

Correlation functions for nematic liquid crystals

by JOEL L. LEBOWITZ

Department of Mathematics and Physics,
Rutgers University, New Brunswick, New Jersey, U.S.A.

and JOHN W. PERRAM

Department of Mechanical Engineering and Planetary Science,
State University of New York at Stony Brook, N.Y. 11794,
and Matematisk Institut, Odense Universitet,
DK 5230 Odense, Denmark

(Received 12 October 1982 ; accepted 13 July 1983)

We show that the correlation functions of a system of hard ellipsoids whose axes are constrained to be parallel are simply related to the corresponding functions of a hard sphere fluid with the same packing fraction. The existence of simple, accurate approximations for the latter system make the oriented ellipsoid fluid a suitable 'reference system' for the nematically ordered phase of liquid crystals and other orientationally ordered molecular fluids such as polar fluids in an external field. The properties of such fluids, with a given angular distribution $f(\omega)$, may then be obtained via 'standard' perturbation theory. Methods for obtaining $f(\omega)$ near the perfectly ordered state are discussed.

1. INTRODUCTION

In this work, we attempt to supplement current mean field theories [1-3] of nematically ordered fluids by providing non-trivial estimates of the pair distribution function for a simple model of such a fluid. The reader is invited to imagine a fluid consisting of hard ellipsoids (or more simply, spheroids) which are disordered with respect to position but which are all constrained to lie with their long axes along a fixed vector (the director, in liquid crystal parlance). Although correlations between the particles of such a fluid will be short ranged, they will depend on the length and relative direction relative to the director of the intermolecular vector connecting the centres of two particles.

In § 2, we show that the pair distribution function for this system is very simply related to the pair distribution function for a system of hard spheres of the same reduced density. By using the Percus-Yevick equation, which gives a good representation of the latter [4-6], we are able to calculate the former. As the pair distribution function depends on the angle between the intermolecular vector and the director, it proves convenient to represent this angle dependence by expanding the pair distribution function as a series of even Legendre polynomials of the cosine of this angle, with coefficients which are functions of distance. We calculate the first three of these coefficients and present them graphically.

In § 3, we calculate the dependence of the static structure factor $S(k)$ of the aligned ellipsoids on the components of the wave vector k , as this is also simply related to the corresponding function for hard spheres. We show that $S(k)$ for aligned ellipsoids depends on the components of k parallel and perpendicular to the director. The curves of constant S in the k -plane are ellipses with semi-axes whose lengths are inversely proportional to the lengths of minor and major semi-axes respectively of the ellipsoids. Numerically simulated curves of the structure factor of this very simple model look very similar to reported experimental X-ray patterns [7].

In § 4, we address the problem of relating the pair correlation of long molecules no longer perfectly oriented and acting through realistic intermolecular potentials to that of our simple model. To do this, we adapt modern perturbation theories of isotropic molecular fluids by first relating the properties of the realistic system to those of an equivalent reference system which acts through suitably chosen repulsions. It should be stressed, however, that these repulsions depend on both the real attractions and repulsions at short to moderate separations in a complicated way. In turn, the properties of this reference system are related to those of a suitably chosen assembly of hard ellipsoids. Finally, by using a correlation function $\gamma(1, 2)$, which is known to have a weak dependence on orientations, we are able to relate the (imperfectly) nematic ordered ellipsoid system to the fully ordered one we have calculated in § 2.

In § 5, we discuss the problem of how to compute the one particle angular distribution function when one has a knowledge of the two particle function. An immediate consequence of symmetry is that the pair distribution function reported here is not appropriate for the isotropic phase.

This paper is to be regarded as a preliminary report of our method. Although [8] molecular dynamics simulations of long molecules have been reported, these focused upon order parameters and contain no structural information of the type required to test the ideas presented here. To this end, we shall shortly report extensive Monte Carlo simulations of hard ellipsoids with which the ideas above can be tested and illustrated.

2. ORIENTED ELLIPSOIDS IN THE PERCUS-YEVICK APPROXIMATIONS

Consider a system of N rigid particles at positions $\mathbf{r}_1, \dots, \mathbf{r}_N$, and with orientations $\omega_1, \dots, \omega_N$, which interact with each other via a pair potential function $U(1, 2) = U(\mathbf{r}_1 - \mathbf{r}_2, \omega_1, \omega_2)$ and with an external field $U(1) = W(\mathbf{r}_1, \omega_1)$. The linear transformation

$$\mathbf{r} = \mathbf{B}\mathbf{R},$$

where \mathbf{B} is a positive matrix with unit determinant then changes the equilibrium state of this system, i.e. all correlation functions and thermodynamic properties, into a state of the system with interactions $U'(1, 2) = U(\mathbf{B}\mathbf{R}_1, \mathbf{B}\mathbf{R}_2, \omega_1, \omega_2)$, $U'(1) = W(\mathbf{B}\mathbf{R}_1, \omega_1)$. In particular, a system of parallel hard ellipsoids becomes, with a proper choice of \mathbf{B} , a system of hard spheres.

We begin by studying an assembly of N parallel hard ellipsoids of volume $(\pi/6)abc$, whose principal axes have lengths a, b, c . In what follows, we call, \mathbf{A} , the diagonal matrix with eigenvalues a^{-2}, b^{-2}, c^{-2} , the molecular shape matrix. If the principal axis frame coincides with the laboratory cartesian frame, then two such ellipsoids whose centres are separated by the vector \mathbf{r} will or will not

overlap according as to whether the quantity

$$P^2 = \mathbf{r}^T \mathbf{A} \mathbf{r} \quad (1)$$

is less than or greater than unity respectively. If $h(\mathbf{r})$ denote the total correlation function for this system, then a direct correlation function $c(\mathbf{r})$ may be defined via the Ornstein-Zernike relation

$$h(\mathbf{r}) = c(\mathbf{r}) + \rho \int c(\mathbf{s})h(\mathbf{r}-\mathbf{s}) d\mathbf{s}, \quad (2)$$

where ρ is the number density. The Percus-Yevick [4] equation for this system is then

$$c(\mathbf{r}) = 0 \quad \text{if } P > 1 \quad (3)$$

supplemented by the exact core condition

$$h(\mathbf{r}) = -1 \quad \text{if } P < 1. \quad (4)$$

To solve the set of equations (2-4), we define new coordinates \mathbf{R} by means of the transformation

$$\mathbf{R} = \mathbf{A}^{1/2} \mathbf{r}. \quad (5)$$

Applying this transformation to (2-4), we have, defining

$$H(\mathbf{R}) = h(\mathbf{r}) \quad \text{and} \quad C(\mathbf{R}) = c(\mathbf{r}), \quad (6)$$

$$R^2 = \mathbf{r}^T \mathbf{A} \mathbf{r} \quad (7)$$

that,

$$H(\mathbf{R}) = C(\mathbf{R}) + \rho(abc) \int C(\mathbf{S})H(\mathbf{R}-\mathbf{S}) d\mathbf{S} \quad (8)$$

and

$$C(\mathbf{R}) = 0 \quad \text{if } R^2 > 1, \quad (9 a)$$

$$H(\mathbf{R}) = 1 \quad \text{if } R^2 < 1. \quad (9 b)$$

Evidently $H(\mathbf{R})$ depends only on the modulus of \mathbf{R} . The solution to the problem posed by the equations (8), (9) is of course the solution of the Percus-Yevick integral equation for hard spheres of diameter unity at a reduced density $\rho(abc)$ which was first given by Wertheim and Thiele [5-6].

The dependence of these functions on the vector \mathbf{r} is most simply illustrated by studying the solution for the case of oblate spheroids with

$$a = b < c \quad (10)$$

and changing from the cartesian system \mathbf{r} to a system of polar coordinates. For this case, $h(\mathbf{r})$ depends only on the distance r and the azimuthal angle θ since

$$R^2 = (r/a)^2(1 - (1 - a^2/c^2) \cos^2 \theta). \quad (11)$$

We may then expand $h(\mathbf{r})$ in a series of Legendre polynomials $P_{2l}(\cos \theta)$ of even order. The projection of $h(\mathbf{r})$ onto the first three harmonics is shown in figure 1 at a reduced density $\rho a^2 c = 0.85$. In this example, the axis ratio c/a is 3.0, chosen purely to illustrate the method.

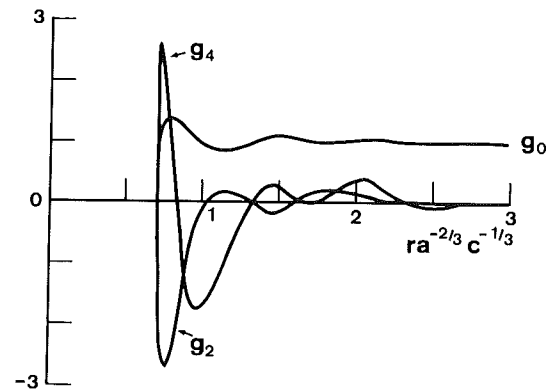


Figure 1. Showing the projections of the pair correlation function $h(1, 2)$ for parallel ellipsoids onto the first three Legendre polynomials.

3. STRUCTURE FACTORS

In order to test the practical utility of the ideas described in this note, it is necessary to have detailed experimental and/or computer simulation data on the structure of orientationally ordered systems. Such data are lacking at present. We are currently engaged in carrying out such simulations [9]. We note that the structure factor $S(\mathbf{k})$ of a perfectly ordered nematic phase is a function of the wave vector \mathbf{k} , and not just its magnitude. We have

$$S(\mathbf{k}) = 1 + \rho \int h(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r}. \quad (12)$$

Applying the transformation (5) to (21), we find

$$S(\mathbf{k}) = 1 + \rho(abc) \hat{H}((\mathbf{k}^T \mathbf{A}^{-1} \mathbf{k})^{1/2}) \quad (13)$$

where $\hat{H}(K)$ is the Fourier transform of the total correlation function for hard spheres. If k_{\parallel} and k_{\perp} are the wave vectors parallel to and perpendicular to the director, (13) predicts that the X-ray or neutron scattering pattern should be elliptic.

In fact, if $a = b < c$, we have that the curves of constant scattering amplitude in the $(k_{\perp}, k_{\parallel})$ plane are the family of ellipses

$$\frac{K_{\perp}^2}{A^2} + \frac{K_{\parallel}^2}{B^2} = K^2,$$

where K_{\perp} , K_{\parallel} are dimensionless wave numbers defined by

$$K_{\perp} = k_{\perp} \rho^{-1/3}, \quad K_{\parallel} = k_{\parallel} \rho^{-1/3}.$$

The constants A , B are given by

$$A = \left(\frac{\pi c}{6\eta a} \right)^{1/3}, \quad B = \left(\frac{\pi a^2}{6\eta c^2} \right)^{1/3},$$

where

$$\eta = \frac{4\pi}{3} \rho a^2 c$$

is the packing fraction of the ellipsoids.

We can get a picture of the scattering amplitude for the model by drawing a sequence of ellipses, for various values of K . We choose the increments in K as being inversely proportional to the value of $S(K)$ for hard spheres of unit diameter in the Percus-Yevick approximation. This is shown in figure 2, which bears a striking qualitative resemblance to the observed scattering pattern for real nematics [7]. The ellipses are more eccentric than those observed, reflecting the greater order present in the model, but the first two peaks are apparent.

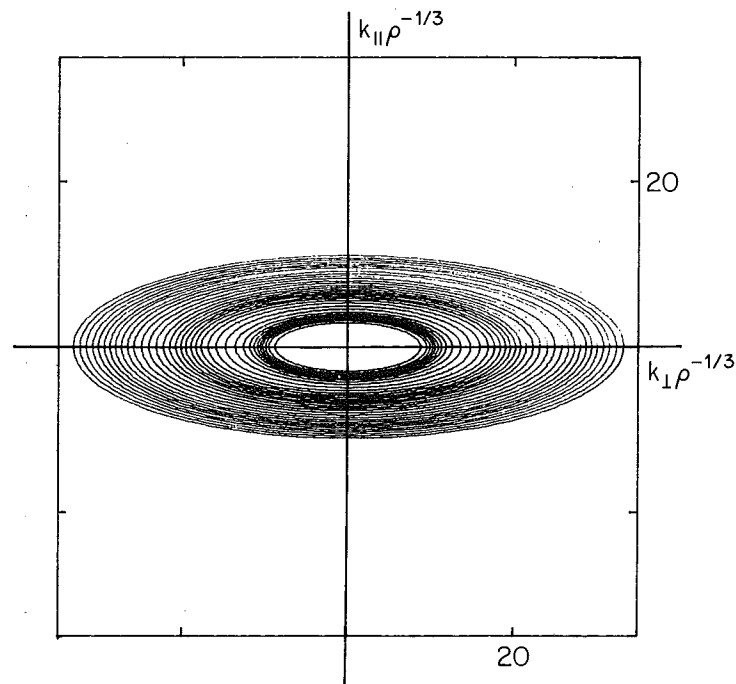


Figure 2. Showing computed contours of the structure factor $S(\mathbf{k})$ of parallel ellipsoids. The density of ellipses in the plane is proportional to the scattering intensity.

4. GENERAL SYSTEM AND PERTURBATION THEORY

The above analysis is, of course, not restricted to the Percus-Yevick approximation, or to the pair correlation, or to pure hard core systems.

We now show how to relate the singlet and pair distribution functions for a real nematic ordered fluid where the molecules act via an arbitrary pair potential $U(1, 2)$ to the properties of this system of parallel ellipsoids. In the interests of simplicity we shall suppose that the molecules have spheroidal symmetry, but make no other restrictions. For such molecules, $U(1, 2)$ is a function of the intermolecular vector $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$, and vectors $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$, which express the orientation of the molecules' long axes relative to the laboratory frame. We follow Kohler *et al.* [10] and study the potential $U(1, 2)$ as a function of separation R for fixed values of the orientations of the three vectors. The next step is to split U for each orientation set into a purely repulsive reference potential U_R and an attractive perturbation potential U_A , as described in [10].

Using techniques described in [11], the properties of the full system are related to the properties of the reference system with potential U_R .

The next stage in the calculation is to calculate the properties of the soft reference system in terms of a system of hard ellipsoids. This is accomplished using the orientational analogue of the so-called blip function expansion introduced by Andersen *et al.* [11]. If U_E denotes the potential of interaction of hard ellipsoids, being infinity if the two ellipsoids overlap and zero otherwise, then we write the identity

$$\exp(-U_R(1, 2)/kT) = \exp(-U_E(1, 2)/kT) + B(1, 2). \quad (14)$$

Using standard first order perturbation theory, we expand the free energy and the one particle distribution function $\rho_R^{(1)}(1)$, to first order in $B(1, 2)$. $\rho^{(1)}(1)$ is defined as usual for the interaction U , and is a function of the orientation of particle 1 in the nematic phase, defined in terms of configurational hamiltonian H by

$$\rho_R^{(1)}(1) = \frac{\frac{1}{(N-1)!} \int \dots \int \exp(-H_R/kT) \, d2 \dots d\mathbf{N}}{\frac{1}{N!} \int \dots \int \exp(-H_R/kT) \, d1 \dots d\mathbf{N}} \quad (15)$$

to first order in $B(1, 2)$.

The elements of the molecular shape matrix are then found from the conditions that the two systems have the same second virial coefficient,

$$0 = \int \int B(1, 2) \, d1 \, d2 \quad (16)$$

and that the first order correction to the free energy be zero,

$$0 = \int \int B(1, 2) y_E(1, 2) \, d1 \, d2, \quad (17)$$

where the function $y_E(1, 2)$ for hard ellipsoids is defined by

$$y_E(1, 2) = (1 + h_E(1, 2)) \exp(U_E(1, 2)/kT). \quad (18)$$

We note that when $U(1, 2)$ is itself a pure hard core potential then $U_R = U_E$ and $B = 0$.

It now remains to relate $y_E(1, 2)$ to the properties of the parallel ellipsoid system which we have calculated. To do this, we make use of the observation from the theory of isotropic molecular fluids that the function y is a relatively weak function of orientations. It is usual [12-15] to replace it by its (orientation independent) value for a fluid acting through a potential $\bar{U}(1, 2)$ defined by the angle average of the Boltzmann factor,

$$\bar{U}(1, 2) = -kT \log \langle \exp(-U_E(1, 2)/kT) \rangle_{1,2}, \quad (19)$$

where $\langle \rangle_{1,2}$ denotes the unweighted average over orientational coordinates. For nematically ordered fluids we may take advantage of this weak dependence by observing that only configurations where the molecules are approximately parallel to the director are likely to be significant. If this is so, we may equate $y_E(1, 2)$ with its value $\hat{y}_E(1, 2) = \hat{y}_E(\mathbf{r}_{12})$ for parallel ellipsoids. Within this approximation, we then have the following expression for the pair distribution function $g_E(1, 2)$ for nematically ordered hard ellipsoids

$$g_E(1, 2) = \hat{y}_E(1, 2) \exp(-U_E(1, 2)/kT). \quad (20)$$

5. ORIENTATIONAL DISTRIBUTION

We may now proceed further and derive an approximate equation for the one particle angular distribution function defined in (15). Differentiating $\rho^{(1)}(\mathbf{1}) = \rho f(\boldsymbol{\omega}_1)$ with respect to angular coordinates, we have, after a little manipulation of the BGY hierarchy for this system,

$$\begin{aligned} \frac{\partial}{\partial \boldsymbol{\omega}_1} \log \rho_{\mathbb{E}}^{(1)}(\mathbf{1}) &= \frac{\partial}{\partial \boldsymbol{\omega}_1} \log f(\boldsymbol{\omega}_1) \\ &= \rho \int f(\boldsymbol{\omega}_2) y_{\mathbb{E}}(1, 2) \frac{\partial}{\partial \boldsymbol{\omega}_1} (\exp(-U_{\mathbb{E}}(1, 2)/kT) \\ &\quad - \exp(-\tilde{U}_{\mathbb{E}}(1, 2)/kT)) d2. \end{aligned} \quad (21)$$

We may now replace $y_{\mathbb{E}}(1, 2)$ by $\hat{y}_{\mathbb{E}}(1, 2)$, which is independent of orientations and integrate (21) to obtain,

$$\begin{aligned} \log(f(\boldsymbol{\omega}_1)) &= \log X + \rho \int f(\boldsymbol{\omega}_2) \hat{y}_{\mathbb{E}}(\mathbf{r}) (\exp(-U_{\mathbb{E}}(\mathbf{r}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)/kT) \\ &\quad - \exp(-\tilde{U}_{\mathbb{E}}(\mathbf{r})/kT)) d\boldsymbol{\omega}_2 d\mathbf{r}, \end{aligned} \quad (22)$$

where we have written out explicitly the arguments of the different quantities. Equation (22) is an integral equation for the unknown orientational distribution function f : X is an integration constant which may be found from its normalization. Since $\hat{y}_{\mathbb{E}}(\mathbf{r})$ refers to specified space axes, with the z -axis, say, in the direction along which the long axes of all the ellipsoids are aligned, (22) can be expected to be useful (as can the perturbation expansion) only when there is a fair degree of ordering in the system. In particular, (22) does not have any isotropic solutions and hence is not expected to show any transition [16].

This work was supported by grants from the Danish Natural Science Research Council and the United States Air Force Office of Scientific Research under grant No. 82-0016. One of us (J.W.P.) would like to express his gratitude to G. Stell and the State University of New York for their hospitality, and especially to Dr. Alex King for helpful conversations and the kind use of his Apple computer. We should further like to acknowledge helpful discussions with J. Percus, M. S. Wertheim and M. Kalos, as well as the hospitality of the Computing Center of the Courant Institute at New York University where some of the computations have been performed.

REFERENCES

- [1] ONSAGER, L., 1949, *Ann. N.Y. Acad. Sci.*, **51**, 627.
- [2] MAIER, W., and SAUPE, A., 1958, *Z. Naturf. (a)*, **13**, 564.
- [3] GELBART, W. M., and BARON, B. A., 1977, *J. chem. Phys.*, **66**, 207.
- [4] PERCUS, J. K., and YEVICK, G. Y., 1958, *Phys. Rev.*, **110**, 1.
- [5] WERTHEIM, M. S., 1963, *Phys. Rev. Lett.*, **10**, 321.
- [6] THIELE, E., 1963, *J. chem. Phys.*, **39**, 474.
- [7] LEADBETTER, A. J., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press).
- [8] TSYKALO, A. L., and BAGMET, A. D., 1978, *Czech. J. Phys. B*, **28**, 1113.
- [9] PERRAM, J. W., WERTHEIM, M., LEBOWITZ, J. L., and WILLIAMS, G. (in preparation).
- [10] KOHLER, F., PERRAM, J. W., and QUIRKE, N., 1979, *J. chem. Phys.*, **71**, 4128.
- [11] ANDERSON, H. C., CHANDLER, D., and WEEKS, J. D., 1971, *J. chem. Phys.*, **54**, 5237 ; 1971, *Ibid.*, **55**, 5421 ; 1972, *Ibid.*, **57**, 1918.

- [12] PERRAM, J. W., and WHITE, L. R., 1972, *Molec. Phys.*, **24**, 1133 ; 1974, *Ibid.*, **28**, 527.
- [13] WHITE, L. R., 1974, Doctoral Thesis, A.N.U.
- [14] SMITH, W. R., 1974, *Can. J. Chem.*, **52**, 2022.
- [15] This theory is sometimes referred to as the Reference Average Mayer (RAM) theory.
A more accurately descriptive title, which nevertheless preserves an ovine acronym
is the Boltzmann Angle Average (BAA) theory.
- [16] KAYSER, R. F., and RAVECHÉ, H., 1978, *Phys. Rev. A*, **17**, 2067.