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1995 J. Phys.: Condens. Matter 7 8839

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A model for homogeneous and inhomogeneous hard molecular fluids: ellipsoidal fluids

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Received 7 July 1995, in final form 4 September 1995

Abstract. The thermodynamic and structural properties of a fluid of hard axially symmetric ellipsoids are studied on the basis of two approximations, namely that (a) the orientations of the molecules can be restricted to a discrete number of directions and (b) the direct correlation function can be written as a superposition of three geometrical functions with weights which depend on the density of the fluid. The variational principle of Anderson and Chandler is used to determine the weights. The equation of state of the fluid is derived for a range of values of the ratio of axes (elongation) from 0.35 to 5.0. For comparison new simulations have been performed on the same systems. Except at the greatest elongation, the theoretical pressure agrees very well with the simulated pressure of the restricted orientation model as well as with that of a fluid of freely rotating ellipsoids. When the elongation is 5.0, the pressure of the fluid of freely rotating ellipsoids lies somewhat above the pressure of the restricted orientation model, although for this model the theory and simulation are still in accord. Thus far the theory has not revealed a transition to a nematic state although there is some evidence from simulation that when the elongation is 5.0, the isotropic state of the restricted orientation model is not stable.

The direct correlation function of the homogeneous phase is used in conjunction with a density functional in order to investigate the density profile of the fluid confined to a slit. Except in the neighbourhood of a wall there is very good agreement between the theory and simulation. The discrepancy near the wall is to be expected from the simple form of functional used. Overall it appears that the approximation developed is adequate for describing the thermodynamic properties of the homogeneous and inhomogeneous isotropic state, but that it needs some improvement for studying the properties of the nematic state.

1. Introduction

In previous papers [1–4], the authors and collaborators have studied theoretically the structure of inhomogeneous fluids of hard molecules of various shapes including ellipsoids and cylinders. We have used a model in which the orientations of the molecules are restricted to certain directions. Qualitatively, at least for bulk densities which are not too high and for shapes which are not too anisotropic, reasonable agreement was found between the theoretical predictions and the results of computer simulation of the same systems. In addition, many of the significant features of fluids of freely rotating molecules were reproduced.

However, at high densities and for very anisotropic molecules there were serious discrepancies between the theoretical predictions and the results of simulation. For example, according to the simplest version of the theory, a fluid of disc-shaped cylinders with a ratio of length to diameter of 0.25 would make a transition to a nematic state at a packing fraction of 0.18 and a further transition to a spatially-ordered state at a packing fraction of 0.202 [5].

A simulation by one of us [6] for the same model at a packing fraction of 0.238 revealed no such phase transitions and no long-range order.

The theory as applied hitherto involved one extreme simplification not required by the basic theory but introduced in order to implement and simplify the calculations. The remarkable thing is that even with this simplification the theory gave satisfactory results over a wide range of parameters; it is not surprising to find that ultimately it breaks down. In this paper we consider the effect of improving upon this original simple approximation. A preliminary account of part of this work has appeared in [7].

As with many other density functional theories of the structure of inhomogeneous fluids both simple and molecular (see [8] for a review of many such theories), the present theory requires at the outset a knowledge of the direct correlation function (dcf) of the homogeneous fluid. For many simple fluids, especially the much explored hard sphere fluid, there does exist a good and tractable approximation for this function, namely the PY solution. This partly explains the success of such theories. For fluids of molecules of non-spherical shape no such approximations exist. *Ab initio* calculations of the structure of some homogeneous molecular fluids do exist [9, 10] but the results are expressed only in a numerical form not well suited as an input to calculations of the structure of the inhomogeneous fluid.

An alternative approach follows the seminal work of Onsager [11] on the isotropic-nematic transition and is well adapted to the study of very anisotropic molecules. It is based upon a virial expansion in which the higher-order terms are approximated using the PY results for hard spheres and re-summed. The free energy is, in this way, expressed in terms of the first few virial coefficients [12–15]. The validity of the approximation is not clear although reasonable agreement with simulation is obtained for very oblate or prolate ellipsoids.

In a wide-ranging study of the thermodynamics of homogeneous fluids of hard anisotropic molecules, Rosenfeld and collaborators [16, 17] have motivated and introduced approximations based on the idea that the direct correlation function of the fluid in the core region could be written as a superposition of geometrical functions. In what they call the strong-coupling limit (high density for hard molecules), they showed that it is necessary to include the overlap volume of two molecules [17]. In [16] Rosenfeld also introduced a scaled field theory in which the direct correlation function was written as a superposition of scaled geometrical functions of two molecules. The weights of these basis functions were chosen according to a conformal equation of state based on that for mixtures of hard spheres.

Our own approach is similar in spirit to that of Rosenfeld and is also based on a direct correlation function which is written as a superposition of scaled geometrical functions of two molecules. In our earlier work [1–5], the main concern was to find a simple analytic form of direct correlation function which could be used in a density functional from which to derive the structure of an inhomogeneous system. The simplifying approximation was made that the direct correlation function for two axially-symmetric molecules oriented with their axes aligned in the directions α, β could be represented by the form,

$$c_{\alpha\beta}(\mathbf{r}) = A f_{\alpha\beta}(\mathbf{r}) + B F_{\alpha\beta}(\mathbf{r}) \quad (1)$$

where $f_{\alpha\beta}(\mathbf{r})$ and $F_{\alpha\beta}(\mathbf{r})$ are, respectively, the Mayer function and the overlapping volume of the two molecules when their vector separation is \mathbf{r} . In fact the first term is essential in the low density limit while the second is, for reasons already given by Rosenfeld, necessary in the high density one. Equation (1) interpolates simply between these limits. The form given by equation (1) ensures that the direct correlation function satisfies the PY closure relation, namely that it vanishes when the molecules do not overlap. The variables A and

B were parameters chosen to ensure that the dcf satisfies two relations also satisfied by the PY solution of the problem. These conditions lead to two algebraic equations for A and B which are easily solved. The functions $f_{\alpha\beta}(\mathbf{r})$ and $F_{\alpha\beta}(\mathbf{r})$ are purely geometrical; the parameters A and B depend upon the density.

The discrepancy between this theory and simulation referred to above could be traced to the fact the direct correlation function of equation (1) did not properly describe the equation of state of the homogeneous fluid. *Ipso facto*, it could not properly describe the structure of the inhomogeneous one. Apart from this the form of equation (1) for the direct correlation function does not reproduce the PY approximation even for the hard sphere fluid. This is a deficiency than can be remedied by adding a third geometrical function to the form (1) [18].

In this paper we study the consequences of adding such a term on the properties of both homogeneous and inhomogeneous hard ellipsoidal (HE) fluids. We further extend the generality of the *ansatz* by allowing the coefficients of the geometric functions to depend on orientation. Thus we choose the dcf to be of the form,

$$c_{\alpha\beta}(\mathbf{r}) = A_{\alpha\beta} f_{\alpha\beta}(\mathbf{r}) + B_{\alpha\beta} F_{\alpha\beta}(\mathbf{r}) + D_{\alpha\beta} S_{\alpha\beta}(\mathbf{r}) \quad (2)$$

To define the direct correlation function completely we need to specify the function $S_{\alpha\beta}(\mathbf{r})$ and to provide a satisfactory method for choosing the parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$, $D_{\alpha\beta}$.

In choosing the function $S_{\alpha\beta}(\mathbf{r})$, we have been guided by a number of considerations. The success of Rosenfeld's scaled field theory [16] suggests that a set of geometrical basic functions derived from the dimensions of overlapping ellipsoids should be suitable. The overlapping volume is already a member of such a set. A suitable measure of the area of overlap is another. In addition we should like the approximate dcf to satisfy the PY closure relation. This requires that

$$S_{\alpha\beta}(\mathbf{r}) = 0 \quad (3)$$

when the two ellipsoids do not overlap. We also require that the dcf given by equation (2) should become the PY approximation in the limit that the ellipsoids become spheres. Finally, in order to keep the theory as simple as possible, the tractability of the resulting expressions is also a consideration. These thoughts have led us to choose $S_{\alpha\beta}(\mathbf{r})$ by re-scaling the dimensions of the ellipsoids by a factor t and looking at the change in overlapping volume as t tends to unity. Explicitly,

$$S_{\alpha\beta}(\mathbf{r}) = \lim_{t \rightarrow 1} \partial [t^3 F_{\alpha\beta}(\mathbf{r}/t)] / \partial t \quad (4)$$

Because $F_{\alpha\beta}(\mathbf{r})$ is zero when two ellipsoids do not overlap, $S_{\alpha\beta}(\mathbf{r})$ also possesses this property, i.e. $c_{\alpha\beta}(\mathbf{r})$ as given by equation (2) satisfies the PY closure relation. In addition, the PY result for hard spheres is of the form (2). In fact for hard spheres, the expression (2) is a cubic polynomial in r (without a quadratic term) as is the PY solution. Since both are sums of three linearly-independent terms, the three constants A , B and D can be chosen uniquely to make them identical.

To determine the parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$, $D_{\alpha\beta}$, in general, we use a straightforward generalization of a variational principle due originally to Anderson and Chandler [19] which is applicable to the present case. This principle has already been extended and exploited by Rosenfeld and collaborators [17, 20] in studies of fluids of hard molecules with distributed charges. However, explicit calculations exist only in cases where the cores are spherical or conformal with spherical (e.g. hard parallel ellipsoids). The present calculations include perpendicular ellipsoids and most of the complexity of the computation stem from this fact (see section 4.1.).

If the *ansatz* (2) were of the form of an exact solution of the PY equations, the variational principle would ensure that the pair distribution function, $g_{\alpha\beta}(\mathbf{r})$, would be zero when the molecules overlap. In the case of spheres, the form (2), as is explained above, is exact and the variational principle does lead to the PY solution. Once the dcf has been obtained, the equation of state of the fluid can be derived from either the virial or compressibility routes. The direct correlation function can, as originally planned, then be used as an input to a theory from which the structure of the fluid in external potentials and when subject to constraints can be derived.

While the ideas presented in this introduction could be applied quite generally the cost in both computer time and memory would be formidable. In order to reduce this they have so far been applied to the restricted orientation model (ROM) in the form in which it was introduced in [1]. This means that the molecules have been permitted to orient in a discrete number of directions. In practice for ellipsoids, the directions chosen were those with the axes of symmetry of the ellipsoids parallel to one of the co-ordinate axes. Since ellipsoids also have a centre of symmetry, in this model they can orient in only three distinct directions. The variables α and β in equation (2) can therefore each take only the three values 1, 2 and 3 corresponding to alignment parallel to the x -, y -, and z -axes, respectively. Further, from the symmetry of the ellipsoids it follows that only two of the functions $F_{\alpha\beta}(\mathbf{r})$ are independent, say $F_{11}(\mathbf{r})$, $F_{12}(\mathbf{r})$, referring to ellipsoids with parallel and perpendicular axes. The remaining functions of the set can be obtained from these by appropriate permutations of the co-ordinates. The other sets of functions $f_{\alpha\beta}(\mathbf{r})$, $S_{\alpha\beta}(\mathbf{r})$ as well as $c_{\alpha\beta}(\mathbf{r})$ possess the same symmetry. It follows, too, that the parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$ and $D_{\alpha\beta}$, have only six independent values namely,

$$A_{\alpha\alpha} = A_{\parallel} \quad A_{\alpha\beta} = A_{\perp} \quad \alpha \neq \beta, \quad (5)$$

with similar definitions for B_{\parallel} , B_{\perp} , D_{\parallel} , D_{\perp} .

These six parameters have been determined by means of the variational principle for a range of densities or packing fractions, and the resultant direct correlation function is then used to derive both the equation of state of the homogeneous fluid and the structure of the fluid confined between planar walls. The results have then been compared with those of simulation. As simulation results do not exist for the ROM over the range of parameters used, we have generated appropriate ones ourselves. In addition, to assess how well the ROM represents realistic systems, we have compared our results for homogeneous systems with those of other workers for the more realistic case of freely rotating molecules.

We have also used the theory to search for an isotropic–nematic transition, but over the range of parameters so far investigated no such transition has appeared. Nevertheless, for reasons given in section 5, we believe that for sufficiently anisotropic ellipsoids such a transition will appear. It is the case that in the simulations of the ROM with ellipsoids with elongations of 5.0 evidence for the transition has been found. However for the most anisotropic molecules, as we discuss below, it takes a long time for stable equilibrium to be achieved and for one to establish unequivocally the existence of a transition.

2. The basic functions and the pressure

The mathematical expressions for the basic functions $f_{\alpha\beta}(\mathbf{r})$ and $F_{\alpha\beta}(\mathbf{r})$ for ellipsoids have already been given in [3]. However, as we shall need to refer to them frequently we repeat them here for convenience. If $2b$ is the length of the axis of symmetry and $2a$ the length

of the other axes, then

$$f_{33}(r) = -\theta \left(1 - \frac{x^2 + y^2}{4a^2} - \frac{z^2}{4b^2} \right) \quad f_{13}(r) = -\theta(1 - f(x, y, z, u)) \quad (6)$$

where

$$f(x, y, z, u) = \frac{(ax)^2}{(a^2 + ub^2)^2} + \frac{y^2}{a^2(1+u)^2} + \frac{(bz)^2}{(b^2 + ua^2)^2} \quad (7)$$

and u is a function of x, y and z defined implicitly by

$$g(x, y, z, u) = \frac{(ubx)^2}{(a^2 + ub^2)^2} + \frac{(uy)^2}{a^2(1+u)^2} + \frac{(uaz)^2}{(b^2 + ua^2)^2} = 1. \quad (8)$$

The surface defined by

$$f(x, y, z, u) = 1 \quad (9)$$

is convex, axially symmetric about the y -axis and meets the x -, y - and z -axes at distances from the origin of $a + b, 2a, a + b$ respectively. This is the surface of the excluded volume of two perpendicular ellipsoids.

The two independent overlapping volumes are

$$F_{33}(r) = \int d^3r' \theta \left(1 - \frac{x'^2 + y'^2}{a^2} - \frac{z'^2}{b^2} \right) \theta \left(1 - \frac{(x-x')^2 + (y-y')^2}{a^2} - \frac{(z-z')^2}{b^2} \right) \quad (10)$$

and

$$F_{13}(r) = \int d^3r' \theta \left(1 - \frac{z'^2 + y'^2}{a^2} - \frac{x'^2}{b^2} \right) \theta \left(1 - \frac{(x-x')^2 + (y-y')^2}{a^2} - \frac{(z-z')^2}{b^2} \right). \quad (11)$$

The remaining functions, $S_{\alpha\beta}(r)$, can be obtained from these by differentiation.

For the variational principle used in the following section, we also require the Fourier transforms of these functions. Those for the overlap functions and the derived functions can be obtained by convolution. If a Fourier transform is defined by

$$\tilde{\psi}(k) = \int dr \psi(r) \exp(ik \cdot r) \quad (12)$$

then

$$\tilde{F}_{\alpha\beta}(k) = (2\pi)^{-3} \tilde{D}_\alpha(k) \tilde{D}_\beta(k) \quad (13)$$

where

$$\tilde{D}_3(k) = \int dr \theta \left(1 - \frac{x^2 + y^2}{a^2} - \frac{z^2}{b^2} \right) \exp(ik \cdot r) = -\frac{4\pi a^2 b}{K} \frac{d}{dK} \left(\frac{\sin K}{K} \right) \quad (14)$$

$$K = (ak_x, ak_y, bk_z). \quad (15)$$

Similarly,

$$\tilde{f}_{33}(k) = \frac{4\pi a^2 b}{K} \frac{d}{dK} \left(\frac{\sin 2K}{K} \right). \quad (16)$$

The Fourier transform of the perpendicular Mayer function is given by

$$\tilde{f}_{31}(k) = - \int dr \exp(ik \cdot r) \quad (17)$$

where the integral is taken over the excluded volume defined by

$$f(x, y, z, u) = g(x, y, z, u) < 1 \quad (18)$$

and the functions f and g are defined by equation (6) and (7). In addition we require u to satisfy

$$a/b < u < b/a \quad \text{if } a < b \quad b/a < u < a/b \quad \text{if } a > b. \quad (19)$$

It is possible to integrate equation (17) over one variable, say, y , in a straightforward way. If at the same time we collect together the contributions from the negative and positive values of x and z , we find that

$$\tilde{f}_{31}(k) = -(8/k_y) \int_0^{a+b} dx \int_0^{z_M} dz \cos(k_x x) \cos(k_z z) \sin(k_y y(x, z)). \quad (20)$$

Here $y(x, z)$ lies on the surface of the excluded volume and is given by equations (7) and (8). The function $z_M(x)$ is the maximum value of z for a given value of x and is determined from

$$y(x, z_M) = 0. \quad (21)$$

To find the function $y(x, z)$ explicitly, y can be eliminated between equations (6) and (7) to yield

$$\frac{1}{u^2} - 1 = (b^2 - a^2) \left[\frac{x^2}{(a^2 + ub^2)^2} - \frac{z^2}{(b^2 + ua^2)^2} \right]. \quad (22)$$

This equation determines u as a function of x and z . When the result is substituted into equations (6) or (7), it provides y as a function of x and z . Note that there is a symmetry

$$\tilde{f}_{31}(k_x, k_y, k_z) = \tilde{f}_{31}(k_z, k_y, k_x) \quad (23)$$

a property which we exploited in performing the integral.

Finally, it is not difficult to show from equation (3) that, for any component of the third basic function,

$$\tilde{S}(k) = \lim_{t \rightarrow 1} \{\partial [t^6 \tilde{F}(kt)] / \partial t\}. \quad (24)$$

Once the parameters $A_{\alpha\beta}$, $B_{\alpha\beta}$, $D_{\alpha\beta}$ have been determined, the direct correlation function is known and it is possible to derive the equation of state of the homogeneous fluid. As is well known there are two standard equations, the compressibility and the virial equations, from which the pressure can be derived. With the exact direct correlation function the final result is the same whichever route is chosen. However, an approximate direct correlation function, even the PY one, usually leads to different answers. The discrepancy is a measure of the accuracy of the approximation. We therefore derive both equations for the present case.

As is shown in [3], the compressibility equation for our approximation is

$$\beta \frac{dP_c}{d\rho} = 1 - \frac{\rho_B}{9} \sum_{\alpha, \beta} \tilde{c}_{\alpha\beta}^-(0) = 1 - \frac{\rho_B}{3} [\tilde{c}_{\parallel}(0) + 2\tilde{c}_{\perp}(0)] \quad (25)$$

where ρ_B is the bulk density of the fluid and

$$\beta = 1/kT.$$

The usual derivation of the virial pressure [21] leads to

$$\beta P_V = \rho_B + \frac{\rho_B^2}{18} \sum_{\alpha, \beta} \int d\mathbf{r} z \frac{\partial}{\partial z} [f_{\alpha\beta}(r)] c_{\alpha\beta}(r). \quad (26)$$

Note that the derivative of the Mayer function is non-zero only at the surface of the excluded volume. Hence, only the values of the direct correlation function on this surface contribute.

Now, of the basic functions, only the Mayer functions are non-zero on the surface of the excluded volume and these are constant and equal to -1 on this surface. Hence the direct correlation functions can be taken outside the integrals and the remainder integrated explicitly by parts. The result is [3]

$$\beta P_V = \rho_B - \frac{\rho_B^2}{6} [D_{11} \tilde{f}_{11}(0) + 2D_{13} \tilde{f}_{13}(0)]. \quad (27)$$

Equations (25) and (27) are used to obtain the equations of state discussed in section 5.1.

3. The variation principle

We seek a variational principle which in some sense leads to the best approximation possible for a direct correlation function of the form of equation (2). Such a principle is a straightforward generalization of that due originally to Anderson and Chandler [19] and has been established by Rosenfeld [20] and used by him and co-workers [18, 20] for more general mean spherical approximations, for which

$$c_{\alpha\beta}(\mathbf{r}) = c_{\alpha\beta i}(\mathbf{r}) + c_{\alpha\beta o}(\mathbf{r}) \quad (28)$$

where $c_{\alpha\beta i}(\mathbf{r})$ is zero outside the excluded volume $V_{\alpha\beta}$ and $c_{\alpha\beta o}(\mathbf{r})$ is zero inside and known outside; the problem is to obtain the best approximation for $c_{\alpha\beta i}(\mathbf{r})$. Now the exact pair distribution function $g_{\alpha\beta}(\mathbf{r})$ should be zero inside $V_{\alpha\beta}$ and the Anderson and Chandler function is minimized when this condition is satisfied. In the present instance this function is

$$I = \frac{\rho_B^2}{2N_0^2} \sum_{\alpha\beta} \int d\mathbf{r} c_{\alpha\beta}(\mathbf{r}) - \frac{1}{2(2\pi)^3} \int d\mathbf{k} \text{Tr}[q(\mathbf{k})] - \frac{1}{2(2\pi)^3} \int d\mathbf{k} \ln \text{Det}[1 - q(\mathbf{k})] \quad (29)$$

where

$$q_{\alpha\beta}(\mathbf{k}) = \rho_B \tilde{c}_{\alpha\beta}(\mathbf{k}) / N_0 = (\rho_B / N_0) \int d\mathbf{r} c_{\alpha\beta}(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (30)$$

N_0 is the number of independent directions, 3 in the present case, and $q(\mathbf{k})$ is the $N_0 \times N_0$ square matrix with elements $q_{\alpha\beta}(\mathbf{k})$.

For the properties of the homogeneous fluid the programme then is to substitute equation (2) for $c_{\alpha\beta s}(\mathbf{r})$ in the expression (29) for I and then to minimize the resulting function I with respect to the 6 parameters $A_{\parallel}, A_{\perp}, B_{\parallel}, B_{\perp}, D_{\parallel}, D_{\perp}$. The results are discussed in section 5.

4. Numerical and computational details

4.1. Numerical methods

To abbreviate the notation and to allow for generalizations, we write the direct correlation function in the form,

$$c_{\alpha\beta}(\mathbf{r}) = \sum_{i=1}^p A_{\alpha\beta}^{(i)} H_{\alpha\beta}^{(i)}(\mathbf{r}) \quad (31)$$

where $A_{\alpha\beta}^{(i)}$ and $H_{\alpha\beta}^{(i)}(\mathbf{r})$ are, respectively, the parameters and the basic functions which constitute the approximation for $c_{\alpha\beta}(\mathbf{r})$. Then the parameters are the solutions of the equations,

$$\frac{\partial I}{\partial A_{\alpha\beta}^{(i)}} = 0 \quad \forall i, \alpha, \beta. \quad (32)$$

For I defined by equation (29) and the direct correlation function defined by equation (31), this equation becomes

$$\tilde{H}_{\alpha\beta}^{(i)}(0) + \frac{1}{(2\pi)^3} \int d\mathbf{k} \tilde{H}_{\alpha\beta}^{(i)}(\mathbf{k}) \tilde{G}_{\beta\alpha}(\mathbf{k}) = 0 \quad (33)$$

where

$$\tilde{G}(\mathbf{k}) = [1 - \tilde{q}(\mathbf{k})]^{-1} \quad (34)$$

Since the integral in equation (33) can decay slowly as $k \rightarrow \infty$ and most integrations have to be performed numerically, it is helpful to expand the last term and rewrite equation (33) as

$$\tilde{H}_{\alpha\beta}^{(i)}(0) + \int d\mathbf{r} H_{\alpha\beta}^{(i)}(\mathbf{r}) q_{\beta\alpha}(\mathbf{r}) + \frac{1}{(2\pi)^3} \int d\mathbf{k} \tilde{H}_{\alpha\beta}^{(i)}(\mathbf{k}) [\tilde{q}^2(\mathbf{k}) \tilde{G}(\mathbf{k})]_{\beta\alpha} = 0 \quad (35)$$

The first integrand in equation (35) is a superposition of products of the basic functions, $H_{\alpha\beta}^{(i)}(\mathbf{r})$, which are non-zero in the same region of space. Since the molecules are hard, when at least one of the functions is a Mayer function, the corresponding integration can be carried out analytically. In the remaining cases the integrals can be evaluated in k -space using conventional quadrature methods.

The third term in equation (35) had to be evaluated in k -space. The greatest difficulties were encountered in the evaluation and use of the perpendicular Mayer function, $\tilde{f}_{31}(\mathbf{k})$. In fact, in the evaluation of this Mayer function we resorted to a number of different techniques, but the one we found most effective and accurate is that given in section 2.

The integrals in equation (35) all represent geometrical properties which are independent of the fluid density. Once they have been determined, equation (35) can be solved for the six parameters $A_{\alpha\beta}^{(i)}$ for any given bulk density. In practice, the equations were solved by a Newton-Raphson method.

4.2. Simulation

To provide a test of the approximation, various hard ellipsoidal fluids were simulated by us using standard Monte Carlo methods [22]. Most of the simulations were performed on the bulk fluid in isothermal-isobaric ensembles although a few were performed on a fluid confined to a slit with hard walls in a canonical ensemble.

To avoid the overlap of the ellipsoids, the criteria of Perram and Wertheim [23] were employed and this technique allowed us to check the pressure for the bulk systems by using the formula

$$\frac{\beta P}{\rho_B} = 1 + \lim_{\varepsilon \rightarrow 0} \frac{1}{3N\varepsilon} \sum_{i < j} F_{ij} \quad (36)$$

The function F_{ij} is the Perram and Wertheim overlap function defined so that $F_{ij} < 1$ when ellipsoids i and j overlap, $F_{ij} = 1$ when i and j just touch and $F_{ij} > 1$ otherwise. The sum in equation (36) is carried out over all pairs of ellipsoids i and j for which $(1 + \varepsilon)^2 \geq F_{ij} \geq 1$, with N being the number of ellipsoids in the simulation and ε is a small quantity $\approx 0.005a$. For improved statistics we employed the histogramming technique described in [24]. The bulk density was obtained through

$$\eta = v_e \rho_B = N v_e / \bar{h}^3 \quad (37)$$

where η is the bulk packing fraction, ρ_B the bulk density, v_e the volume of a molecule and \bar{h} is the average box length during the data collecting period of the simulation (i.e. after the equilibration period).

The pressure of the confined fluids was obtained from the sum rule [1].

$$\beta P = \sum_{\alpha} \rho_{\alpha w} \quad (38)$$

where $\beta = 1/kT$, P is the pressure and $\rho_{\alpha w}$ is the density of particles of orientation α at the wall. These densities were obtained by fitting a cubic polynomial to the density profile close to the wall (usually to the closest 6–8 simulation points) and extrapolating to contact. The corresponding bulk density was identified with the average density near the centre of the slit where, apart from small statistical fluctuations, the density profiles were constant. In all our simulations of a fluid in a slit only the isotropic phase of the fluid was seen.

The simulation parameters are summarized in table 1. One Monte Carlo cycle is defined as one attempted move for each particle. As usual, a certain number of initial cycles were discarded to allow the system to reach equilibrium before sampling began. All simulations were begun with the fluid in a perfect nematic state i.e. with all molecules in the same direction. It was assumed that equilibrium was achieved when \bar{h} and the number of molecules oriented in any given direction fluctuated about some mean values. It was found that the time for equilibrium to be achieved increased markedly as η increased, especially so as the molecules became more anisotropic. The cases $b > a$ took particularly long times. This behaviour was no doubt due, at least in part, to the fact that the orientations of the molecules were restricted to a discrete number of directions. For a molecule to change direction a drastic change of configuration is required especially in the cases of the most anisotropic molecules. It may be that a more subtle form of sampling of the phase space available, akin to that developed for simulating long chain molecules (see e.g. [25]), is required if longer molecules and more dense systems are to be studied.

Table 1. Parameters for the MC simulations. N represents the number of ellipsoids in the simulation. The last two columns give respectively the system studied (I for inhomogeneous and H homogeneous) and the ensemble used.

Run	b	N	Cycles generated	Cycles discarded	η	$\beta P/\rho_B$	System	Ensemble
1	0.5	750	82 000	20 000	0.231	3.06 ± 0.03	I	NVT
2	0.5	750	75 000	15 000	0.318	4.89 ± 0.08	I	NVT
3	0.5	750	100 000	15 000	0.392	7.57 ± 0.21	I	NVT
4	3.0	700	299 000	100 000	0.271	4.30 ± 0.07	H	NPT
5	3.0	700	325 000	150 000	0.337	6.18 ± 0.08	H	NPT
6	3.0	730	1 649 000	1 398 000	0.395	8.79 ± 0.22	H	NPT
7	5.0	750	1 042 000	400 000	0.211	3.95 ± 0.22	H	NPT

5. Results and discussion

5.1. Homogeneous fluids

Equation (35) for the parameters, $A_{\alpha\beta}^{(i)}$, of the direct correlation function were solved for several values of the ratio b/a in the range 0.35 to 5.0 and for values of the packing fraction, η , defined by

$$\eta = 4\pi a^2 b \rho_B / 3 \quad (39)$$

from zero to 0.6 at intervals of 0.01. Since all the lengths in the theory can be scaled by the length a , we quote the results in units for which $a = 1$. The system is then described by just the two parameters, b and η .

As the packing fraction tends to zero the direct correlation function tends exactly to the Mayer function. Because of the form, equation (2), chosen for the direct correlation function this is also a consequence of the present approximation. Thus as $\eta \rightarrow 0$, one finds that the parameters of equation (2) satisfy

$$A_{\alpha\beta} \rightarrow 1 \quad B_{\alpha\beta} \rightarrow 0 \quad D_{\alpha\beta} \rightarrow 0. \quad (40)$$

As an illustration of the results obtained for the parameters, we show a plot of six parameters as functions of packing fraction for the case $b = 5.0$ in figure 1. Although the parameters for the parallel and perpendicular components of B and D are quite close to each other as is assumed in scaling theory, this is not true of the components of A . The different components of the parameter D are so close that they cannot be distinguished from each other on the scale of the figure and are displayed as single lines. However the components of B are not as close as for the more nearly isotropic molecules [7].

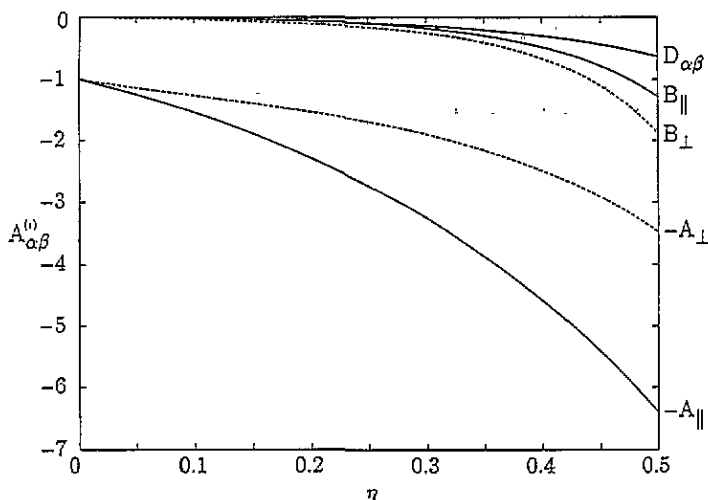


Figure 1. The weights, $A_{\alpha\beta}^{(i)}$, in the direct correlation function of equations (2) and (31) plotted as functions of the packing fraction, η , for $b = 5$. The curves for D_{\parallel} and D_{\perp} are too close to separate on this figure.

Fortunately, for applications to other problems such as the structure of the inhomogeneous fluid, these curves have a simple monotonic structure and can be very well approximated by Padé approximants of the form

$$A = \left(\delta + \sum_{i=1}^N a_i \eta^i \right) / \left(1 + \sum_{i=1}^{N+1} b_i \eta^i \right) \quad (41)$$

where δ is one or zero according to equation (40). With $N = 3$, the error in fitting the curves over the whole range studied here is at most 10^{-4} . This means that for one value of b , the direct correlation function for any packing fraction, can be expressed in terms of 42 constants, the five values of the constants in equation (41) for each of the six parameters. These constants are tabulated in tables 2 and 3 for the cases of $b = 0.5$ and 5.0 , respectively. The Padé approximant representation, (41), of the results is very sensitive to the values of

the parameters. As can be seen from the tables, although the curves of $D_{\alpha\beta}$ in figure 1 are very close the values of the corresponding coefficients, a_i , b_i , are easily distinguished. It may well be that an alternative representation could be found in which the coefficients, a_i , b_i , are less sensitive to the value of A in equation (41). One would like ultimately to provide simple formulae for the constants a_i and b_i as functions of the semi-major axis, b , but as yet we have the results for an insufficient number of values of b to do this with any confidence.

Table 2. The Padé coefficients for the parameters $A_{\alpha\beta}^{(i)}$ when $b = 0.5$. The values of the coefficients a_i , b_i in equation (41) give the weighting parameters as functions of η .

	A_{\parallel}	A_{\perp}	B_{\parallel}	B_{\perp}	D_{\parallel}	D_{\perp}
a_1	-1.066 969	0.835 972	-0.552 611	-1.022 326	-0.801 193	-0.829 756
a_2	0.268 681	2.594 193	-2.335 471	-2.654 038	-1.258 933	-2.070 948
a_3	-0.466 343	-0.479 055	0.467 843	2.447 446	-0.628 142	1.138 736
b_1	-3.915 922	-1.773 800	-4.476 443	-4.205 317	-2.721 396	-1.673 312
b_2	6.443 093	3.580 753	7.810 699	6.730 723	2.707 957	-1.993 637
b_3	-5.598 099	-6.697 645	-6.415 088	-5.030 957	-1.563 664	5.400 749
b_4	2.176 021	4.140 165	2.136 955	1.578 775	0.679 518	-2.781 704

Table 3. As table 2 but with $b = 5.0$.

	A_{\parallel}	A_{\perp}	B_{\parallel}	B_{\perp}	D_{\parallel}	D_{\perp}
a_1	3.223 339	1.483 077	-0.090 351	-0.403 844	-0.128 378	-0.086 895
a_2	5.110 642	1.730 769	-1.274 128	1.538 752	-1.028 397	-1.352 933
a_3	-5.562 093	17.464 436	-0.740 478	-5.224 476	-0.982 240	-8.287 195
b_1	-1.311 733	-1.437 952	4.698 872	-4.211 953	2.890 324	7.302 807
b_2	2.176 159	8.564 663	-35.320 405	16.259 273	-9.642 629	13.087 716
b_3	-4.981 834	-8.983 340	65.708 371	-33.637 285	2.514 553	-82.494 883
b_4	3.716 553	-0.767 937	-40.367 085	23.912 027	5.540 408	74.089 245

Once the parameters, $A_{\alpha\beta}^{(i)}$, are known it is possible to insert them into equations (25) and (27) and so derive the equation of state from both the compressibility and the virial. As was pointed out in [7], for the case $b = 1$, that is for spheres, we obtain the results of the PY approximation and the two curves are not identical. It is usual in this case to use the linear combination from Carnahan and Starling [26] for the pressure and this is in good agreement with the results of computer simulation. When the ellipsoids are not spherical, the original argument of Carnahan and Starling is no longer valid and it is doubtful whether the same combination of the two formulae is appropriate. This itself merits investigation. We have therefore chosen to display both formulae (25) and (27), as well as the linear combination chosen by Carnahan and Starling, the CS curve. For the values $b = 0.5$, 3 and 5 the resultant curves are displayed in figures 2-4 where the compressibility factor, $\beta P/\rho$, is plotted as a function of packing fraction, η . Also shown in these figures are the results of computer simulations of three different kinds. The first set, indicated by daggers on the figure, have been performed by us on the same model of a homogeneous fluid. The second set, indicated by diamonds, come from simulations by Frenkel and Mulder [27, 28], on a fluid of *freely rotating* ellipsoids with the same dimensions and the same packing fractions. The third set have been obtained by simulation of the inhomogeneous fluid and deducing

the pressure of the homogeneous fluid from the density profile by means of equation (38) and the procedure given in section 4.2.

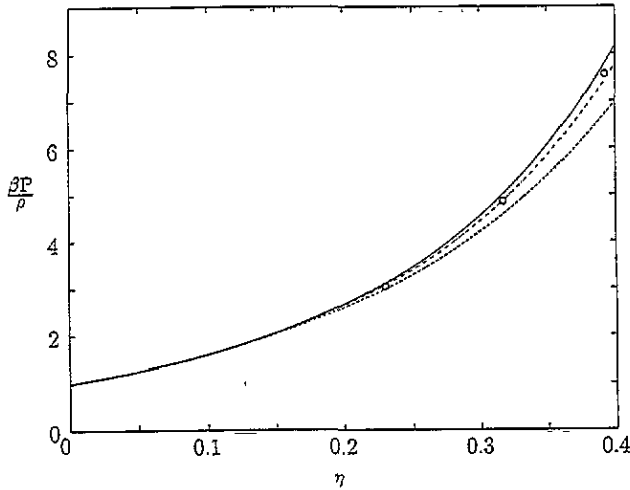


Figure 2. The compressibility factor, $Z = \beta P/\rho$, of a fluid of hard ellipsoids with elongation $b = 0.5$ as a function of the packing fraction, η . The continuous curve is from the compressibility, the dashed curve from the virial and the dot-dash curve from the CS combination. The circles show the results derived from simulations of the inhomogeneous fluid as discussed in section 4.2.

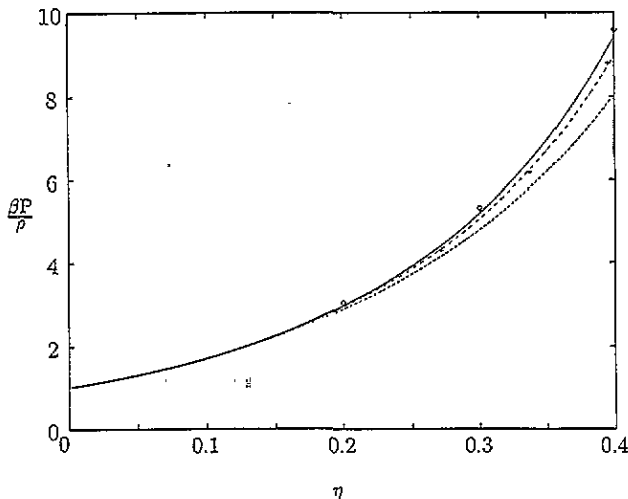


Figure 3. The compressibility factor, $Z = \beta P/\rho$, of a fluid of hard ellipsoids with elongation $b = 0.5$ as a function of the packing fraction, η . The curves have the same meaning as in figure 2. The points show results from simulations of a homogeneous fluid; the daggers derive from the simulations of the ROM reported in this paper, the diamonds are obtained from simulations of a similar fluid with freely rotating molecules by Frenkel and Mulder [25, 12].

For $b = 0.5$ and 3.0 (see figures 2 and 3), as for the previous cases [7], simulations of the restricted orientation model (ROM) are in good accord with the theory especially with the CS curve. However, when $b = 3.0$, the pressure in the fluid of freely rotating

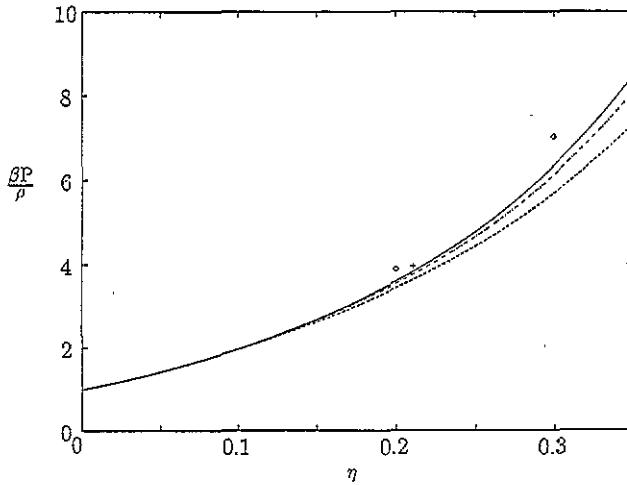


Figure 4. As figures 2 and 3, but with $b = 5.0$.

molecules appears to be higher than that of the ROM. The fluid of more elongated molecules ($b = 5.0$, figure 4) shows this latter difference is greater and more evident in figure 4. Also, the pressure in the ROM when $b = 5.0$ and $\eta = 0.211$ is slightly greater than that given by the theory, although the error is such that one cannot be sure of this.

We have also searched for any local instability in the isotropic phase over the range of parameters studied. As shown in [5], the condition for such an instability is

$$\Delta = \text{Det}[3\delta_{\alpha\beta}/\rho_B - \tilde{c}_{\alpha\beta}(0)] = 0 \tag{42}$$

This determinant factorizes and the condition is equivalent to

$$\Delta_0 = 3/\rho_B - \tilde{c}_{\parallel}(0) + 2\tilde{c}_{\perp}(0) = 0 \tag{43}$$

For values of b in the range, $0.35 < b < 5$, this function does not vanish and the isotropic phase is locally stable. Figure 5 displays plots of Δ_0 versus η for $b = 0.5, 5.0$ from which it can be seen that Δ_0 tends to fall as η increases from zero. However, it reaches a minimum at a finite value of η and thereafter increases. These results are typical, the curves for intermediate values lying between these two. This negative result agrees with our own simulations and with those of simulations of the fluid of freely rotating molecules [15, 24, 25, 27, 28] with values of b in the range $0.5 < b < 3.0$. However when $b = 5.0$ our simulations show evidence that the isotropic state is unstable, although as explained in section 4.2 simulations of such anisotropic molecules in the ROM take a very long time to reach equilibrium and our systems have not yet done so; others [15, 24, 25, 27, 28] have observed such a transition in a fluid of freely rotating ellipsoids although there is not yet precise agreement on the value of b at which the transition sets in.

5.2. Inhomogeneous fluids

Once one has obtained the direct correlation function for the homogeneous fluid one can insert it into one of the many density functionals which depend upon it in order to derive the structure of the inhomogeneous state. It is well known [9] that the best results are obtained if a weighted or averaged density is used rather than the local one. However, this uses considerably greater computer time and memory and, in any case, local theories

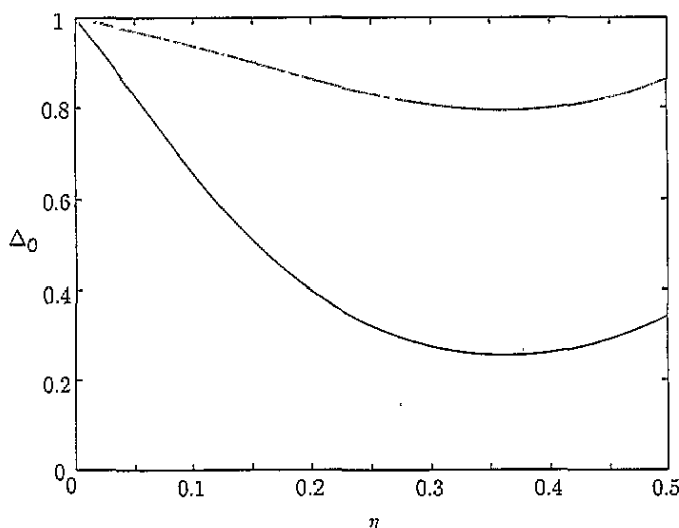


Figure 5. A plot of Δ_0 (defined in equation (44)) as a function of the packing fraction, η , for the cases of $b = 0.5$ and 5.0 . The isotropic state is locally unstable when Δ_0 is negative. The corresponding curves for intermediate values of b lie between these two curves, showing that in all these cases, according to the theory the isotropic state is locally stable.

can produce satisfactory results for confined hard fluids except very close to the walls. Furthermore, the weighting function is itself a matter for investigation when the molecules are no longer spheres. Accordingly, in this first analysis of the problem of the fluid confined between hard parallel planar walls using the new direct correlation function, we have used the HNC functional. The method and many of the basic equations have already been given in [1] and [3] and will not be repeated here.

The density functional requires as input the functions

$$\bar{c}_{\alpha\beta}(z) = \int dx dy c_{\alpha\beta}(\mathbf{r}) \quad (44)$$

which in turn require the functions

$$\bar{F}_{\alpha\beta}(z) = \int dx dy F_{\alpha\beta}(\mathbf{r}) \quad (45)$$

$$\bar{f}_{\alpha\beta}(z) = \int dx dy f_{\alpha\beta}(\mathbf{r}) \quad (46)$$

$$\bar{S}_{\alpha\beta}(z) = \int dx dy S_{\alpha\beta}(\mathbf{r}). \quad (47)$$

The first two of these functions have been given in [3]. Due to the relationship (4), any component of $\bar{S}(z)$ can be expressed in terms of the corresponding component of $\bar{F}(z)$. In fact one can show that

$$\bar{S}(z) = 5\bar{F}(z) - z\bar{F}'(z). \quad (48)$$

Equations (2), (45), (46) and (48) determine between them the direct correlation function as it appears in the density functional.

The equations for the components of the density which minimize the HNC functional have been given in [3] and we have now solved them for the new form of direct correlation

function. The results for the cases of $b = 0.5$ and 2.0 are displayed in figures 6 and 7, where they are compared with our own simulation results on the same systems. As was expected, except very close to a wall, the results agree with each other. At the wall the present improved theory overestimates the density, a property shared with the HNC functional in the spherical case. One would expect this discrepancy to be diminished, or even disappear, in a weighted density approximation. In fact, at the wall the simpler theory [3] agrees rather better with the simulation. However, this is fortuitous. For the simpler theory predicts an isotropic–nematic transition where there isn't one and this spurious effect shows up in the structure of a confined fluid [5]. Calculations and simulations with the improved theory have not yet been extended to the region where one might expect to see a transition.

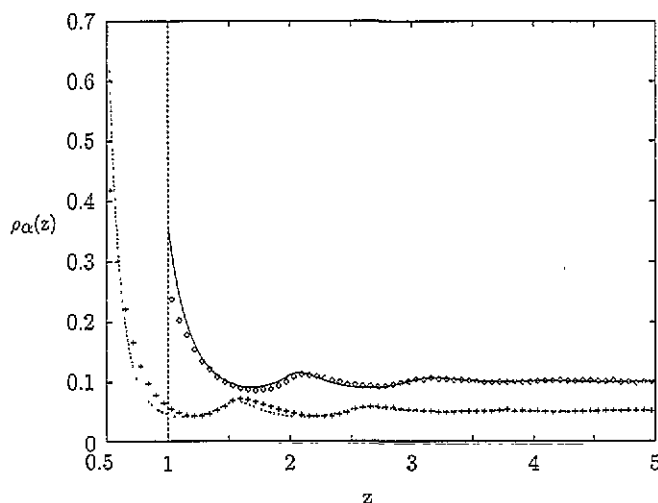


Figure 6. The density profiles of the molecules with axes parallel and perpendicular to the walls of the hard ellipsoidal fluid with $b = 0.5$ confined between two walls. One wall is situated at $z = 0$ and only half the profile is illustrated. The curve is derived from the theory discussed in this paper and the points come from the simulations discussed in section 4.2.

Recently, Rosenfeld [29] has proposed a density functional for an inhomogeneous fluid comprised of general hard convex molecules based upon geometrical properties of the individual molecules. When the excess free energy is truncated at the second order, it leads to a form similar to that treated in this paper [29]. As yet, it has not been applied explicitly to particular systems so that one cannot compare the results with ours. Nevertheless, with similar ingredients the two functionals can be expected to lead to similar results.

5.3. Summary and conclusions

We have been investigating the properties of the restricted orientation model of homogeneous and inhomogeneous hard ellipsoidal fluids on the basis of the approximation (2) for the direct correlation function of the homogeneous fluid, and with the parameters determined by the Anderson–Chandler variational principle. The twin objectives have been to study (a) how well the approximation represents the true properties of the ROM and (b) for the homogeneous fluid, how closely the properties of the ROM resemble those of the fluid in which the molecules can rotate freely. Because of limitations in computer time and memory the investigation has so far been confined to ellipsoids for which the ratio b lies in the range of 0.35 to 5.

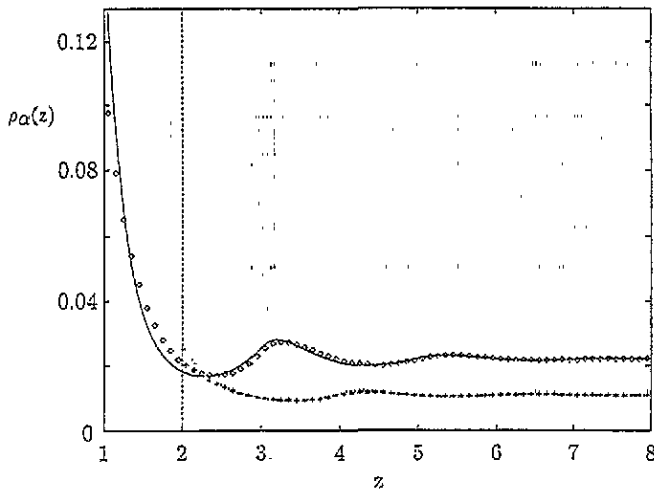


Figure 7. As figure 6 but with $b = 2.0$.

For the range of values of b studied the two equations of state still enclose the simulated values for the pressure which themselves, for $b < 3.0$, are close to the values obtained from the simulation of freely rotating molecules. For $b = 5.0$, the pressure of the fluid of freely rotating molecules is greater than that of the ROM especially at the higher densities. For $0.35 < b < 3.0$ we do not expect to see an isotropic–nematic transition and one does not appear in either the theory or simulation. For more prolate ellipsoids transitions have been observed in the simulation of the fluid of freely rotating molecules and we have some evidence from simulation that the isotropic state of the ROM is unstable when $b = 5.0$ and the density is sufficiently great. However, the present theory does not predict such a transition. It appears that the condition for an isotropic–nematic transition is more sensitive to the form of the direct correlation function than the equation of state and that a more general form than that adopted in this paper will be required; this is a matter for further investigation.

Nevertheless, the present theory will predict an isotropic–nematic transition for sufficiently anisotropic molecules; this follows from the general arguments originally given by Onsager [11, 27]. To verify that this is a consequence of the present theory, consider what happens as $\rho_B \rightarrow 0$. Then according to equation (40), the theory leads to

$$c_{\alpha\beta}(r) = f_{\alpha\beta}(r) \quad (49)$$

and the condition (43) for the instability of the isotropic phase becomes

$$\frac{3}{\rho_B} + \tilde{f}_{\perp}(0) - \tilde{f}_{\parallel}(0) = 0. \quad (50)$$

The Fourier transforms of the Mayer functions here are simply the negatives of the respective excluded volumes, $-V_{\perp}$ and $-V_{\parallel}$. In the limit of b becoming large, i.e. prolate ellipsoids, these become

$$V_{\perp} = 4\pi ab^2 \quad V_{\parallel} = 32\pi a^2 b/3 \quad (51)$$

and V_{\perp} dominates on equation (50). The isotropic state is therefore locally unstable when

$$\eta = a/b. \quad (52)$$

As b/a becomes very large $\eta \rightarrow 0$ and the use of equation (49) is justified.

Similarly, at the other extreme of oblate ellipsoids one can still use equation (49), but now

$$V_{\perp} = 4\pi a^3. \quad (53)$$

This term still dominates equation (50) but now one finds that the instability occurs when $\eta = b/a$ which becomes small as $a \rightarrow 0$, thus justifying the use of equation (49) in this instance, too. The theory can therefore describe the transition but, for prolate ellipsoids it overestimates the value of b at which it can take place.

The structure of the inhomogeneous fluids has also been investigated using the same approximation for the direct correlation function but with the HNC functional to describe the inhomogeneous system. The results again agree with simulated ones except very close to the wall. An improved form of density functional will be required to improve upon this and this is subject to further research.

Altogether then it appears that thus far the model can provide a satisfactory equation of state and a satisfactory description of the structure of the inhomogeneous isotropic fluid. However, it needs improvement if the nematic state is to be described quantitatively. Further calculation is also required to extend the results of the theory to fluids with more anisotropic molecules and a more efficient sampling method is required for the simulation of such fluids. Nevertheless, the present approach should also provide a practical first stage in the development of theories of fluids of molecules interacting through softer and longer ranged potentials.

Acknowledgment

This work was supported in part by grant GR/J24256 of the EPSRC for which the authors are grateful.

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