Integral equation theory for fluids ordered by an external field: Separable interactions

Aurélien Perera

*Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, Case Courrier 121, 4 Place Jussieu,
75252 Paris Cedex 05, France**

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The structural and thermodynamical properties of classical fluids orientationally ordered by an external field are investigated by means of integral equation theories. A general theoretical framework for handling these theories is developed and detailed for the particular case of separable interactions between fluid particles. This approach is then illustrated for the case of two (off lattice) models: the ferromagnetic Heisenberg model and a simple liquid crystal model, for which the numerical solution of integral equations such as the Percus-Yevick, the hypernetted chain, and the reference hypernetted chain closure equations are presented and compared with Monte Carlo simulation results and the analytical solution of the mean spherical approximation. The zero-field case is also examined, and the spontaneous ordering is analyzed in detail, mainly in what concerns the appearance of infinite wavelength singularity in the Ornstein-Zernike equation and the relation with the one-body closure equations and the long range orientational ordering that occurs. In particular, it is shown that the Wertheim one-body closure equation appears as a sum rule compatible with the Ornstein-Zernike equation. The relation between the elastic constant and the long range tail of the pair correlation function is made explicit. In particular, the long range behavior of the various terms in the expansion of the pair correlation function is depicted. The numerical investigation of the two models shows that it is not possible to discriminate between the four integral equations, as to which one would be the most accurate in all cases. The general trends in the thermodynamical and structural properties seem to indicate that the Percus-Yevick approximation is generally better in the strong ordering case, whereas the reference hypernetted chain approximation might be better suited to the study of the isotropic phase and the low ordering regimes. [S1063-651X(99)00909-5]

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I. INTRODUCTION

The integral equation theories for orientationally inhomogeneous systems are not developed to the same point as they are for the spatially inhomogeneous systems. This can be explained by the fact that such studies have been largely preempted by lattice theories for spinlike models [1] or by phenomenological approaches for liquid crystalline type models [2–4], which capture the essential features of ordered fluids and mainly provide analytical approaches to most of the physical properties of such fluids. Yet one might be curious about how to relate these approaches to standard liquid state theories. Such methods have already been applied to investigate the isotropic phase of fluids with angle dependent molecular interactions [5–7]. In the absence of a formalism allowing a calculation of the structural properties of the ordered phases, the usual way to handle the thermodynamics of these phases is through density functional theories, where one make the assumption that the direct correlation function of the isotropic phase, near its limit of stability, can be used to tailor that of the coexisting ordered phase [8,9]. Although this type of argument can be refined in several ways [10], it would be desirable to obtain a direct correlation function of the ordered phase by some other methods. The main problem in applying integral equation techniques to such cases is the appearance of the one-body orientational distribution function in the Ornstein-Zernike (OZ) equation, which in turn implies that a second closure relation must be imposed in order to solve a closed system of equations. The appropriate choice of the one-body closure is then a crucial step.

Recently, two works have tackled this problem directly. Sokolowska solved the mean spherical approximation (MSA) for the ordered continuum ferromagnetic Heisenberg fluid [11] and for a nematic model [12], providing the first analytical solution for the direct correlation function of such fluids. The so-called Wertheim equation for one-body closure has been used in these works. Lado and co-workers [13,14] numerically solved the reference hypernetted chain (RHNC) equation and a variant of the Zerah-Hansen closure equation for the continuum ferromagnetic Heisenberg, and one-body closure was derived from the first equation of the BGY hierarchy. Both approaches investigated the influence of zero and finite ordering fields on the properties of the ordered fluid. The method adopted by Lado and co-workers was based on the tailored orthogonal polynomial technique, that has been successfully applied for various cases such as polarizable fluids [15] or polydisperse fluids [16]. The basic feature of this method, applied to the Heisenberg fluid, is to expand the pair and direct correlation functions on a basis of rotational invariants that are tailored on the one-body orientational correlation function. These new invariants are then dependent on the form of this function, and must be recomputed every time the one-body function changes. Although formally very general, this method is most efficiently implemented when the analytic form of the one-body distribution can be guessed *a priori* [15,16]. In particular, the Heisenberg fluid was studied in Ref. [13] by assuming a Maier-Saupe form, which indeed appears to be a sound approximation for the case of separable intermolecular interactions. In what concerns nonseparable interactions, the study of fluids made of dipolar hard convex molecules [17] has revealed non-

trivial one-body functions, which in particular cannot be cast in a simple Maier-Saupe form. It is certainly desirable to solve the integral equations for inhomogeneous fluids without any *a priori* knowledge about the form of the one-body distribution function.

A general method is introduced in the present work, where it is shown that it is quite possible to solve standard integral equations by using the natural rotational invariants (there is no need to compute them explicitly), without any assumption about the form of the one-body function, and by keeping the same techniques that are used for the isotropic phase [5,6]. This method can thus be applied to several other interesting cases, such as, for example, the nematic phase of hard convex bodies, as well as dipolar and ferro fluids. The method is described extensively in the present work, and illustrated for the case of the two models of separable interactions which have been used in the recent literature [11,18–21]. It turns out that the use of natural invariants allows one to obtain a direct insight into the meaning of the various one-body closures, and particularly into the appearance of long range spontaneous orientational ordering in the absence of field. The method presented here thus allows one to study the appearance of spontaneous orientational order in a liquid crystalline type fluid. The remainder of this paper is as follows. In Sec. II, the general theoretical framework for separable interaction is detailed, and the choice of the one-body closure is analyzed in terms of the relation to the OZ equation. Expressions for the thermodynamical properties of the ordered fluid are given. The relation between the pair density expansion coefficients which are measured by the computer simulations and the pair distribution function that used in an theory is detailed (this difference is often overlooked when reporting structural data). This last point settles the large separation behavior of the density correlation function, indicating in particular which are the expansion coefficients of the pair correlation function that decay to zero, and which tend to a constant limit. Section III covers the comparison between the simulations and the four integral equations that are solved by the method proposed herein. The conclusions are given in Sec. IV.

II. STATISTICAL MECHANICS OF THE ORDERED FLUIDS

In what follows, we consider a fluid of spherical particles with diameter σ with an orientation specified by the unit vector $\mathbf{u}$. This fluid is subject to an external ordering field of the form $\beta\phi_{\text{ext}}(1) = -BP_a(\mathbf{u}\cdot\mathbf{n})$ which favors an order parallel to the direction $\mathbf{n}$. P_a is a Legendre polynomial of order a, and $\beta = 1/k_BT$ is the inverse Boltzmann temperature. We confine ourselves to separable interactions between the fluid particles of the form

$$\beta u(1,2) = \beta u(r,\mathbf{u}_1,\mathbf{u}_2) = u_0(r) + \beta u_a(r)P_a(\mathbf{u}_1\cdot\mathbf{u}_2),$$
(1)

where $u_0(r)$ is the isotropic part of the interactions (this can be a hard sphere type interaction or any other type). The orientational part is model dependent, and is selected by the parameter a which can take two values: $a=1$ corresponds to a Heisenberg type model, and $a=2$ selects the nematic

model. These two models have been abundantly investigated in the recent literature [11,12,18–21].

A. Expansion of the pair correlation function

In order to formulate the problem clearly, we need to specify the form of rotational invariant which must reflect the symmetry of the pair correlation function in the ordered phase. Clearly, the choice of the interaction in Eq. (1) dictates that the pair correlations are independent of the orientation of the intermolecular vector. The most general expansion that takes accounts of this property, as well as the axial symmetry of the particles, can be written in the form

$$g(1,2) = g(r,\mathbf{u}_1,\mathbf{u}_2) = \sum_{m,n,\mu} g^{mn\mu}(r)R_{\mu 0}^m(\mathbf{u}_1)R_{-\mu 0}^n(\mathbf{u}_2)$$
(2)

where $R_{\mu 0}^m(\mathbf{u}_1)$ are the usual Wigner elements [22]. The only rotational invariant operation that leaves $g(1,2)$ unchanged is any arbitrary rotation of the set $(\mathbf{u}_1,\mathbf{u}_2)$ around the director by an azimuthal angle ϕ. This invariance leads the appearance of a unique index μ in the above expansion.

It is useful to write down the Fourier transform of this equation. In fact, only the zeroth-order Fourier-Hankel transform will appear due the separability of the interaction,

$$\tilde{g}(1,2) = \int d\vec{r}\exp(i\vec{k}\cdot\vec{r})g(1,2)$$

$$= \tilde{g}(k,\mathbf{u}_1,\mathbf{u}_2) = \sum_{m,n,\mu}\tilde{g}^{mn\mu}(k)R_{\mu 0}^m(\mathbf{u}_1)R_{-\mu 0}^n(\mathbf{u}_2),$$
(3)

with

$$\tilde{g}^{mn\mu}(k) = 4\pi\int_0^\infty dr\, r^2 g^{mn\mu}(r)\frac{\sin(kr)}{kr}.$$
(4)

Equation (2) can be cast in a matricial form, by introducing the following matrix $\mathbf{G}_\mu$ with matrix elements $\{\mathbf{G}_\mu\}_{mn} = g^{mn\mu}(r)$ and the vector $\underline{\Gamma}_\mu(1)$ with elements $\{\Gamma_\mu\}_m = R_{\mu 0}^m(1)$,

$$g(1,2) = \sum_\mu \underline{\Gamma}_\mu^t(1)\mathbf{G}_\mu\underline{\Gamma}_\mu(2),$$
(5)

where the superscript t indicates a transpose. The matrix notation is quite convenient, and will be often used in what follows. The expansion in Eq. (2) has some symmetry properties worth noting. First the particle exchange symmetry $g(1,2) = g(2,1)$ implies $g^{mn\mu}(r) = g^{nm\mu}(r)$. The reality of the pair correlation function implies $g^{mn-\mu}(r) = g^{mn\mu}(r)$. As a consequence, the matrices $\mathbf{G}_\mu$ are symmetrical and invariant under the change $\mu \to -\mu$. Similar considerations hold also for the direct correlation matrix $\mathbf{C}_\mu$ and the matrix of the Fourier transforms $\tilde{\mathbf{G}}_\mu$ and $\tilde{\mathbf{C}}_\mu$. For notation simplicity, the explicit r and k dependences are omitted in the matrix notation.

In the absence of an external field ($B=0$) and far from any spontaneous order, these equations naturally reduces to

the *isotropic fluid* limit. In this case, the rotational invariance property leaves $g(1,2)$ unchanged under any arbitrary rotation of the set $(\mathbf{u}_1, \mathbf{u}_2)$. It is easy to show that expansion (2) still holds, but with the restriction $m = n$. Using the addition theorem of the spherical harmonics, this expansion can then be written more simply as

$$g_I(1,2) = \sum_m g_m(r) P_m(\mathbf{u}_1 \cdot \mathbf{u}_2), \qquad (6)$$

where the index I discriminates the isotropic phase. The expansion coefficients between the two expansions (2) and (6) are simple related by $g_I^{mn\mu} \delta_{mn} = g_m(-)^\mu$. As a consequence, the $\mathbf{G}_\mu$ matrices are *diagonal* in the isotropic limit. We now proceed to show how these expansions can be used to cast the OZ and closure relations into manageable forms.

B. Expansion of the one-body closure

The major difference between the integral equation for isotropic fluids and that for ordered fluids is the presence of a one-body closure relation in addition to the usual pairing of the Ornstein-Zernike relation with a two-body closure such as the hypernetted chain approximation. The singlet density function that is nucleated by the external orientationally ordering field can be written as

$$\rho(1) = \rho(\mathbf{u}) = \frac{\rho_N}{4\pi} f(1), \qquad (7)$$

where

$$f(1) = f(x = \mathbf{u} \cdot \mathbf{z}) = \sum_l a_l P_l(x), \qquad (8)$$

where ρ_N is the number density of the ordered phase [the index N denotes the (ferro)nematic-type order, and the index I will be used for the isotropic phase]. In the isotropic phase one has simply $\rho(1) = \rho_I/(4\pi)$. In the relation above, we choose the normalization such as $a_0 = 1$:

$$\int d\mathbf{u} \, \rho(\mathbf{u}) = \rho_N. \qquad (9)$$

We note that the order parameters S_m of the ordered fluid are related to the expansion coefficients a_m above by the relation

$$S_m = \langle P_m(1) \rangle = \frac{1}{4\pi} \int d\mathbf{u} \, P_m(\mathbf{u}) f(\mathbf{u}) = \frac{a_m}{2m+1}. \qquad (10)$$

There are three exact relations involving $\rho(1)$ that are available from first principles [23]. All three equations can be cast under a similar form,

$$i\vec{L}_1[\ln \rho(1) + \beta \phi_{\text{ext}}(1)] = \int d\mathbf{u}_2 \vec{K}(\mathbf{u}_1, \mathbf{u}_2) \qquad (11)$$

and differ by the form of the kernel $\vec{K}$. ($i\vec{L}_1$ is the angular momentum operator acting on the orientation of particle 1). The first one can be derived from the BGY equation under the assumption of pairwise additivity of the pair interactions. The corresponding kernel reads

$$\vec{K}_{\text{BGY}}(\mathbf{u}_1, \mathbf{u}_2) = -\rho(2) \int d\vec{r} \, g(1,2) i\vec{L}_1 \beta u(1,2). \qquad (12)$$

The second equation involves $c(1,2)$, the pair direct correlation function (dcf) and the corresponding kernel is

$$\vec{K}_C(\mathbf{u}_1, \mathbf{u}_2) = \tilde{c}^{(0)}(\mathbf{u}_1, \mathbf{u}_2) i\vec{L}_2 \rho(2), \qquad (13)$$

where $\tilde{c}^{(0)}$ is the zeroth-order Fourier-Hankel transform of the direct correlation function. Finally, the last equation involves $h(1,2)$, the pair correlation function, and the corresponding kernel can be written as

$$\vec{K}_H(\mathbf{u}_1, \mathbf{u}_2) = -\tilde{h}^{(0)}(\mathbf{u}_1, \mathbf{u}_2) \rho(2) i\vec{L}_2 \beta \phi_{\text{ext}}(2). \qquad (14)$$

These last two equations are not independent, and in fact can be interrelated through the Ornstein-Zernike equation [23], as shown in Sec. II A. There are no simple relations between the first equation and the two latter ones. In fact, the first equation can be considered as a ''virial'' form of the one-body closure equation, whereas the last two can be seen as the ''compressibility'' analog of this closure in the sense that they are related to the OZ equation, as will become clear in Sec. II C. At present, it is not clear if these two equations will lead to the same solution for $\rho(1)$ if the pair and direct correlation functions are exactly known [23].

The second equation is sometimes called the Wertheim equation, as it was proposed by this author in the context of the liquid-vapor interface problem [24]. It is quite convenient to deal with, as the direct correlation function is generally a short ranged function; thus $\tilde{c}^{(0)}(1,2)$ is well defined. We will now look into the details of this equation for our problem.

For the symmetry of our problem with $\mathbf{u} = (\theta, \phi)$, the angular momentum operator is simply [25] $i\vec{L} = (-\sin(\phi), \cos(\phi), 0) \partial_\theta$. Using the expansions in Eqs. (2)–(4), we can write the solution of the Wertheim equation for orientationally ordered fluids as

$$\rho(1) = \frac{\rho_N}{4\pi} \frac{\exp(-\beta \phi_{\text{ext}}(1) + W(1))}{Z} \qquad (15)$$

where the normalization constant Z is imposed such that $\rho(1)$ obeys Eq. (9), and

$$W(1) = W(x = \mathbf{u} \cdot \mathbf{z}) = \sum_m W_m P_m(x), \qquad (16)$$

with

$$W_m = -\rho_N \sum_n \frac{a_n}{2n+1} \left(\frac{n(n+1)}{m(m+1)} \right)^{1/2} \tilde{c}^{mn1}(0). \qquad (17)$$

We note that only the $\mu = 1$ expansion coefficients of the dcf $c^{mn\mu}$ appear in the one-body closure. This feature is very important in what follows, and is not present in the BGY version of the one-body closure as written in Eq. (12). In practice, Eqs. (15) and (17) are sufficient to solve for the one-body equation when the moments of the dcf are available. These equations can be easily solved by successive interactions starting with an initial guess for $f(1)$ [for example, $f(1) = \exp(-\beta \phi_{\text{ext}}(1))$], and a_m are determined at

each iterative step using the last equality in Eq. (10). We can also write the one-body equation in the form of matrix equation. If we expand the equations in Eqs. (11) and (13) in terms of $f(1)$, we can cast these equations in the form

$$(\mathbf{I} - \mathbf{R}_1 \widetilde{\mathbf{C}}_1^{(0)}) \underline{\mathbf{A}} = \underline{\mathbf{B}}, \tag{18}$$

where we have adopted the matrix notation of Eq. (5), that is $\widetilde{\mathbf{C}}_{1;mn}^{(0)} = \widetilde{c}^{mn1}(0)$. The vectors $\underline{\mathbf{A}}$ and $\underline{\mathbf{B}}$ are defined by their components through the relations $\underline{\mathbf{A}}_m = \rho_N a_m \sqrt{m(m+1)}/(2m+1)$ and $\underline{\mathbf{B}}_m = B\sqrt{a(a+1)}R^{am1}$, $\mathbf{I}$ is the identity matrix, and a is the model selecting parameter introduced in Eq. (1). In the equation above, we have introduced a new matrix $\mathbf{R}_\mu$ with matrix elements

$$R^{mn\mu} = \int d\mathbf{u}\, \rho(\mathbf{u}) R_{\mu 0}^m(\mathbf{u}) R_{-\mu 0}^n(\mathbf{u}). \tag{19}$$

This matrix is very important in the solution of the integral equations for orientationally inhomogeneous fluids, and will appear recurrently in this work and subsequent ones. The matrix elements in Eq. (19) can be thought as an orthogonality relation between the Wigner elements, weighted by the one-body function. If one uses this relation to define tailored Wigner elements such that the $\mathbf{R}_\mu$ matrices reduce to the identity (the orthogonality of the new tailored Wigner elements) one recovers the solution method used in Ref. [13].

From Eq. (19) and the properties of the Wigner elements [25], it can be seen that the matrix $\mathbf{R}_\mu$ has the same symmetry properties as the correlation functions. In particular, one can show that

$$R^{mn\mu} = \rho_N \sum_l a_l \begin{pmatrix} m & n & l \\ \mu & -\mu & 0 \end{pmatrix} \begin{pmatrix} m & n & l \\ 0 & 0 & 0 \end{pmatrix} \tag{20}$$

where the matrix symbols above are the $3-j$ elements [25].

If we now expand the one-body equation in terms of $\ln f(1)$, we obtain a different matrix equation

$$(\mathbf{I} - \widetilde{\mathbf{C}}_1^{(0)} \mathbf{R}_1) \underline{\mathbf{\Lambda}} = \underline{\mathbf{\Theta}}, \tag{21}$$

where the vectors $\underline{\mathbf{\Lambda}}$ and $\underline{\mathbf{\Theta}}$ are now defined as $\underline{\mathbf{\Lambda}}_m = W_m \sqrt{m(m+1)}$ and $\underline{\mathbf{\Theta}}_m = B\sqrt{a(a+1)}\delta_{am}$ and where W_m are given by Eq. (17). We note that, in the absence of an external ordering field ($B=0$), Eqs. (18) and (21) show that these matrix equations are now eigenequations for the vectors $\underline{\mathbf{A}}$ and $\underline{\mathbf{\Lambda}}$, respectively, with unit eigenvalue. In particular, the matrices $(\mathbf{I} - \mathbf{R}_1 \widetilde{\mathbf{C}}_1^{(0)})$ and $(\mathbf{I} - \widetilde{\mathbf{C}}_1^{(0)} \mathbf{R}_1)$ are singular in the zero-field limit if there is a nontrivial solution for $\rho(1)$. We see in Sec. II C that this singularity in the matrix equation is responsible for the divergence of the pair correlation function in the limit $k=0$, which is responsible for the turbid appearance of systems orientationally ordered in the absence of any external field [3].

C. Expansion of the Ornstein-Zernike equation

The Ornstein-Zernike equation for inhomogeneous fluids can be written as [23]

$$\eta(1,2) = h(1,2) - c(1,2) = \int d3\, \rho(3) h(1,3) c(3,2) \tag{22}$$

This equation is more conveniently written after a Fourier transform, which allows one to write the convolution product as a product of the transforms. After expanding the various terms, and using the orthogonality of the Wigner elements, it is straightforward to show that this equation can be written in a matricial form as

$$\widetilde{\mathbf{N}}_\mu = \widetilde{\mathbf{H}}_\mu - \widetilde{\mathbf{C}}_\mu = \widetilde{\mathbf{H}}_\mu \mathbf{R}_\mu \widetilde{\mathbf{C}}_\mu = \widetilde{\mathbf{C}}_\mu \mathbf{R}_\mu \widetilde{\mathbf{H}}_\mu, \tag{23}$$

where the last equality expresses simply the commutativity of the convolution in Eq. (22). We recall that it is understood that the $\widetilde{\mathbf{C}}$ and $\widetilde{\mathbf{H}}$ are k dependent. By a simple manipulation, one can rewrite these equations into two equivalent forms:

$$(\mathbf{I} + \mathbf{R}_\mu \widetilde{\mathbf{H}}_\mu)(\mathbf{I} - \mathbf{R}_\mu \widetilde{\mathbf{C}}_\mu) = \mathbf{I},$$

$$(\mathbf{I} - \widetilde{\mathbf{C}}_\mu \mathbf{R}_\mu)(\mathbf{I} + \widetilde{\mathbf{H}}_\mu \mathbf{R}_\mu) = \mathbf{I}. \tag{24}$$

These equations are no more complex to solve as those encountered in the expansion of the isotropic fluid equations for nonseparable interactions [5,6]. In practice, it is preferable to use the following equation in order to compute $\widetilde{\eta}^{mn\mu}(k) = \widetilde{h}^{mn\mu}(k) - \widetilde{c}^{mn\mu}(k)$:

$$\widetilde{\mathbf{N}}_\mu = \widetilde{\mathbf{C}}_\mu \mathbf{R}_\mu \widetilde{\mathbf{C}}_\mu (\mathbf{I} - \mathbf{R}_\mu \widetilde{\mathbf{C}}_\mu)^{-1} = (\mathbf{I} - \widetilde{\mathbf{C}}_\mu \mathbf{R}_\mu)^{-1} \widetilde{\mathbf{C}}_\mu \mathbf{R}_\mu \widetilde{\mathbf{C}}_\mu \tag{25}$$

The OZ equation can be used to obtain directly the factorization of the third closure equation for the one body function (14). Indeed, using Eq. (24), one obtains directly from Eqs. (18) and (21), respectively, the following result at $k=0$ and for $\mu=1$:

$$(\mathbf{I} + \mathbf{R}_1 \widetilde{\mathbf{H}}_1^{(0)}) \underline{\mathbf{B}} = \underline{\mathbf{A}},$$

$$(\mathbf{I} + \widetilde{\mathbf{H}}_1^{(0)} \mathbf{R}_1) \underline{\mathbf{\Theta}} = \underline{\mathbf{\Lambda}}. \tag{26}$$

The case of the isotropic fluid is interesting in particular. All the matrices are then diagonal, and the $R^{mn\mu}$ matrix elements reduce to $\rho_I/(2m+1)(-)^\mu$. The OZ equations decouple entirely for each component

$$\widetilde{\eta}_m(k) = \frac{\rho_I [\widetilde{c}_m(k)]^2/(2m+1)}{(1 - \rho_I \widetilde{c}_m(k)/(2m+1))}, \tag{27}$$

which is a result that was derived previously [7,20].

D. Spontaneous ordering in the absence of an ordering field

Another interesting case is the zero ordering field limit, when spontaneous order can appear and persist in the system. In this case, we see from the eigenequation in Eq. (21) that, in the $k=0$ limit, the OZ equation is singular for $\mu=1$ with a nontrivial $\rho(1)$. In particular, one cannot invert $\mathbf{\Pi}_1 = (\mathbf{I} - \widetilde{\mathbf{C}}_1 \widetilde{\mathbf{R}}_1)$ in Eq. (24), and some care must be taken before performing this operation. The singularity in the $\mathbf{\Pi}_1$ matrix in fact reflects the growth of long ranged orientational correlations in $g^{mn1}(r)$ with $\mu=1$. From the expansion equa-

tion (2), we see that $\mu=1$ expansion terms correspond to the angular average of the following Wigner elements:

$$g^{mn1}(r)\approx\langle R_{10}^m(1)R_{-10}^n(2)+R_{-10}^m(1)R_{10}^n(2)\rangle. \quad (28)$$

Using the definition of the Wigner elements in terms of spherical harmonics [25], we can write, in particular,

$$R_{10}^m(\mathbf{u})=\frac{\sqrt{1-z^2}}{\sqrt{m(m+1)}}\frac{d}{dz}P_m(z)(x-iy)=\gamma_m(z)(x-iy),$$
$$(29)$$

with the Cartesian notation $z=\cos(\theta)$ and $e^{-i\phi}=x-iy$ for the components of any unit vector $\mathbf{u}(\theta,\phi)$. Therefore, one has

$$g^{mn1}(r)\approx\langle\gamma_m(z_1)\gamma_n(z_2)\mathbf{u}_1^\perp\cdot\mathbf{u}_2^\perp\rangle, \quad (30)$$

where the vector $\mathbf{u}_1^\perp=(x,y,0)$ is orthogonal to the direction of the order (taken here to be the $\mathbf{z}$ direction). Thus the $g^{mn1}(r)$ component measures the orientational correlations in the plane perpendicular to the director, and thus has a $1/r$ long ranged tail when spontaneous order is present in the system. It is interesting to note that it is the transverse fluctuations that are responsible for the long range order in the unoriented nematics, not the longitudinal ones that reflect the director long wavelength distortions and are associated with the elastic behavior of these ordered fluids. It is these transverse correlations that are responsible for the turbid appearance of real unoriented nematics, and the strong forward scattering observed in these materials. These transverse excitations at $k=0$ and zero field are often called Goldstone modes, and the Wertheim equation, or equivalently the OZ equation in the limit $k=0$, does contain these modes, independently of the two-body closure relation that might be used. It is an open question as to whether the use of the BGY one-body closure together with the OZ equation will lead to these modes. In particular, one would like to know if the two limits $k=0$ and $B=0$ coincide to produce the Goldstone modes. The numerical information from Ref. [13] does not allow a clearcut answer of this problem. The exact algebraic long range decay of these transverse correlations is known from renormalization group theory to be $1/r^{1+\eta}$ [1]. However, in the present case, in the absence of an exact closure, the classical Ornstein-Zernike form should be expected, that is, $g^{mn1}(r)\approx1/r$. Thus the Fourier transform of this function will have a small k singularity of the form $\tilde{g}^{mn1}(k\to0)\approx1/k^2$. In order to see the consequence in the OZ equations (24), we perform a small k expansion of the matrices:

$$\tilde{\mathbf{C}}_1=\tilde{\mathbf{C}}_1^{(0)}+k^2\tilde{\mathbf{C}}_1^{(2)}+\cdots,$$

$$\tilde{\mathbf{H}}_1=\frac{1}{k^2}\tilde{\mathbf{H}}_1^{(-2)}+\tilde{\mathbf{H}}_1^{(0)}+k^2\tilde{\mathbf{H}}_1^{(2)}+\cdots. \quad (31)$$

Combining these expansion into the OZ equations (24) for the term in $1/k^2$ in the expansion we obtain

$$(\mathbf{I}-\tilde{\mathbf{C}}_1^{(0)}\mathbf{R}_1)\tilde{\mathbf{H}}_1^{(-2)}=0. \quad (32)$$

Comparing this equation with Eq. (21) we see that a solution for $\tilde{\mathbf{H}}_1^{(-2)}$ compatible with the eigenequation (21) is to postulate that

$$\tilde{\mathbf{H}}_1^{(-2)}=\kappa\underline{\mathbf{\Lambda}}\otimes\kappa\underline{\mathbf{\Lambda}}, \quad (33)$$

where $\otimes$ denotes a tensorial product between the two eigenvectors $\underline{\mathbf{\Lambda}}$, and κ is an arbitrary constant. For separable systems with spontaneous ordering, the exact form of the long range part of the pair correlation is then known from the expression for Λ [Eq. (21)]:

$$\lim_{r\to\infty}h^{mn1}(r)=\kappa^2\frac{W_mW_m}{r} \quad (34)$$

with W_m given by Eq. (17). The constant κ will be related soon in what follows to the elastic constant of the fluid. This result allows one to solve the case of spontaneous ordering quite precisely and numerically, as the long range decay can be handled exactly. We come back to this point in Sec. III. It is quite remarkable that the limit in Eq. (34) is reminiscent of that observed in ionic fluids. In that sense the term κW_m plays the role of a ''charge.'' This analogy is used in the actual numerical solution of the integral equations in order to handle the long range part of the distribution function, as is explained in Sec. III.

E. Expansion of the two-body closures

A closure relation relating the pair and direct correlation functions is needed in order to have a closed set of equations to solve. The RHNC closure equation can be written as

$$g(1,2)=\exp(-\beta u(1,2)+\eta(1,2)+b^{000}(1,2;\bar{\sigma})), \quad (35)$$

where b^{000} is the isotropic part of the bridge function, which is empirically known in some cases (hard sphere and Lennard-Jones fluids). The effective diameter $\bar{\sigma}$ (or equivalently, the effective density) involved in $b^{000}(r)$ must be adjusted by a free-energy minimization [26]. Following Fries and Patey [5], this type of equation can be rewritten as:

$$c(1,2)=-\beta u(1,2)+b(1,2)-\int_r^\infty dr'h(1,2)\frac{d}{dr'}w(1,2),$$
$$(36)$$

where $w(1,2)=-\beta u(1,2)+\eta(1,2)+b^{000}(r)$ is the argument of the exponent in Eq. (35). In this form the equation can be readily expanded and thus written in a solvable form:

$$c^{mn\mu}(r)=-\beta u^{mn\mu}(r)-b^{000}(r)\delta_{m0}\delta_{n0}\delta_{\mu0}$$
$$-\sum_{\substack{m_1n_1\mu_1\\m_2n_2\mu_2}}P\int_r^\infty dr'h^{m_1n_1\mu_1}(r')\frac{d}{dr'}w^{m_2n_2\mu_2}(r'),$$
$$(37)$$

where the coefficient P depends on all nine indices, and is explicitly given by

$$P = (2m+1)(2n+1) \begin{pmatrix} m_1 & m_2 & m \\ \mu_1 & \mu_2 & -\mu \end{pmatrix} \begin{pmatrix} m_1 & m_2 & m \\ 0 & 0 & 0 \end{pmatrix}$$

$$\times \begin{pmatrix} n_1 & n_2 & n \\ -\mu_1 & -\mu_2 & \mu \end{pmatrix} \begin{pmatrix} n_1 & n_2 & n \\ 0 & 0 & 0 \end{pmatrix}. \tag{38}$$

The above relation must be completed by the exact one valid for $r < \sigma$:

$$c^{mn\mu}(r) = -\delta_m \delta_n \delta_\mu - \eta^{mn\mu}(r) \quad \text{for } r < \sigma \tag{39}$$

Of course, neglecting the bridge term $b^{000}(r)$ gives the HNC equation.

The Percus-Yevick (PY) equation can also be written in terms of the direct correlation function as

$$c(1,2) = F(1,2)(1 + \eta(1,2)), \tag{40}$$

where $F(1,2) = \exp(-\beta u(1,2)) - 1$ is the Mayer function. This equation is readily expanded as

$$c^{mn\mu}(r) = F^{mn\mu}(r) + \sum_{\substack{m_1 n_1 \mu_1 \\ m_2 n_2 \mu_2}} P F^{m_1 n_1 \mu_1}(r) \eta^{m_2 n_2 \mu_2}(r), \tag{41}$$

where the coefficient P is given by Eq. (38). We show in the Appendix how the Mayer coefficients $F^{mn\mu}(r)$ can be analytically computed for the case of separable interactions. Finally, the MSA states that $c(1,2) = -\beta u(1,2)$. For the case of interactions of the form of Eq. (1), by using the addition theorem of the spherical harmonics and the relation between the Wigner elements and the spherical harmonics [25], one can resume the MSA as

$$c^{mm\mu}(r) = -(-1)^\mu \beta u_m(r) \quad \text{for } r > \sigma, \tag{42}$$

where m is restricted to the values $m = 0$ or $m = a$. The MSA for such a model has been solved analytically [11,12]. We have tested our numerical algorithm by reproducing the results for the MSA. Despite the fact that it is amenable to analytical solutions, we note that the MSA has severe drawbacks, one of which is that the embodied direct correlation function has exactly the symmetry of the *isotropic* pair interaction. For this particular reason, this theory cannot give any valuable information in the case of the antiferromagnetic Heisenberg model [21], for which it predicts no ordering transition [27]. The numerical details for the practical solution of the coupled set of three equations is given in Sec. III.

F. Infinite field limit: $B = \infty$

In this limit, one has rigorously

$$\rho(1) = \rho_N \delta(\mathbf{u} - \mathbf{n}), \tag{43}$$

where $\mathbf{n}$ is the direction of the field, along which all the particles are pointing ($\mathbf{u} = \mathbf{n}$). Using the spherical harmonics expansion of the Dirac δ function [25] with Eq. (8), one obtains $a_m = (2m+1)$ for all the expansion parameters. Using Eq. (10), this is equivalent to stating that all the order parameters S_m are unity. We can select the director orientation (or, equivalently, the field orientation) to be that of the $\mathbf{z}$ axis. Then using $R^m_{\mu 0}(\mathbf{u} \| \mathbf{z}) = \delta_{\mu 0}$ [25], we find the new expansion of the correlation functions,

$$h(r, (\mathbf{u}_1, \mathbf{u}_2) \| \mathbf{z}) = \sum_{m,n} h^{mn0}(r), \tag{44}$$

which is independent of the orientation, as expected. In particular, the pair interaction becomes, by using the equation above

$$\beta u(r, (\mathbf{u}_1, \mathbf{u}_2) \| \mathbf{z}) = u0(r) + u_a(r). \tag{45}$$

In other words, the fluid particle interaction is now purely isotropic. Needless to say, this conclusion is only valid for separable interactions. For the general case of nonseparable interactions one finds [28] that the pair interaction depends only on the angle $(\mathbf{r}, \mathbf{u})$ in the same limit.

G. Thermodynamics of the orientationally ordered fluid

Various thermodynamic properties can be written in terms of the pair and direct correlation functions. The corresponding expressions vary substantially from the isotropic fluid case, mainly due to the presence of the one-body function.

1. Excess internal energy

The excess internal energy is the canonical average of the sum of all the interactions in the system, which in our case contains a contribution from the external field, in addition to the usual pair interaction term. The general expression for the excess internal energy for the case of inhomogeneous fluids is then given by

$$\beta U^{ex} = \frac{1}{2} \int d\mathbf{1}\, d\mathbf{2} \rho(1) \rho(2) g(1,2) \beta u(1,2)$$

$$+ \int d\mathbf{1}\, \beta \phi_{\text{ext}}(1) \rho(1), \tag{46}$$

where the last term is the external field contribution. For the particular case of orientationally ordered fluids with spatial homogeneity, this expression reduces to

$$\beta U^{ex}/N = \frac{\rho_N}{2(4\pi)^2} \int d\vec{r}\, d\mathbf{u}_1 d\mathbf{u}_2 f(1) f(2) g(1,2) \beta u(1,2)$$

$$+ \int d\mathbf{u}_1 \beta \phi_{\text{ext}}(\mathbf{u}_1) f(1) \tag{47}$$

Upon expansion of the various terms involved, this can be written in a compact way as the trace of a matrix product:

$$\beta U^{ex}/N = \frac{2\pi}{\rho_N} \int_0^\infty dr\, r^2 \sum_\mu \text{Tr}[\mathbf{G}_\mu \mathbf{R}_\mu \mathbf{U}_\mu \mathbf{R}_\mu] - B S_a, \tag{48}$$

where S_a in the last term is the order parameter introduced in Eq. (10) for the model selected with the parameter a. We note that if the pair potential decays faster than $1/r^3$, then the eventual long ranged part in $g(1,2)$ due to the spontaneous ordering will not induce a divergence in the internal energy. Thus the energy will remain finite in the vicinity and below the Curie point, as expected. However, in the case of dipolar

fluids, some care must be taken in the evaluation of the long range contributions. This type of problem will be considered in a subsequent work.

2. Virial pressure

One can similarly derive a compact expression for the virial pressure which is defined generally for inhomogeneous fluids as

$$\frac{\beta P}{\rho} = 1 - \frac{1}{6\rho} \int d\mathbf{1} \, d\mathbf{2} \rho(1)\rho(2)g(1,2)r \frac{d}{dr} \beta u(1,2) \tag{49}$$

which for orientationally ordered fluids with spatial inhomogeneity reduces to

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi}{3} \rho_N \int_0^\infty dr \, r^3 \int \int d\mathbf{u}_1 d\mathbf{u}_2 f(1) f(2) g(1,2)$$

$$\times \frac{d}{dr} \beta u(1,2) \tag{50}$$

One can expand the various functions and write a compact expression also involving a trace

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi}{3\rho_N} \int_0^\infty dr \, r^3 \sum_\mu \text{Tr}[\mathbf{G}_\mu \mathbf{R}_\mu d\mathbf{U}_\mu \mathbf{R}_\mu] \tag{51}$$

where the matrix $d\mathbf{U}_\mu$ contains the expansion coefficients of the derivative of the potential $d\beta u^{mn\mu}(r)/dr$. Provided the pair potential decays faster than $1/r^3$, there are no diverging contribution to the viral pressure.

3. Compressibility

The correct expression of the compressibility for inhomogeneous fluids is given by [23]

$$\frac{\chi_T}{\chi_T^0} = 1 + \frac{1}{\langle N \rangle} \int d\mathbf{1} \, d\mathbf{2} \rho(1)\rho(2)h(1,2) \tag{52}$$

where $\chi_T^0 = 1/(\rho k_B T)$ is the compressibility of the ideal gas. For ordered fluids which are spatially homogeneous, this equation can be simplified to give

$$\frac{\chi_T}{\chi_T^0} = 1 + \frac{\rho_N}{(4\pi)^2} \int \int d\mathbf{u}_1 d\mathbf{u}_2 f(1) f(2) \tilde{h}^{(0)}(\mathbf{u}_1, \mathbf{u}_2). \tag{53}$$

By introducing the generalized structure factor for ordered fluid as the angle average of Fourier transform of the pair density $\rho^{(2)}(1,2) = \rho(1)\rho(2)g(1,2)$ [more exactly the Fourier transform of $\rho(1)\rho(2)h(1,2)$, which decays to zero], after performing the angular integrals one finds

$$\tilde{S}(k) = 1 + \frac{1}{\rho_N} \tilde{\mathbf{T}}_{00} \tag{54}$$

where the matrix $\tilde{\mathbf{T}}$ is defined as $\mathbf{T} = \mathbf{R}_0 \tilde{\mathbf{H}}_0 \mathbf{R}_0$. Then the compressibility is related to the structure factor of the ordered phase exactly by the same expression that of the isotropic phase

$$\frac{\chi_T}{\chi_T^0} = \tilde{S}(0) \tag{55}$$

We note that, as opposed to the case of isotropic fluids, where it is relatively easy to relate the compressibility to the direct correlation function, this operation is not trivial here. Hence, the expression given in Ref. [13] is incorrect. We also note that above expression is free of the divergences that appear in case of spontaneous order as it only involves $\tilde{h}^{mn0}(k=0)$ and not the $\mu=1$ expansion terms. We note that the compressibility can diverge in case of the appearance of long range order in the *isotropic* part of the pair correlation, as this can be the case near a liquid-gas critical point. In no case this divergence can be due to instabilities in the orientational order. Finally, using Eqs. (10) and (20) (namely, $R^{m00} = \rho_N S_m$), the above expression can also be written in a more straightforward way as

$$\frac{\chi_T}{\chi_T^0} = 1 + \rho_N \sum_{mn} \tilde{h}^{mn0}(0) S_m S_n \tag{56}$$

in terms of the order parameters of the one-body function. In this form the *isotropic* fluid limit is trivial and leads to the known result $\chi_T/\chi_T^0 = 1 + \rho_I \tilde{h}^{000}(0) = 1/[1 - \rho_I \tilde{c}^{000}(0)]$.

4. Magnetic susceptibility

In the presence of an external field, one can compute the response of the fluid using the general expression [13]

$$\beta \chi = \frac{1}{V} \boldsymbol{\nabla}_\mathbf{B} \otimes \beta \underline{\mathbf{M}}, \tag{57}$$

where the symbol $\otimes$ denotes a tensorial product, and where the net magnetization is given by

$$\beta \underline{\mathbf{M}} = \boldsymbol{\nabla}_\mathbf{B} \ln(Z), \tag{58}$$

with the Canonical ensemble the partition function Z given by

$$Z = \frac{1}{N! \Lambda^{3N}} \int d\mathbf{1}...d\mathbf{N} \exp(-\beta \Phi^{\text{ext}} - \beta U_N), \tag{59}$$

where βU_N is the total energy of the system and $\beta \Phi^{\text{ext}} = \Sigma_i \beta \phi(i) = -\Sigma_i \beta P_a(\mathbf{u}_i \cdot \mathbf{z})$ is the total contribution of the external field which is chosen to be in the direction of the z axis. It is clear that explicit expressions for the magnetization and susceptibility will depend on the actual form chosen for the ordering external field. It is quite straightforward to obtain the net magnetization of the fluid in term of the singlet density. For the Heisenberg model, one obtains, explicitly,

$$\beta \underline{\mathbf{M}} = \rho_N S_1 \mathbf{z}. \tag{60}$$

It is not surprising that the net magnetization of the Heisenberg model is directly related to the rank-1 order parameter S_1. Similarly, one can relate the magnetic susceptibility to the pair density, and subsequently to the pair correlation function. A straightforward calculation shows that the tensor $\beta \chi$ is diagonal. For the Heisenberg model, one obtains explicitly:

$$\beta\chi_{xx}=\beta\chi_{yy}=-\sum_{m,n}R^{m11}\widetilde{h}^{mn1}(0)R^{n11}-R^{111}, \quad (61)$$

$$\beta\chi_{zz}=\sum_{m,n}R^{m10}\widetilde{h}^{mn0}(0)R^{n10}+R^{110}. \quad (62)$$

The presence of the $\mu=1$ component of the pair correlation function in the transverse components of the susceptibility tells us immediately that these will diverge in case of spontaneous magnetization below the Curie point. These are known results from the classical ferromagnetic Heisenberg model [1]. The longitudinal part is always finite, as it involves only $\mu=0$ terms. It is interesting to examine the isotropic limit of the susceptibility (62). In this case one has $\widetilde{h}^{mn\mu}=(-)^{\mu}\widetilde{h}_m\delta_{mn}$ and $R^{111}=-R^{110}=\rho_I/3$. Therefore, all three components of the susceptibility tensor are equal, and one has $\beta\chi=(\rho_I/3)[1+(\rho_I/3)\widetilde{h}_1(0)]$, which is related to the Kerr constant [29]. This expression diverges at the limit of stability of the isotropic phase. Similar expressions can also be derived for the nematic model ($a=2$).

5. Elastic constants

The general expressions for the elastic constants of ordered fluids have been given by Poniewiersky and Stecki [30], and can be cast in a fourth-rank tensorial form

$$\beta K_{ijkl}=\frac{1}{2}\int d\mathbf{r}\,d\mathbf{u}_1 d\mathbf{u}_2 \mathbf{V_{ij}}(1,2)\mathbf{W_{kl}}(1,2) \quad (63)$$

where the two second rank tensors are given by

$$\mathbf{V}(1,2)=[i\vec{L}_1\rho(1)]\otimes[i\vec{L}_2\rho(2)],$$
$$\mathbf{W}(1,2)=c(1,2)\vec{r}\otimes\vec{r}. \quad (64)$$

Expression (63) can be greatly simplified for separable interactions. In particular, the r integration can be performed directly over the second tensor $\mathbf{W}(1,2)$, leading to the second moment of the direct correlation function, which was introduced in the small-k expansion used in Eq. (31) in the form of the matrix $\widetilde{\mathbf{C}}_1^{(2)}$ in terms of the expansion coefficients of the dcf. The integration over the angles shows that the three elastic constants $K_1=K_{xxxx}$ (splay), $K_2=K_{xxyy}$ (twist), and $K_3=K_{zzxx}$ (bend) merge into a unique constant for separable interactions:

$$\beta K=\beta K_1=\beta K_2=\beta K_3=-\frac{\rho_N^2}{3}\mathbf{A}\widetilde{\mathbf{C}}_1^{(2)}\mathbf{A}, \quad (65)$$

where $\mathbf{A}$ is the eigenvector in Eq. (18). It is interesting to relate this elastic constant to the long range decay of the pair correlation function in Eq. (34) in the case of spontaneous ordering in the absence of any external field. We note that, using Eqs. (15), (17), (11), and (13), this equation can be rewritten in term of the full pair correlation in the Fourier space as

$$\lim_{k\to 0}\widetilde{h}(k,\mathbf{u}_1,\mathbf{u}_2)=\kappa^2\frac{i\vec{L}_1\rho(1)i\vec{L}_2\rho(2)}{k^2}. \quad (66)$$

We start with the OZ equation (22) and insert in it the small-k-vector expansion of the direct correlation function up to second order,

$$\widetilde{c}(k,\mathbf{u}_1,\mathbf{u}_2)=\widetilde{c}^{(0)}(\mathbf{u}_1,\mathbf{u}_2)+k^2\widetilde{c}^{(2)}(\mathbf{u}_1,\mathbf{u}_2)+o(k^4),$$
$$(67)$$

as well as Eq. (66). Making then use of the one-body closure equation (11) with Eq. (13) to simplify the $\widetilde{h}$ contribution from the left hand side, then multiplying both sides by $i\vec{L}_2\rho(2)$, integrating over the angle $\mathbf{u}_2$ and, once again making use of the one-body closure equation, one obtains a relation involving κ^2 and the integral of the second moment of the dcf, which is identical to the expression involving the elastic constant (65). In other words, one has

$$\kappa^2=\frac{1}{\beta K}. \quad (68)$$

By construction, this relation should hold only in the zero field limit.

6. Long range behavior of the orientational correlations

In what concerns the calculation of the expansion coefficients $g^{mn\mu}(r)$ by computer simulations, it is important to point out the actually measured property is the pair density function $\rho^{(2)}(1,2)=\rho(1)\rho(2)g(1,2)$, and not the pair correlation function itself $g(1,2)$. This difference is not important in the isotropic phase, because $\rho(1)=\rho_I/(4\pi)$ is a constant, but it is crucial for the ordered phase. Using the expansion of $\rho^{(2)}(1,2)$,

$$\rho^{(2)}(1,2)=\sum_{m,n,\mu}\rho_2^{mn\mu}(r)R_\mu^m(1)R_{-\mu}^n(2), \quad (69)$$

it is easy to see that the canonical ensemble angular average $\langle R_\mu^m(1)R_{-\mu}^n(2)\rangle$ points to $\rho_2^{mn\mu}(r)$, and not to $g^{mn\mu}(r)$. Using the orthogonality of the Wigner elements, one can relate the expansion coefficients of the pair density function to the expansion coefficients of the pair distribution function $g^{mn\mu}(r)$:

$$\rho_2^{mn\mu}(r)=\sum_{m',n'}R^{m'n'\mu}g^{m'n'\mu}(r)R^{n'n\mu}. \quad (70)$$

This relation allows us to settle an issue that was not clearly stated in the past literature concerning the behavior of pair correlations at large distance. Both in the isotropic and ordered phases, the pair distribution function $g(1,2)$ goes to unity in this limit [as $\lim_{r\to\infty}g^{000}(r)=1$ and all other $g^{mn\mu}(r)$ decay to zero in the same limit]. It is the pair density function $\rho^{(2)}(1,2)$ that depends on the order parameters in this limit. Using the relation $R^{m00}=R^{0m0}=\rho_N a_m/(2m+1)=\rho_N S_m$, where S_m is the order parameter of order m [e.g., Eq. (10)], the above relation indicates that

$$\lim_{r\to\infty}\rho_2^{mn\mu}(r)=\rho_N^2 S_m S_n \delta\mu 0. \quad (71)$$

In particular, when $m=n$, one finds the often quoted limit $\lim_{r\to\infty}\rho_2^{mm0}(r)/\rho_N^2=S_m^2$. It is important to note that, as only

TABLE I. The thermodynamical properties for the ferromagnetic Heisenberg model from Monte Carlo simulations. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1 [the total excess internal energy $E/(Nk_BT)$, the compressibility factor $Z=\beta P/\rho$, and the first and second rank order parameters (S_1 and S_2, respectively)].

	$B=0$				$B=1$			
T^*	E/Nk_BT	Z	S_1	S_2	E/Nk_BT	Z	S_1	S_2
10.0	-0.015	5.561	0.071	0.043	-0.814	5.281	0.532	0.192
8.0	-0.022	5.603	0.061	0.035	-1.023	5.085	0.591	0.238
7.0	-0.052	5.591	0.114	0.035	-1.180	5.072	0.625	0.277
6.0	-0.146	5.495	0.248	0.051	-1.400	4.907	0.666	0.324
5.0	-0.511	5.089	0.492	0.158	-1.774	4.397	0.726	0.399
4.0	-1.169	4.354	0.682	0.345	-2.251	3.879	0.773	0.473
3.0	-2.069	3.293	0.789	0.499	-3.106	2.917	0.831	0.577
2.0	-3.744	1.287	0.869	0.659	-4.774	1.236	0.887	0.700

the $\mu=1$ expansion coefficients have a long range critical decay, the above mentioned asymptotic limit is attained exponentially. These results are well known for lattice systems [1], and it is interesting to find their off-lattice analog here, in term of the standard liquid state theory. Finally, one can compute the "two-point" correlation function often quoted in lattice theories of the Heisenberg model, which is related to the canonical angular average of the dot product $\mathbf{u}_1 \cdot \mathbf{u}_2$. One then finds

$$\langle \mathbf{u}_1 \cdot \mathbf{u}_2 \rangle = \sum_{mn} R^{m11} g^{mn1}(r) R^{n11} + \sum_{mn} R^{m10} g^{mn0}(r) R^{n10}. \tag{72}$$

The large-r limit of this function is simply $\lim_{r \to \infty} \langle \mathbf{u}_1 \cdot \mathbf{u}_2 \rangle = \rho_N^2 S_1^2$. It is particularly interesting to examine the large-r behavior of this function in the case of spontaneous ordering with zero field. It is then clear that, as the $\mu=1$ component are all long ranged, this asymptotic limit is reached algebraically in $1/r$. These findings are in perfect agreement with that known from lattice theories [1].

III. RESULTS

The two model interactions of the type (1) studied in the present work are explicitly given by

$$\beta u(1,2) = \beta u_{HS}(r) - \alpha \frac{\exp(-\kappa(r-\sigma))}{r} P_a(\mathbf{u}_1 \cdot \mathbf{u}_2), \tag{73}$$

where $\beta u_{HS}(r)$ is the usual hard sphere interaction [$\beta u_{HS}(r) = \infty$ if $r < \sigma$ and $\beta u_{HS}(r) = 0$ if $r > \sigma$] and $a=1$ in the anisotropic part of the interaction selects the Heisenberg model and $a=2$ selects the nematic model. In the present work, we consider only the ferromagnetic Heisenberg model with $\alpha > 0$. The antiferromagnetic model can equally be solved by the present method [27]. In all the results reported here $\kappa = \sigma$ and $\alpha = 1$. The external field is chosen to be model dependent in order to follow the symmetry of the particles interaction:

$$\beta \phi_{ext}(1) = -B P_a(\mathbf{u}_1 \cdot \mathbf{u}_2) \tag{74}$$

We have solved numerically the three coupled equations consisting of the one-body equations (15)–(17), the OZ equation (25), together with one of the closure equations, Eq. (37) for RHNC or HNC, Eq. (41) for PY, and finally Eq. (42) for MSA, and obtained the expansion coefficients a_m, $c^{mn\mu}$ and $h^{mn\mu}$ for several thermodynamical points in the $\{\rho^*, T^*\}$ space, where the reduced density ρ^* is defined as $\rho^* = \rho \sigma^3$ and the reduced temperature is $T^* = k_B T/\alpha$. The hard sphere bridge function [31] was used in the RHNC closure. The RHNC equation contains, in addition, a self consistent determination of the effective density contained in the bridge term [26]. We have neglected this additional step here, and taken the effective density to be the current density ρ_N. The RHNC results are virtually identical in both approaches in the isotropic phase. This might not be the case in the ordered phase. Once these functions are known, one can determine some of the thermodynamical properties of the ordered fluid. We have compared our results with computer simulations.

A. Monte Carlo simulations

Monte Carlo simulations have been performed, with $N = 500$ particles, by using standard NVT ensemble techniques [32,18]. Interactions (73) have been truncated at half box size and appropriate long range corrections have been applied for the internal energy and the virial pressure [18]. The order parameters of the system have been monitored both in the presence of the field and without it. The finite size effects do not allow a clearcut evidence of the phase transition when the system is spontaneously ordered. Each simulation of a state point was conducted with an equilibration run of about 1–2 million steps followed by a production run of about 2–5 million steps. Long runs were needed to obtain high order correlation functions which are particularly noisy in the isotropic phase, mainly due to their low magnitude.

We would like to stress again that only the expansion coefficients $\rho_2^{mn\mu}(r)$ of the pair density function $\rho^{(2)}(1,2)$ are measured in the computer simulations. The thermodynamical properties for both models measured at fixed density $\rho^*=0.7$ are reported in Tables I and III.

B. Numerical solution of the integral equations

The Fourier transform is at the heart of the numerical solution of the integral equations. Fortunately, for the case of

TABLE II. (a) The thermodynamical properties for the ferromagnetic Heisenberg model from RHNC theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1 (in addition to the quantities defined for Table I, are listed the isothermal compressibility χ_T/χ_0 and the elastic constant K_{elast}). (b) The thermodynamical properties for the ferromagnetic Heisenberg model from HNC theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Tables I and II(a). (c) The thermodynamical properties for the ferromagnetic Heisenberg model from the PY theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Tables I and II(a). (d) The thermodynamical properties for the ferromagnetic Heisenberg model from the MSA theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Tables I and II(a).

			$B=0$						$B=1$			
T^*	E/Nk_BT	Z	χ_T/χ_0	S_1	S_2	K_{elast}	E/Nk_BT	Z	χ_T/χ_0	S_1	S_2	K_{elast}
						(a)						
10.0	−0.015	5.699	0.0571	0	0	0	−0.852	5.482	0.0603	0.542	0.204	1.007
8.0	−0.027	5.694	0.0572	0	0	0	−1.080	5.371	0.0621	0.612	0.261	1.564
7.0	−0.042	5.684	0.0574	0	0	0	−1.256	5.277	0.0637	0.651	0.304	2.023
6.3	−0.074	5.655	0.0623	0.063	0.002	0.021	-	-	-	-	-	-
6.2	−0.122	5.629	0.0673	0.188	0.018	0.202	-	-	-	-	-	-
6.0	−0.212	5.578	0.0678	0.303	0.052	0.545	−1.498	5.140	0.0659	0.695	0.357	2.691
5.0	−0.681	5.271	0.0707	0.565	0.211	2.264	−1.841	4.944	0.0693	0.743	0.424	3.690
4.0	−1.277	4.894	0.0757	0.706	0.369	4.503	−2.354	4.659	0.0749	0.793	0.507	5.257
3.0	−2.171	4.436	0.0867	0.805	0.527	8.019	−3.198	4.258	0.0864	0.844	0.605	7.945
2.0	−3.877	4.152	0.1244	0.883	0.689	15.325	−4.870	3.967	0.1245	0.896	0.721	13.46
						(b)						
10.0	−0.015	6.669	0.0740	0	0	0	−0.854	6.464	0.0794	0.549	0.204	1.008
8.0	−0.027	6.661	0.0742	0	0	0	−1.083	6.364	0.0829	0.612	0.262	1.565
7.0	−0.042	6.649	0.0746	0	0	0	−1.159	6.277	0.0857	0.651	0.304	2.025
6.3	−0.076	6.621	0.0846	0.072	0.002	0.027	-	-	-	-	-	-
6.2	−0.126	6.595	0.0923	0.194	0.019	0.214	-	-	-	-	-	-
6.1	−0.171	6.573	0.0928	0.258	0.036	0.387	-	-	-	-	-	-
6.0	−0.216	6.553	0.0932	0.305	0.053	0.553	−1.502	6.154	0.0897	0.695	0.358	2.693
5.0	−0.684	6.285	0.0986	0.565	0.212	2.269	−1.846	5.982	0.0960	0.743	0.425	3.692
4.0	−1.282	5.964	0.1086	0.706	0.369	4.506	−2.360	5.745	0.1070	0.793	0.507	5.259
3.0	−2.179	5.625	0.1327	0.805	0.527	8.014	−3.207	5.454	0.1320	0.844	0.605	7.947
2.0	−3.894	5.850	0.2456	0.883	0.690	15.256	−5.517	5.662	0.2462	0.897	0.723	13.488
						(c)						
10.0	−0.014	5.307	0.0539	0	0	0	−0.842	5.025	0.0579	0.545	0.200	0.988
8.0	−0.024	5.301	0.0539	0	0	0	−1.066	4.866	0.0604	0.606	0.256	1.529
7.0	−0.035	5.293	0.0539	0	0	0	−1.238	4.734	0.0625	0.645	0.297	1.979
6.0	−0.064	5.268	0.0558	0.034	0.000	0.006	−1.478	4.545	0.0656	0.689	0.350	2.638
5.7	−0.162	5.169	0.0793	0.239	0.035	0.333	-	-	-	-	-	
5.5	−0.259	5.080	0.0771	0.333	0.069	0.670	-	-	-	-	-	
5.0	−0.525	4.820	0.0765	0.488	0.158	1.593	−1.820	4.256	0.0702	0.737	0.417	3.636
4.0	−1.178	4.182	0.0815	0.677	0.338	3.892	−2.336	3.806	0.0782	0.789	0.501	5.231
3.0	−2.142	3.256	0.0968	0.799	0.521	7.463	−3.193	3.043	0.0950	0.843	0.604	8.051
2.0	−3.949	1.598	0.1618	0.891	0.709	15.033	−4.906	1.536	0.1604	0.899	0.729	14.219
						(d)						
10.0	−0.009	5.309	0.0537	0	0	0	−0.787	5.039	0.0563	0.518	0.179	0.882
8.0	−0.017	5.302	0.0537	0	0	0	−0.991	4.889	0.0578	0.576	0.228	1.361
7.0	−0.024	5.296	0.0537	0	0	0	−1.151	4.762	0.0592	0.614	0.264	1.767
6.0	−0.038	5.282	0.0537	0	0	0	−1.378	4.573	0.0611	0.659	0.313	2.370
5.5	−0.055	5.264	0.0542	0.024	0.000	0.003	-	-	-	-	-	-
5.4	−0.067	5.252	0.0622	0.067	0.003	0.027	-	-	-	-	-	-
5.3	−0.105	5.214	0.0736	0.156	0.014	0.150	-	-	-	-	-	-
5.2	−0.155	5.162	0.0729	0.227	0.031	0.324	-	-	-	-	-	-
5.0	−0.267	5.049	0.0713	0.328	0.067	0.705	−1.798	4.284	0.0640	0.709	0.377	3.298
4.0	−0.938	4.357	0.0723	0.602	0.252	2.959	−2.212	3.821	0.0687	0.764	0.459	4.787
3.0	−1.895	3.367	0.0802	0.751	0.438	6.152	−3.048	3.017	0.0782	0.822	0.561	7.376
2.0	−3.623	1.597	0.1089	0.854	0.625	11.899	−4.705	1.386	0.1076	0.880	0.684	12.686

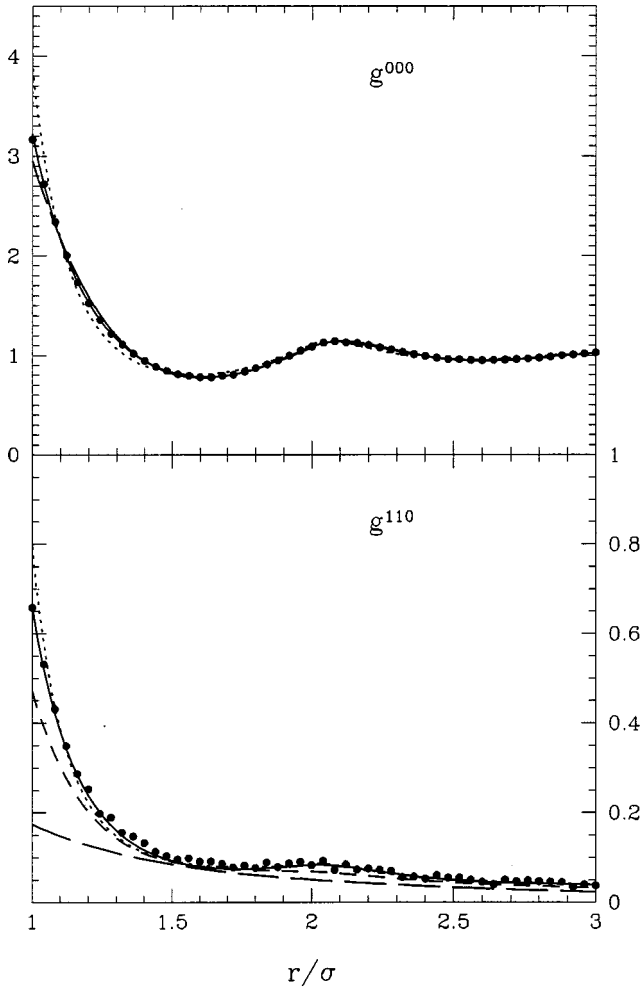FIG. 1. Some expansion coefficients $gmnl(r)$ of the pair correlation function for the Heisenberg model in the isotropic phase at $\rho^*=0.7$ and $T^*=7$. The symbols are as follows: Monte Carlo simulations (dots), RHNC (solid line), HNC (dotted line), PY (dashed line), and MSA (dash-dotted line).

separable interactions only zeroth-order Fourier-Hankel transforms are required. All expansion coefficients have been computed over 1024 points with a mesh of $\Delta r = 0.02$. This ensured an accuracy of at least $\frac{1}{1000}$ in the OZ relations (26) at $k=0$. The rotational invariant expansion have been performed up to $n_{\max}=4$ for the Heisenberg model [a total of 35 unique $(mn\mu)$ combinations], and $n_{\max}=6$ for the nematic model (a total of 30 unique projections). These choices ensure that the convergence of the expansion of the various correlation functions is not affected by the $n_{\max}$ truncation. The symmetry of the nematic model interaction allows only even m and n values to be taken into account. The numerical evaluation of the one-body closure was done by using 1600 points representation of the Legendre polynomials with a standard Simpson type quadrature to evaluate the various integrals. We found it quite important to ensure that the sum rules (18) and (21) are verified to a great accuracy (relative difference less than $\frac{1}{1000}$). Another important point concerns the solution method used in the zero-field case. The long range $1/r$ divergence that appears in all the $\mu=1$ expansion terms $g^{mn\mu}(r)$ must be carefully handled during the iteration procedure. We have used the method generally applied in the

numerical solution of coulombic fluid. The diverging $k=0$ contribution of $\tilde{g}^{mn\mu}(k)$ was removed analytically using Eqs. (34) and (66) and the corresponding long range tail in $g^{mn\mu}(r)$ was added after the numerical inverse Fourier transform. The accuracy of this method is limited by the accuracy in the solution of the one-body function [quite simply because the effective ''charge'' κW_m in Eq. (34) is known to the same accuracy as that used in the one-body equation]. For this reason it was not possible to obtain converging solution for exactly zero field values [$B=0$ in Eq. (74)]. However, we found that the structural and thermodynamical properties of the fluid were insensitive to values of smaller that $B<\frac{1}{500}$. This was particularly tested in the case of the MSA for which an analytical solution is available [11,12], particularly at exactly zero field. The numerical implementation of the code allows one to pass directly from an isotropic solution to an ordered one by slightly lowering the temperature for example. The embodied one-body equation bifurcates to the ordered solution, and the iterative procedure stabilizes this solution as being numerically viable. It was thus possible to cover, at a fixed density, a temperature range above and below the Curie point. The results reported in the Tables II and IV are for fixed density $\rho^*=0.7$.

The actual numerical solution is very similar to that used in the solution of integral equations for the isotropic phase. For each state point, one starts the iterative cycle with a guess of the initial dcf (usually taken to be the solution of the closest state point that was obtained previously). The corresponding coefficients $c^{mn\mu}(r)$ are first Fourier transformed. One solves the one-body equations (15)–(17) within an inner interactive cycle, and the order parameters thus determined are used to build the $\mathbf{R}_\mu$ matrices. Then the OZ equation (25) is solved matricially in order to obtain the $\tilde{\eta}^{mn\mu}(k)$ terms. At this point we take care of the eventual $k=0$ singularity in the case of spontaneous ordering by removing analytically any $1/k^2$ singularity in the $\mu=1$ components. This is actually done by determining a test function of the form $\gamma \exp(-\xi k^2)/k^2$ whose inverse Fourier transform is exactly known. γ is determined accurately [see Eqs. (34), (67), and (69)], and ξ is determined by fitting the small-k behavior of $\tilde{h}^{mn1}$. Then the $\tilde{\eta}^{mn\mu}(k)$ terms are inverse Fourier transformed and the new $c^{mn\mu}(r)$ are determined by the closure relation. The iterative cycle is continued with new dcf which can be obtained by a Picard type mixing of the old and new values obtained numerically. Convergence is attained when the difference between two iterates is smaller than 10^{-6}. At each iteration steps, the numerical accuracy of the sum rules (18) and (21), as well that of the OZ at $k=0$ is checked to be at least about $\frac{1}{10\,000}$.

C. Ferromagnetic Heisenberg fluid

The lattice version of the Heisenberg model is a standard text book problem. The continuum version has attracted a recent interest among liquid state theorists, and this model has been investigated by computer simulations [18,21,33], by integral equation theories in the isotropic phase [18,21,11,12] and the ordered phase [13], and by mean field theories [19]. The (ρ,T) phase diagram of such a model has been investigated for interaction (71) with $a=1$ (for $\alpha=1$ and $\kappa=\sigma$), both with and without an ordering field. In the
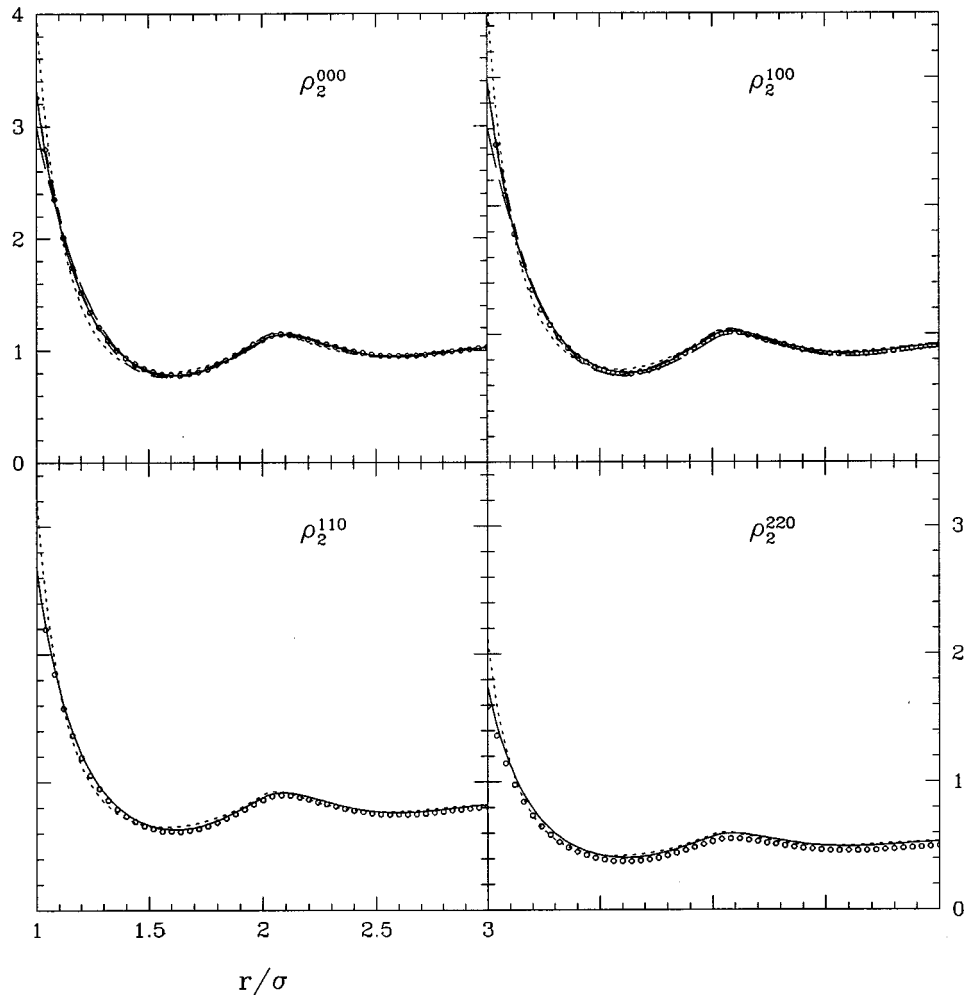
FIG. 2. Some expansion coefficients $\rho_2^{mnl}(r)/\rho^2$ of the normalized pair density function for the Heisenberg model at $\rho^* = 0.7$ and $T^* = 2$ for field value $B^* = 1$. The symbols are as in Fig. 1.

case $B = 0$, this phase diagram has a Curie line below which the fluid is spontaneously ordered. In Table I we report the thermodynamical properties measured from computer simulations at the density $\rho^* = 0.7$ as the temperature is varied, for $B = 0$ and 1. The integral equations results for the same density are reported in four tables, Table II(a) for the RHNC theory, Table II(b) for the HNC theory, Table II(c) for the Percus-Yevick approximation, and finally Table II(d) for the MSA. For this density, the Curie temperature estimate from the RHNC theory is $T_C^* = 6.4$, in perfect agreement with the result obtained by the RHNC theory in the isotropic phase [18]. When $B = 0$, the spontaneous ordering transition is expected to be second order [3]. In view of Tables I and II, the order parameter variations are indeed continuous. As far as the simulations are concerned, it is difficult to distinguish between first and second order transitions by looking at the order parameter variation. Finite size effects tend to smooth the transition. The integral equations are free from this bias. The exact value of the transition (the Curie point) is also difficult to determine. A direct comparison with the results reported in Ref. [13], for the pair interaction truncated at $r_C = 2.5\sigma$, shows that the Curie temperature is quite different when the cutoff is applied. The numerical solution of all the integral equations shows that in the ordered phase, the one-body function is mostly Maier-Saupe like: $\rho(1)$

$\equiv \rho_N/(4\pi)\exp((B + B_1)\mathbf{u}_1 \cdot \mathbf{n})/Z$, with $B_1 = W_1$ the first term in expansion (16). W_2 is always more than one order magnitude smaller, and higher order W_m nearly decreases at the same rate. As an example, for $\rho^* = 0.7$ and $T^* = 2$, the following values are obtained at zero field within the PY approximation: $W_1 = 7.852$, $W_2 = 0.497$, $W_3 = 0.046$, and $W_4 = 0.0043$ It then seems quite reasonable to retain only the leading W_1 term, although the difference of 10% due to the inclusion of the second term is already appreciable in the one-body density function, especially near $\theta = 0$, where the distribution is very peaked. Thus the Maier-Saupe like approximation (including only the W_1 term in one-body density function), as used in Refs. [13,14], is an additional approximation which is justified in the case of separable potentials, but is not a general rule to follow. As far as the thermodynamical properties are concerned, it is the PY and MSA theories that seem to be the most accurate when order is present. In the isotropic phase the RHNC theory seems more accurate; this result is also in agreement with previous findings [18,13]. The pair distribution function expansion coefficients for the isotropic phase (at $T^* = 7$) are shown in Fig. 1, where all integral equation results are compared with simulation results. In this case the components measured by the simulations (pair density) are identical to those of the
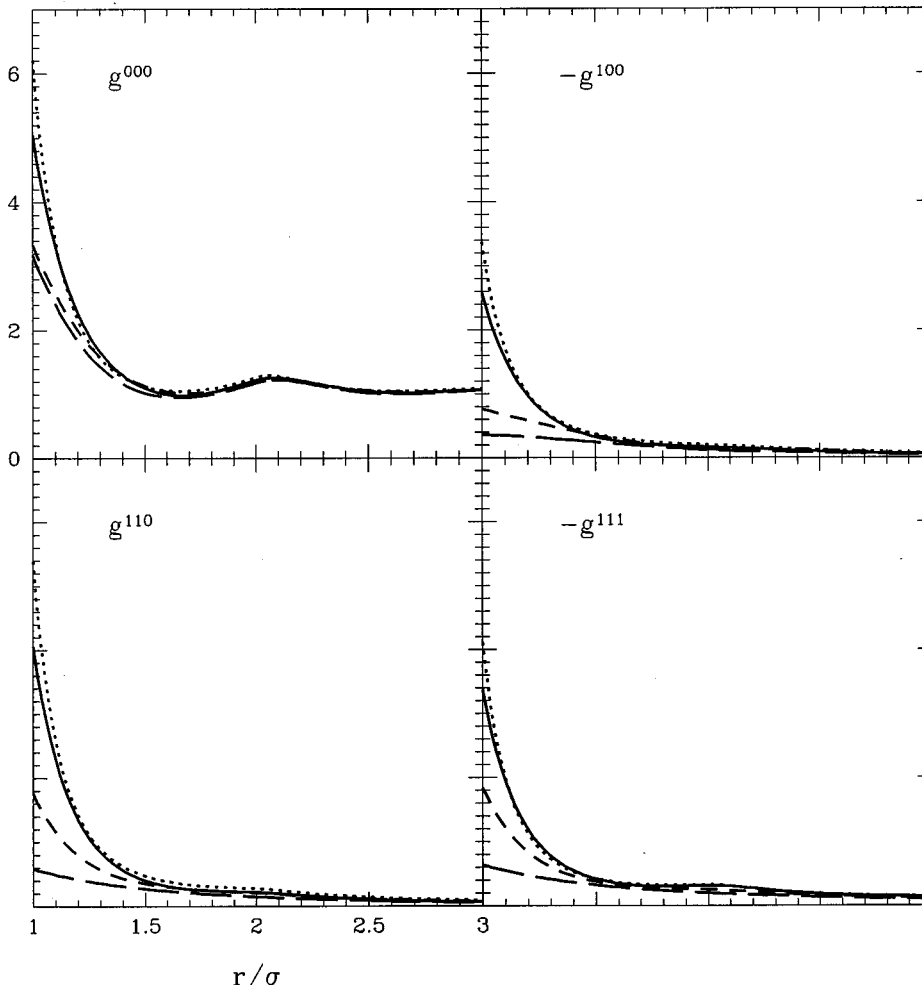
FIG. 3. Some expansion coefficients $g^{mnl}(r)$ of the pair correlation function for the Heisenberg model at $\rho^*=0.7$ and $T^*=2$ for field value $B^*=1$. The symbols are as follows: RHNC (solid line), HNC (dotted line), PY (dashed line), and MSA (dash-dotted line).

pair distribution (to a factor ρ_I^2). The RHNC and PY results seems to be the most accurate as far as the component $g^{000}(r)$ is concerned, while the HNC results seem to be the worst. For the anisotropic component $g^{110}(r)$, again it is the RHNC theory which give the most accurate result, whereas the MSA theory gives the worst results (some of the projections are rigorously zero). The HNC and PY theories bracket the RHNC results, as they do for the hard sphere fluid case. In Fig. 2, we compare the expansion coefficients of the normalized pair density function $\rho_2^{mn\mu}(r)/\rho_N^2$ for an ordered system ($B^*=1$ and $T^*=2$). All integral equation results are quite similar. This is largely imputed to the fact that all the expansion terms with $\mu=0$ are weighted by the term $g^{000}(r)$ which has the largest magnitude, and which all integral equations predict quite reasonably. This situation might be different with another type of interaction where the anisotropic part might be predominant [α larger in Eq. (71), or for dipolar fluids for example]. A closer look reveals that both RHNC and PY results are quite accurate. In Fig. 3, we compare now the components of the pair correlation function $g^{mn\mu}(r)$ between the four integral equations. It is now possible to discriminate letter between the theories. We find that the RHNC results generally interpolate between the HNC and PY results, though they are generally closer to the HNC values. In view of this, one might expect that a Rogers-Young type approach might be more suitable. Indeed, the results obtained in Ref. [13] with a Zerah-Hansen closure are quite good. It is also clear that the MSA theory, which is the

most linearized, also gives the worst structural results. However, a cancellation of the various contributions in Eq. (71) leads to a pair density function that is almost identical for all theories. A similar conclusion is also reached for the struc-
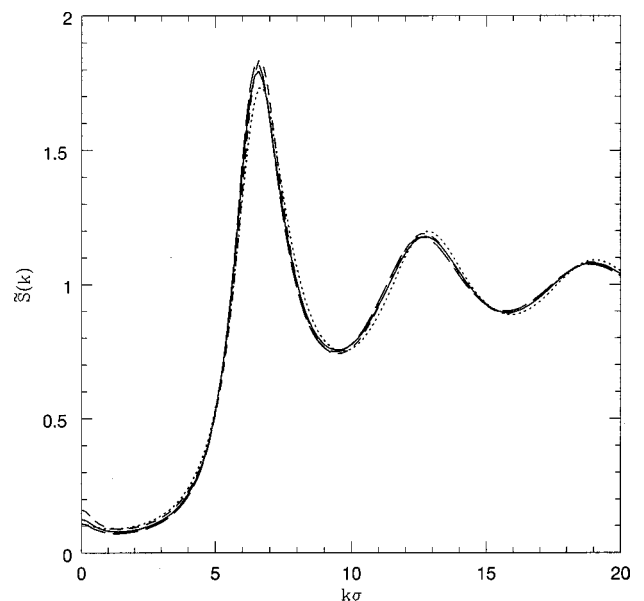

FIG. 4. The structure factor $S(k)$ for the Heisenberg model at $\rho^*=0.7$ and $T^*=2$ for the field value $B^*=1$. The symbols are as in Fig. 3.
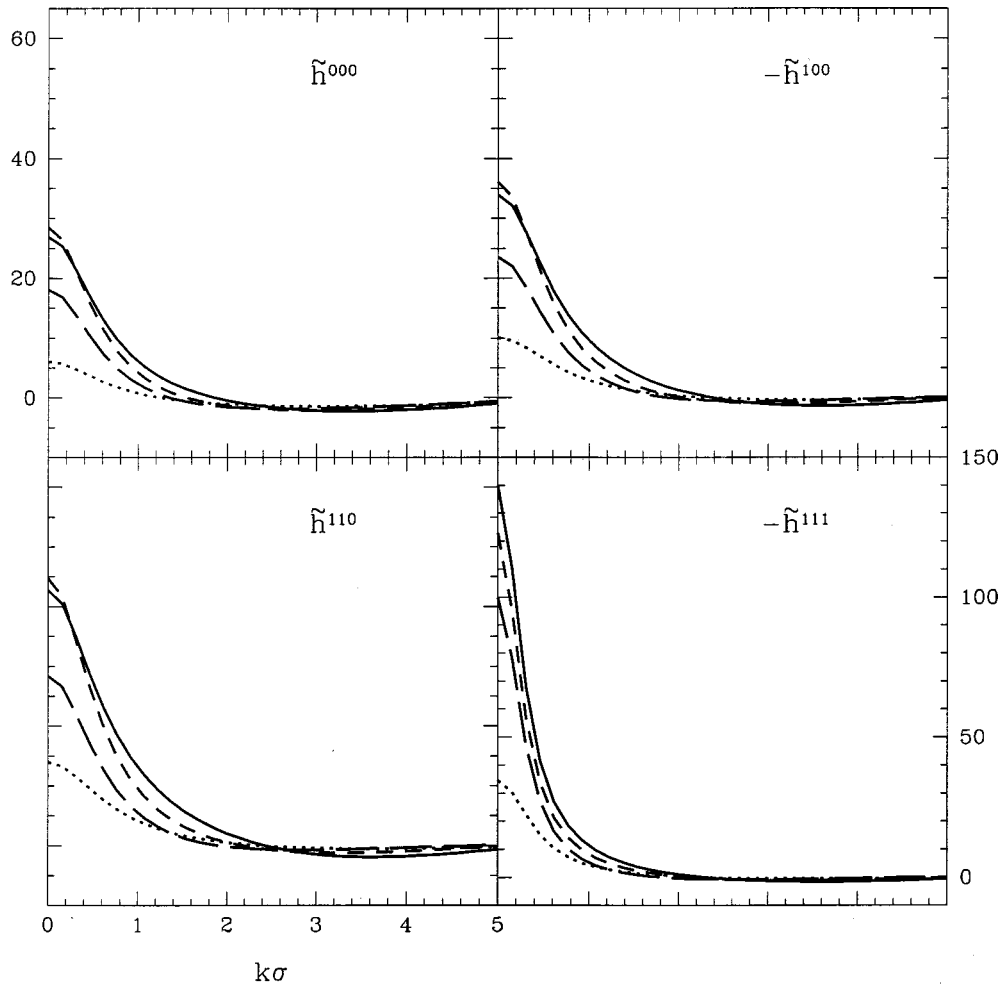
FIG. 5. The one-body density function $f(x)$ for the Heisenberg model at $\rho^*=0.7$ and $T^*=2$ for field value $B^*=0$. The symbols are as in Fig. 3.-

ture factor shown in Fig. 4, which is also a combination of the elementary constituents of the pair correlation function (54), while the latter factors, shown in Fig. 5, are quite different between the four theories. The large $k=0$ value of the $\widetilde{h}^{111}$ component must be noted. This is the diverging component in the zero-field ordered case. Finally, it must be noted that the components g^{110} and $-g^{111}$ are identical in the isotropic case, and become quite different in the ordered case. More generally, one can think of the components $g^{mn\mu}$ as a ''degeneracy'' of the main (isotropic) component g^{mm0}, when an external field is applied. The one-body density function $f(x=\cos(\theta))=\rho(1)/\rho_N$ for $\rho^*=0.7$ and $T^*=2$ at zero field is compared in Fig. 6 between the four theories. All theories reflect the strong ordering by a distribution very peaked around $\theta=0$. The RHNC and HNC curves are almost identical, indicating that the isotropic bridge diagram does not contribute much to the ordering of the particles. This trend is already visible in the pair distribution function. The PY theory predicts a marginally narrower distribution that the RHNC/HNC theory, whereas the MSA theory predicts a broader distribution, probably again reflecting the linearization embodied in this theory. The comparison of the order parameters S_1 and S_2 between the four theories and that calculated by Monte Carlo simulations (Tables I and II) show that the RHNC theory is in somewhat better agreement
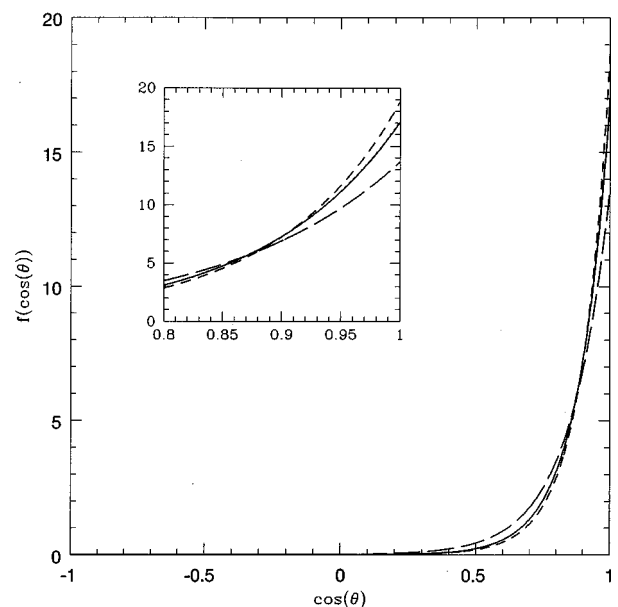

FIG. 6. The expansion coefficient $\widetilde{g}^{mn0}(k)$ of the Fourier transform of the pair correlation function for the Heisenberg model at $\rho^*=0.7$ and $T^*=2$ for field value $B^*=1$ (upper panel). The symbols are as in Fig. 3.

TABLE III. The thermodynamical properties for the nematic model from Monte Carlo simulations. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Table I.

	$B=0$			$B=1$		
T^*	E/Nk_BT	Z	S_2	E/Nk_BT	Z	S_2
10.0	-0.0585	5.7013	0.04	-0.4869	5.4926	0.3563
8.0	-0.0124	5.601	0.051	-0.6500	5.3624	0.4225
7.0	-0.0165	5.6206	0.0420	-0.7873	5.3582	0.4714
6.0	-0.0276	5.6086	0.0613	-1.0999	5.0477	0.5647
5.0	-0.0481	5.4636	0.0875	-1.5637	4.6754	0.6720
4.0	-0.0946	5.5640	0.1247	-2.0171	4.1394	0.7205
3.8	-0.8171	4.5666	0.5507	-	-	-
3.6	-0.9740	4.5139	0.5848	-	-	-
3.4	-1.3429	4.1331	0.6721	-	-	-
3.2	-1.5615	3.7883	0.7051	-	-	-
3.0	-1.8752	3.4275	0.7500	-3.0616	3.0189	0.8253
2.0	-3.6815	1.4757	0.8624	-4.7215	1.3260	0.8808

with the computer simulation results. Finally, the last column in Tables II shows the variation of the elastic constant with the temperature. We note the rapid increase with the lowering of the temperature, reflecting that larger elasticity of the fluid at low temperatures.

D. Nematic model

This model corresponds to $a=2$ in Eq. (73) (we again keep $\alpha=1$ and $\kappa=\sigma$). This type of model was used by Luckhurst and Romano [34] in order to investigate by computer simulations a nematic model which was not Maier-Saupe like (with a short range orientational interaction). In the absence of field, this model has an isotropic-nematic (I-N) transition which differs from that of the Heisenberg model as it is a first order transition. This is a well known result, and can be obtained by a symmetry consideration in the Landau–de Gennes Hamiltonian in its mean field version [3,4]. This first order transition is visible from Tables IV at the finite jump of the second rank order parameter S_2, which goes from 0 to approximately 0.4 at the transition temperature. It is harder to localize from the computer simulations in Table III due to finite size effects. From what was seen in Sec. II F, it must be noted that this fluid has exactly the same Yukawa liquid-gas phase diagram as the previous Heisenberg model when $B=\infty$. This model offers several analogies with the Heisenberg model. In particular, at $B=0$, it has the equivalent of the Curie line in the (ρ,T) phase diagram, below which the fluid is in a nematic liquid crystalline phase. At $\rho^*=0.7$ the RHNC estimate of the isotropic-nematic transition temperature is $T^*_{IN}\approx4.35$. We did not investigate the finite field liquid-gas coexistence in the present work, and report only the temperature dependence of the thermodynamical properties for fixed density $\rho^*=0.7$, both at $B=1$ and $B=0$. The computer simulation results are reported in Table III, and the integral equation results in Tables IV. The general conclusion is quite similar to that of the previous paragraph as concerns the various integral equations. In Fig. 7. some components of the pair density are compared between simulation and theoretical results, for the cases T^*

$=2$ and $B=1$. Once again we see that the RHNC and PY results are the closest to that of the simulations, and the discrimination between the four approaches is harder than when comparing the components of the pair distribution function. Finally, in Fig. 8. The long range behavior of the $\mu=1$ component $g^{221}(r)$ when crossing the transition temperature T_{IN}. There is a clear shift in the large r values below $T^*_{IN}\approx4.35$. The first order nature of the transition is seen most clearly when examining the same variation in terms of the pair density $\rho_2^{220}(r)$. We see that the isotropic components are now almost invisible in the upper part of Fig. 8, whereas the jump in the order parameter is visible for temperatures lower than T^*_{IN}. These large variations of the orientational components are not reflected in the isotropic component $g^{000}(r)$, which is quite similar across temperature variations. The order parameter S_2, computed by Monte Carlo simulations (Table III), is generally in good agreement with that calculated by all four theories (Tables IV), both at zero fields $B=0$ and 1. The one-body density function is now symmetric with respect to $\theta=0$, reflecting the symmetry of the pair interaction and that of the ordering field, which is the major difference than the Heisenberg model (which is a vectorial model). The elastic constants (Tables IV) indicate that the fluid is more elastic at lower temperatures, and the temperature dependence is quite similar to that observed in the case of the Heisenberg model.

IV. CONCLUSION

A general framework for solving integral equations, for fluids orientationally ordered by an external field, is outlined in the present work for the particular case of the separable interactions. The major difference with nonseparable interactions is that the degrees of freedom introduced by the coupling between the intermolecular axis and the orientations of the particles are totally absent from the former case. In that sense, this type of interaction is suitable to study the continuum analog of lattice models. Thus, by developing a liquid state approach to this class of problem, one can expect some feedback from the lattice model physics, which is generally richer, and often with exact results [1]. In particular, the critical behavior of such models is well classified, and there are considerable problems obtaining similar results, even for simple liquids. Despite many recent investigations [18,13,19], this is still an open field of investigation.

In the present work, the basic relations between the one-body closure relations and the Ornstein-Zernike equation are presented, and it is shown that two of the three available closures are readily embodied in the OZ equation in the $k=0$ limit, and in that sense they can be considered as sum rules for ordered systems. The status of the one-body closure derived from the BGY hierarchy is less clear, although numerical evidence from the integral equations [13] indicate that it gives quite good results.

From a technical point of view, it is shown here that the integral equation techniques are no more difficult to solve for orientationally ordered systems than they are for isotropic ones. The present work shows that it is possible to write all the equations and expressions for thermodynamical properties in a compact matrix form. In particular, the spontaneous ordering that can occur in the absence of an external field is

TABLE IV. The thermodynamical properties for the nematic model from RHNC theory. Results for $\rho^*=0.7$ and for field values B^* $=0$ and 1. The notations are as in Tables I and II(a). (b) The thermodynamical properties for the nematic model from HNC theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Tables I and II(a). (c) The thermodynamical properties for the nematic model from the PY theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Tables I and II(a). (d) The thermodynamical properties for the nematic model from the MSA theory. Results for $\rho^*=0.7$ and for field values $B^*=0$ and 1. The notations are as in Tables I and II(a).

|	$B=0$					$B=1$				
T^*	E/Nk_BT	Z	χ_T/χ_0	S_2	K_{elast}	E/Nk_BT	Z	χ_T/χ_0	S_2	K_{elast}
					(a)					
10.0	−0.007	5.715	0.0569	0	0	−0.548	5.593	0.0588	0.391	1.534
8.0	−0.013	5.710	0.0570	0	0	−0.740	5.507	0.0607	0.465	2.714
7.0	−0.017	5.706	0.0570	0	0	−0.917	5.421	0.0625	0.523	3.916
6.0	−0.025	5.699	0.0571	0	0	−1.191	5.278	0.0655	0.596	5.943
5.0	−0.043	5.687	0.0572	0	0	−1.600	5.049	0.0695	0.679	9.256
4.4	−0.069	5.665	0.0577	0	0	-	-	-	-	-
4.34	−0.416	5.458	0.1288	0.391	4.004	-	-	-	-	-
4.32	−0.459	5.429	0.1106	0.414	4.485	-	-	-	-	-
4.3	−0.494	5.404	0.1027	0.432	4.905	-	-	-	-	-
4.2	0.645	5.302	0.0898	0.498	6.602	-	-	-	-	-
4.1	−0.771	5.217	0.0859	0.544	8.027	-	-	-	-	-
4.0	−0.889	5.141	0.0841	0.581	9.342	−2.194	4.701	0.0755	0.759	14.480
3.0	−2.029	4.395	0.0887	0.777	22.245	−3.105	4.189	0.0869	0.829	23.054
2.0	−3.805	3.666	0.1254	0.874	43.030	−4.814	3.558	0.1248	0.890	39.839
					(b)					
10.0	−0.008	6.675	0.0739	0	0	−0.549	6.572	0.0770	0.392	1.540
8.0	−0.013	6.671	0.0740	0	0	−0.743	6.494	0.0802	0.466	2.725
7.0	−0.018	6.667	0.0740	0	0	−0.921	6.415	0.0835	0.524	3.932
6.0	−0.026	6.662	0.0741	0	0	−1.196	6.287	0.0887	0.597	5.964
5.0	−0.044	6.649	0.0744	0	0	−1.606	6.082	0.0963	0.679	9.279
4.5	−0.063	6.633	0.0749	0	0	-	-	-	-	-
4.45	−0.066	6.629	0.0751	0	0	-	-	-	-	-
4.42	−0.069	0.626	0.0752	0	0	-	-	-	-	-
4.32	−0.467	6.427	0.1935	0.417	4.552	-	-	-	-	-
4.3	−0.503	6.404	0.1709	0.436	4.969	-	-	-	-	-
4.2	−0.651	6.315	0.1391	0.500	6.648	-	-	-	-	-
4.1	−0.778	6.242	0.1300	0.546	8.070	-	-	-	-	-
4.0	−0.895	6.174	0.1263	0.582	9.375	−2.201	5.777	0.1080	0.760	14.502
3.0	−2.037	5.542	0.1374	0.777	22.301	−3.115	5.362	0.1329	0.830	23.071
2.0	−3.820	5.200	0.2493	0.874	43.108	−4.831	5.113	0.2470	0.891	39.858
					(c)					
10.0	−0.007	5.312	0.0538	0	0	−0.541	5.163	0.0562	0.387	1.503
8.0	−0.012	5.309	0.0538	0	0	−0.726	5.050	0.0585	0.458	2.633
7.0	−0.016	5.307	0.0538	0	0	−0.896	4.942	0.0608	0.514	3.781
6.0	−0.024	5.303	0.0539	0	0	−1.161	4.751	0.0647	0.586	5.735
5.0	−0.038	5.294	0.0539	0	0	−1.565	4.433	0.0704	0.669	8.997
4.0	−0.075	5.263	0.0542	0	0	−2.164	3.924	0.0788	0.753	14.297
3.8	−0.094	5.245	0.0549	0.013	0.005	-	-	-	-	-
3.6	−1.143	4.212	0.1020	0.631	11.352	-	-	-	-	-
3.0	−1.962	3.401	0.1025	0.764	20.435	−3.096	3.083	0.0958	0.828	23.301
2.0	−3.892	1.551	0.1621	0.884	44.413	−4.857	1.478	0.1601	0.894	42.152
					(d)					
10.0	−0.005	5.313	0.0537	0	0	−0.495	5.179	0.0551	0.362	1.291
8.0	−0.008	5.310	0.0537	0	0	−0.645	5.086	0.0563	0.421	2.181
7.0	−0.011	5.307	0.0537	0	0	−0.785	4.992	0.0576	0.468	3.088
6.0	−0.016	5.303	0.0537	0	0	−1.013	4.825	0.0599	0.535	4.692
5.0	−0.025	5.295	0.0537	0	0	−1.387	4.526	0.0637	0.620	7.567
4.0	−0.045	5.276	0.0537	0	0	−1.978	4.013	0.0693	0.713	12.521
3.5	−0.070	5.251	0.0537	0.004	0.000	-	-	-	-	-
3.4	−0.874	4.432	0.1090	0.532	8.157	-	-	-	-	-
3.2	−1.223	4.070	0.0935	0.617	11.680	-	-	-	-	-
3.0	−1.549	3.733	0.0901	0.676	14.963	−2.910	3.140	0.0789	0.800	20.963
2.0	−3.516	1.709	0.1113	0.841	34.637	−4.636	1.451	0.1080	0.873	37.451
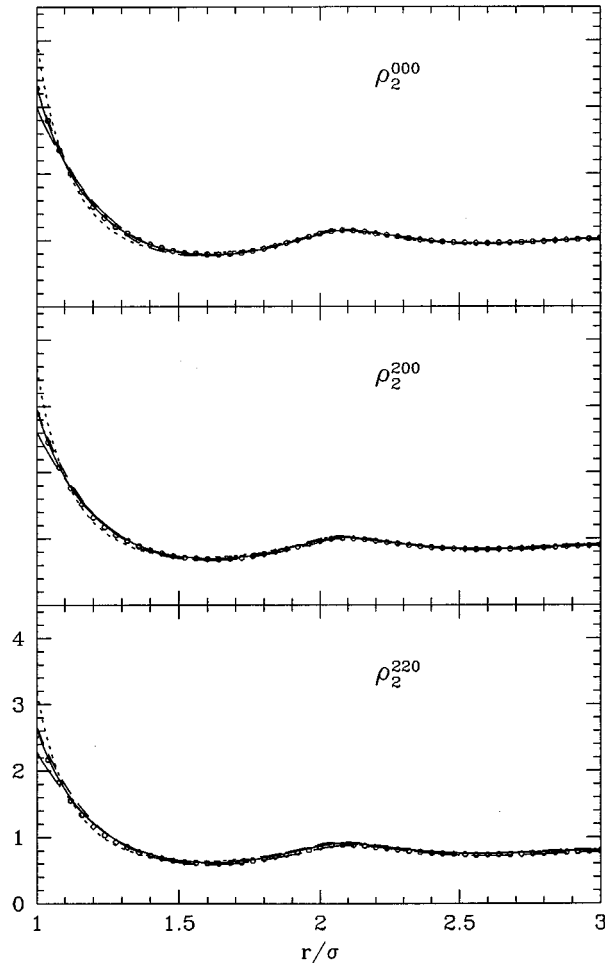
FIG. 7. Some expansion coefficients $\rho_2^{mnl}(r)/\rho^2$ of the normalized pair density function for the Nematic model at $\rho^*=0.7$ and $T^*=2$ for field value $B^*=1$. The symbols are as in Fig. 1.
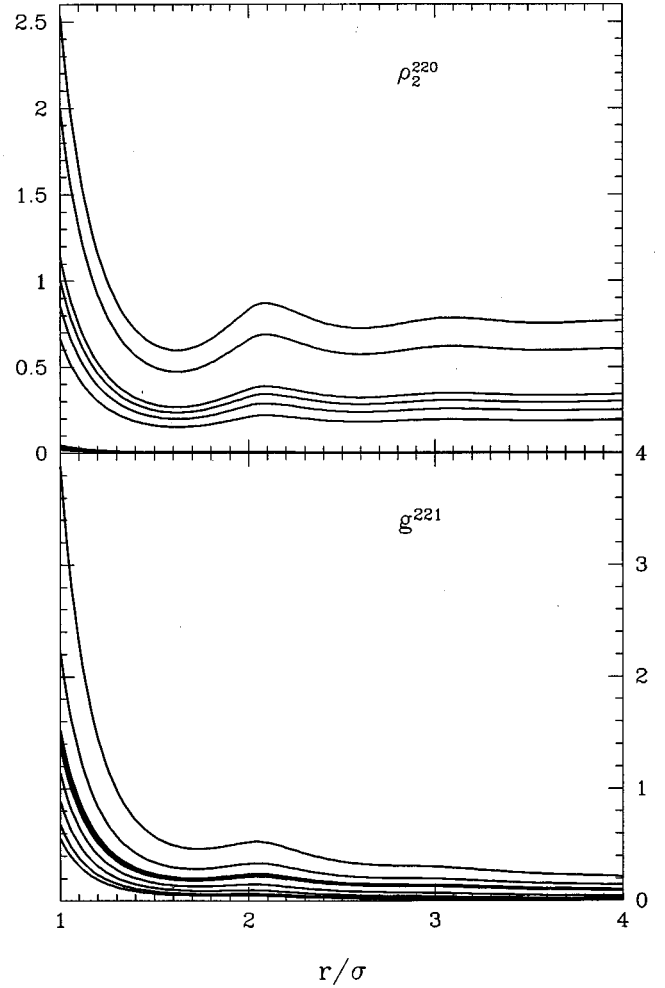

FIG. 8. The expansion coefficient of the normalized pair density $\rho_2^{220}(r)/\rho^2$ (upper panel) and the pair correlation function $g^{221}(r)$ (lower panel) for the nematic model at $\rho^*=0.7$ and for field value $B^*=0$. From top to bottom, the temperatures are $T^*=2$, 3, 4, 4.1, 4.2, 4.3, 4.4, 5, 6, and 7.

obtained by all the integral equations closures investigated in this work, for sufficiently low temperatures. This systematization opens the way for investigating several interesting cases such as ferrofluids.

Nonseparable interactions are more realistic, and also they involve more rotational invariants in the expansion of the correlation functions, precisely due the additional orientational couplings that must be taken into account. However, the situation is quite similar to that presented here, mainly in what concerns the relation between the OZ and the one-body closure equation [28]. The numerical effort is more involved, but not more than that involved in the solution of the integral equations for hard convex bodies, for example. This step is quite necessary, however, if one aims at exploring more complex phases such as smectic phases, for which only density functional theories are able to tackle this problem in a nonphenomenological approach.

APPENDIX: INVARIANT EXPANSION OF THE MAYER FUNCTION FOR SEPARABLE INTERACTIONS

In order to solve the Percus-Yevick approximation (41), it is necessary to obtain the expansion coefficients of the Mayer function $F_M^{mn\mu}(r)$. For the case of a separable potential of the form of Eq. (1), we show how these coefficients can be obtained analytically by using a recurrence method outlined below. We basically need to expand the function

$$f(r,x)=\exp(-\gamma(r)P_a(x))-1 \qquad (A1)$$

on a basis set of Legendre polynomials. The direct Taylor expansion of the exponential leads to products of Legendre polynomials of different orders. The double product can be expanded as [25]

$$P_{m_1}(x)P_{m_2}(x)=\sum_{m_3}(2m_3+1)\begin{pmatrix} m_1 & m_2 & m_3 \\ 0 & 0 & 0 \end{pmatrix}^2 P_{m_3}(x).$$
$$(A2)$$

Using this relation, one can successively expand products of higher orders. Thus, the general expansion of Eq. (A1) reads now

$$f(r,x) = -1 + \sum_n \frac{(-)^n}{n!} \gamma(r)^n \sum_{m_n} \alpha_{m_n} P_{m_n}(x), \quad \text{(A3)}$$

where

$$\alpha_{m_n} = \sum_{m_2,\dots,m_{n-1}} (2m_2+1)\cdots(2m_n+1)$$

$$\times \begin{pmatrix} a & a & m_2 \\ 0 & 0 & 0 \end{pmatrix}^2 \cdots \begin{pmatrix} a & m_{n-1} & m_n \\ 0 & 0 & 0 \end{pmatrix}^2 \quad \text{(A4)}$$

with the selection rule $|a-m_{n-1}| \le m_n \le a+m_{n-1}$ obeyed for each index m_n. In practice, the above expansion can be computed numerically very efficiently, and the expansion converges quite rapidly (it is sufficient to retain about $m_n = 10$ to obtain a precision of $\frac{1}{10\,000}$ near $r=\sigma$).

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