields. In fact, numerical results for the latter case are also given in this paper.

A method is described which allows the integral equation theories commonly applied in the theory of isotropic

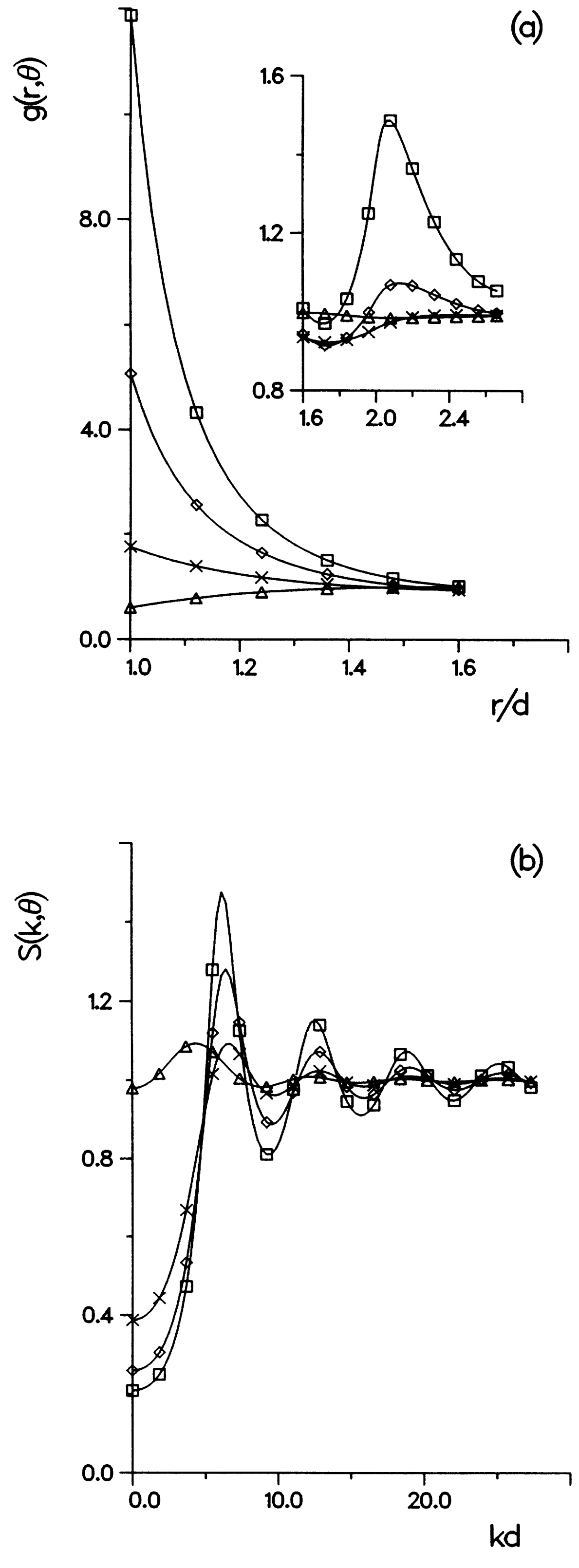

FIG. 5. Functions (a) $g(r,\theta)$ and (b) $S(k,\theta)$ for the ferrofluid at $\rho^*=0.2$ and $a^*=3.0$. Results are shown for selected orientations. The curves are as follows: $\theta=0°$ (□), $\theta=30°$ (◇), $\theta=50°$ (×), $\theta=90°$ (△).

fluids (e.g., the HNC,PY,MSA, etc.) to be solved for the orientationally ordered model. The approach followed is closely related to that previously used[9–12] in the theory of isotropic fluids interacting with angle-dependent pair interactions. The correlation functions are expanded in an appropriate symmetry adopted basis set and the problem is reduced to a numerically tractable form.

The pressure and compressibility for particles interacting with both short- and long-range (i.e., dipolar) potentials are considered in detail. For the present anisotropic systems the pair correlation function depends upon the direction as well as the magnitude of the interparticle vector **r**, and hence, *a priori*, the pressure and compressibility are tensors. Although for fluids we know physically that these tensors must be isotropic (i.e., the pressure exerted upon a container must be the same in all directions), the microscopic demonstration of this is a nontrivial problem. In the present paper the compressibility equation is used to prove microscopically that these tensors are isotropic as expected.

We have also considered the virial expression for the equation of state, and reducing the pressure tensor $\overleftrightarrow{\pi}$ to tractable form proved to be a rather difficult but very interesting and worthwhile exercise. Explicit expressions for $\pi_{\parallel}$ and $\pi_{\perp}$ in terms of the coefficients of the $g(12)$ expansion were obtained. The condition that $\pi_{\parallel}=\pi_{\perp}$ was then used to show that complex relationships exist between the coefficients in the $g(12)$ expansion. In other words, in orientationally ordered fluids the fact that the pressure tensor must be isotropic imposes conditions upon $g(12)$. The expressions obtained for $\pi_{\parallel}$ and $\pi_{\perp}$ are also important since the numerical evaluation of these quantities provides a severe test of the theoretical approximation applied. For example, for the models defined by Eqs. (32) (with $n=3$ and 6) it is found that, except at low density, the condition $\pi_{\parallel}=\pi_{\perp}$ is not satisfied by any of the approximate theories (i.e., the HNC, RHNC, and RPY) solved in the present paper.

For the orientationally ordered dipolar case expressions were derived relating the elements of the dielectric tensor $\overleftrightarrow{\epsilon}$ to the pair distribution function. At first sight it may seem peculiar to think of a dielectric tensor in an orientationally ordered dipolar fluid since the existence of such a system presupposes the presence of a saturating electric field. However, if one wishes one can simply think of $\overleftrightarrow{\epsilon}$ as being the dielectric tensor governing the response of an orientationally saturated system to the application of an additional small perturbing field. For the fluid of aligned dipoles electrostriction is linear in field (rather than quadratic as is the case for isotropic dipolar systems) and $\epsilon_{\parallel}$ is found to be simply related to the isothermal compressibility and consequently to the structure factor at $\mathbf{k}=0$. The component $\epsilon_{\perp}$ is related to orientational fluctuations due to rotation about the fixed axis and will differ from 1 only for models where $\mu_{\perp}$ is nonzero. It should also be mentioned that the present formulation for ϵ can be easily generalized to include the usual nematic phase where an average half of the dipoles are "up" and the other held are "down" (i.e., $\mathbf{P}=0$ in the absence of a field). This would permit the calculation of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for relatively realistic model nematics and work in this direction is underway.

Numerical results have been reported and discussed for model ferrofluids and for a closely related system in which the pair potential retains dipolar symmetry but is short ranged varying radially as $1/r^6$. This latter model is useful since comparing its properties with those of the ferrofluid serves to demonstrate some of the features unique to the long-range dipolar interaction. For example, for the short-range potential the structure factor $S(\mathbf{k})$ becomes independent of the direction of $\mathbf{k}$ as $k\rightarrow 0$, whereas for the ferrofluid $S(\mathbf{k})$ remains strongly dependent upon orientation at $k=0$. For the short-range potential the RHNC and RPY theories are found to give similar thermodynamic and structural properties. For the ferrofluid the HNC and RHNC equations were solved at low and high density, respectively. The RPY was not applied in the ferrofluid case since it is known[12] to be very poor for the long-range dipolar interaction. Again we note that at high density the condition $\pi_{\parallel}=\pi_{\perp}$ is not satisfied by any of the theories considered.

Physically, the conclusions we draw from our numerical results are similar to those arrived at by earlier works.[3–5] Ferrofluids can develop a very anisotropic structure driven by the tendency of the dipoles towards alignment in order to form energetically, favorable chainlike configurations. It is also interesting to note that for ferrofluids at high density the internal energy is about five times smaller in magnitude than the energy of an isotropic fluid at the same dipole moment and temperature. Unfortunately, for the ferrofluid problem the usefulness of the integral equation techniques is limited by the fact that with present numerical methods solutions cannot be obtained in the physically interesting low-temperature region.[4]

Finally, we remark that the techniques described in this paper will likely prove most useful in the study of the thermodynamic, dielectric, and structural properties of nematic liquid crystals. Numerical calculations for several such models are currently being carried out.

ACKNOWLEDGMENTS

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APPENDIX A

The purpose of this Appendix is to derive expressions for the elements of the pressure tensor defined by Eq. (28). We begin with Eq. (29) and expand g and u on the basis set ψ^{mnl} [cf. Eq. (5b)] to obtain

$$\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}=\frac{\beta\rho}{2}\sum_{\substack{m,n,l\\m',n',l'}} f^{mnl}f^{m'n'l'}\int_0^\infty dr\, r^2 g^{mnl*}(r)$$
$$\times\int d\Omega_r Y_l^{-(m+n)*}(\Omega_r)\mathbf{r}\nabla[u^{m'n'l'}(r)Y_{l'}^{-(m'+n')}(\Omega_r)]\int\frac{d\chi_1}{2\pi}\int\frac{d\chi_2}{2\pi}e^{i(m'-m)\chi_1}e^{i(n'-n)\chi_2} \tag{A1}$$

$$=\frac{\beta\rho}{2}\sum_{\substack{m,n,l\\l'}} f^{mnl}f^{mnl'}\int_0^\infty dr\, r^2 g^{mnl*}(r)\langle l,-m-n\mid \mathbf{r}\nabla u^{mnl'}(r)\mid l',-m-n\rangle\ . \tag{A2}$$

In order to evaluate the matrix element in (A2) it is convenient to introduce the spherical components of $\nabla(\partial_q, q=0,\pm 1)$ and $\mathbf{r}(r_q=\sqrt{4\pi/3}\,rY_1^q)$ from which one can construct two irreducible tensors of rank 0 and 2, respectively,[27]

$$T(0)=\sum_q r_q^*\partial_q=\mathbf{r}\cdot\nabla \tag{A3a}$$

and

$$T(2,M)=\sum_{q,q'} r_q\partial_{q'}(1q1q'\mid 112M)\ . \tag{A3b}$$

$\Delta\overleftrightarrow{\pi}$ being a symmetric tensor of rank two can be expressed entirely in terms of $T(0)$ and $T(2)$. In fact, since $\Delta\overleftrightarrow{\pi}$ has only two independent components only $T(0)$ and the $M=0$ component of $T(2)$

$$T(2,0)=\frac{1}{\sqrt{6}}\left[3z\frac{\partial}{\partial z}-r\frac{\partial}{\partial r}\right] \tag{A4}$$

need be considered. Thus

$$\mathrm{Tr}\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}=2A_\perp+A_\parallel$$
$$=\frac{\beta\rho}{2}\sum_{m,n,l,l'} f^{mnl}f^{mnl'}\int_0^\infty dr\, r^2 g^{mnl*}(r)\langle l,-m-n\mid T(0)\mid l',-m-n\rangle u^{mnl'}(r) \tag{A5a}$$

and

$$3\left[\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}\right]_{zz}-\mathrm{Tr}\frac{\beta}{\rho}\Delta\overleftrightarrow{\pi}=2(A_\parallel-A_\perp)$$
$$=\frac{\beta\rho}{2}\sum_{m,n,l,l'} f^{mnl}f^{mnl'}\int_0^\infty dr\, r^2 g^{mnl*}(r)\langle l,-m-n\mid \sqrt{6}T(2,0)\mid l',-m-n\rangle u^{mnl'}(r)\ . \tag{A5b}$$

As $\langle l,-m-n\mid T(0)\mid l',-m-n\rangle=r(\partial/\partial r)\delta_{ll'}$, Eq. (A5a) leads immediately to Eq. (31a). In order to evaluate the matrix element in (A5b) we apply the Wigner-Eckart theorem[27]

$$\langle l,-m-n\mid T(2,0)\mid l',-m-n\rangle=(-1)^{l+m+n}\begin{pmatrix} l & 2 & l'\\ m+n & 0 & -m-n\end{pmatrix}\langle l\|T(2)\|l'\rangle \tag{A6a}$$

and use the relations[27]

$$\langle l\|T(2)\|l'\rangle=\sqrt{5}(-1)^{l+l'}\sum_J\begin{Bmatrix}1 & 1 & 2\\ l' & l & J\end{Bmatrix}\langle l\|\mathbf{r}\|J\rangle\langle J\|\nabla\|l'\rangle\ , \tag{A6b}$$

$$\langle l\|\mathbf{r}\|J\rangle=r(-1)^l\sqrt{(2l+1)(2J+1)}\begin{pmatrix}l & 1 & J\\ 0 & 0 & 0\end{pmatrix}\ , \tag{A6c}$$

and

$$\langle J\|\nabla\|l'\rangle=\delta_{J,l'+1}\sqrt{l'+1}\left[\frac{\partial}{\partial r}-\frac{l'}{r}\right]$$
$$-\delta_{J,l'-1}\sqrt{l'}\left[\frac{\partial}{\partial r}+\frac{l'+1}{r}\right]\ , \tag{A6d}$$

where $(\cdots)$ and $\{\cdots\}$ denote the usual 3-j and 6-j symbols of Wigner. Substitution of (A6) into (A5) leads to the desired Eq. (31b).

APPENDIX B

In this appendix the relationship (81) between $H_\parallel^{00}(0)$ and $H_\perp^{00}(0)$ is derived from the OZ equation. Using the form given by Eq. (18) and putting $m=n=0$ we have

$$H^{00}(\mathbf{k})=C^{00}(\mathbf{k})+\rho\sum_{p=-\infty}^{+\infty}H^{0\,-p}(\mathbf{k})C^{p0}(\mathbf{k})\ , \tag{B1}$$

where [cf. Eq. (16)]

$$C^{p0}(\mathbf{k})=\sum_{l}\sqrt{4\pi/(2l+1)}\,\tilde{c}^{\,p0l}(k)Y_l^{-p}(\mathbf{\Omega}_{\mathbf{k}})\ . \tag{B2}$$

If we make the assumption that $c(12)\rightarrow-\beta u(12)$ as $r\rightarrow\infty$, with $u(12)$ given by (52), it is clear that in the limit $\mathbf{k}\rightarrow0$ the only nonzero contributions to (B2) will be

$$\tilde{c}^{\,p00}(0)=\tilde{c}^{\,000}(0)\delta_{p,0}\ , \tag{B3a}$$

$$\tilde{c}^{\,p02}(0)=-\frac{6y_{\parallel}}{\rho}\delta_{p,0}\ , \tag{B3b}$$

and consequently

$$\lim_{\mathbf{k}\rightarrow0}C^{p0}(\mathbf{k})=\left[\tilde{c}^{\,000}(0)-\frac{6y_{\parallel}}{\rho}P_2(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})\right]\delta_{p,0}\ . \tag{B4}$$

From Eq. (B1) it follows that

$$1+\rho\lim_{\mathbf{k}\rightarrow0}H^{00}(\mathbf{k})=\frac{1}{1-\rho\lim\limits_{\mathbf{k}\rightarrow0}C^{00}(\mathbf{k})}=\frac{1}{1-\rho\tilde{c}^{\,000}(0)+6y_{\parallel}P_2(\hat{\mathbf{k}}\cdot\hat{\mathbf{z}})}\ . \tag{B5}$$

Applying Eq. (B5) with $\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}=1$ and $\hat{\mathbf{k}}\cdot\hat{\mathbf{z}}=0$ and recalling the definitions of $H_{\parallel}^{00}(0)$ and $H_{\perp}^{00}(0)$ given in (77) and (80) we obtain

$$1+\rho H_{\parallel}^{00}(0)=\frac{1}{1-\rho\tilde{c}^{\,000}(0)+6y_{\parallel}}\ , \tag{B6a}$$

and

$$1+\rho H_{\perp}^{00}(0)=\frac{1}{1-\rho\tilde{c}^{\,000}(0)-3y_{\parallel}}\ . \tag{B6b}$$

Elimination of $\tilde{c}^{\,000}(0)$ from these equations immediately leads to Eq. (81), which is the desired result.

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[1] J. L. Lebowitz and J. W. Perram, Mol. Phys. **50**, 1207 (1983).

[2] J. K. G. Dhont, J. Chem. Phys. **85**, 5983 (1986).

[3] J. B. Hayter and R. Pynn, Phys. Rev. Lett. **49**, 1103 (1982).

[4] G. A. R. Martin, A. Bradbury, and R. W. Chantrell, IEEE Trans. Magn. **22**, 1137 (1986).

[5] S. Hess, J. B. Hayter, and R. Pynn, Mol. Phys. **53**, 1527 (1984).

[6] A. Stroobants, H. N. W. Lekkerkerker, and D. Frenkel, Phys. Rev. Lett. **57**, 1452 (1986); Phys. Rev. A **36**, 2929 (1987).

[7] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986).

[8] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon, Oxford, 1984).

[9] L. Blum and A. J. Torruella, J. Chem. Phys. **56**, 303 (1972).

[10] L. Blum, J. Chem. Phys. **57**, 1862 (1972); *ibid.* **58**, 3295 (1973).

[11] P. H. Fries and G. N. Patey, J. Chem. Phys. **82**, 429 (1985).

[12] P. H. Fries and G. N. Patey, J. Chem. Phys. **85**, 7307 (1986).

[13] A. Perera, P. G. Kusalik, and G. N. Patey, Mol. Phys. **60**, 77 (1987).

[14] A. Perera, P. G. Kusalik, and G. N. Patey, J. Chem. Phys. **87**, 1295 (1987).

[15] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1962), Vol. II.

[16] J. M. Caillol, Chem. Phys. Lett. **121**, 347 (1985).

[17] S. L. Price, A. J. Stone, and M. Alderton, Mol. Phys. **52**, 987 (1984).

[18] See, e.g., L. E. Reichl, *A Modern Course in Statistical Physics* (Arnold, London, 1980).

[19] See, e.g., Ref. 7.

[20] R. L. Fulton, J. Chem. Phys. **78**, 6865 (1983).

[21] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960), p. 61.

[22] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), Pt. I, p. 572.

[23] L. G. Suttorp and S. R. De Groot, Physica **108A**, 361 (1981).

[24] F. Lado, Phys. Rev. **135A**, 1013 (1964); Mol. Phys. **31**, 1117 (1976).

[25] L. Verlet and J. J. Weis, Phys. Rev. A **5**, 939 (1972).

[26] G. N. Patey, D. Levesque, and J. J. Weis, Mol. Phys. **38**, 219 (1979).

[27] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, New York, 1960).