Molecular field theory of nematics: density functional approach. I. Bulk effects

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Abstract. The molecular field theory of nematics is rephrased in density functional language. The free energy in the nematic state is expressed as a functional expansion around the isotropic state in powers of the nematic order parameters $\bar{P}_l$ and the fractional density change η at the isotropic–nematic transition. The crucial quantities in the expansion are spherical harmonics of the direct correlation functions in the isotropic state. Sensible approximations to these direct correlation functions lead to other well known formulations of nematic field theory. An exact (in our approximation) result for η is obtained in terms of the potential parameters U_l and the order parameters $\bar{P}_l$ at the phase transition. We discuss the relationship of our approach to other microscopic theories of nematics. The theory can be extended to discuss inhomogeneous systems.

1. Introduction

Over the last few years there has been much interest in the so-called liquid crystal mesophases (Chandrasekhar 1977, de Gennes 1974). These systems exhibit symmetry intermediate between that of the isotropic fluid phase and that exhibited by the complicated crystallography of solid phases. They do, however, flow like liquids, although generally the extra symmetries generate a rather complicated hydrodynamics. Liquid crystals have aroused interest partly because of the fundamental statistical mechanics involved, and the wealth of associated order parameters and defects, and partly because of their technological application, particularly in visual display systems. One of the most studied liquid crystal states is the nematic state, in which long molecules preferentially line up in some direction; in these systems there is complete translational invariance, but not complete angular invariance. It is the study of the nematic state and in particular the transition between the isotropic liquid and the nematic state which we undertake in this paper.

The gross features of the statistical thermodynamics of the nematic state are relatively well understood. Heavily anisotropic molecules in a dense fluid may adopt a non-uniform angular distribution, and this distribution gives rise to an effective anisotropic external potential acting on each individual molecule. The consequence is that the non-uniform angular distribution may be stabilised, and for sufficiently low temperatures the resulting thermodynamic state is globally as well as locally stable. All molecular field theories of the nematic state adopt this perspective; they differ in the detail of how exactly to calculate, from microscopic first principles, the effective or pseudo-potential as a function of the distribution. The early theories of Onsager

(1949) who supposed that volume exclusion effects were dominant, and of Maier and Saupe (1958, 1959, 1960) who in contrast supposed that long-range dispersion effects were responsible for the nematic phase, are well known; subsequently it has become evident that some combination of these effects exists, and a summary of more recent work on molecular field theories is given by Luckhurst and Gray (1979).

All molecular field theories involve calculation of a free energy as a function of angular distribution function $f(\omega)$, where ω represents solid angle, and $f(\omega)$ is normalised. Our reformulation of such theories is no exception. What we *are* able to do is to define precisely from a microscopic starting point how the free energy is to be calculated and to show how the terms of a given order in the order parameters (which we define more precisely below) are to be calculated. What we in fact do is to reformulate the Maier–Saupe theory to show that, if correctly interpreted, the predictive value of this theory does not depend on the range of the assumed interparticle potential, as has sometimes been supposed.

In this paper we shall use the density functional language to describe the nematic state near the nematic–isotropic transition. This approach, which in the liquid crystal context has been pioneered by Stecki and Kloczkowski (1979), makes it possible to show that the Helmholtz free energy of a state with given density profile $\rho(r, \omega)$ may be written as a unique functional of $\rho(r, \omega)$. One may then use sensible approximation techniques to write down the free energy. This approach has been fruitful in understanding the behaviour of the electron gas (Hohenberg and Kohn 1964, Kohn and Sham 1965), in describing atomic liquids (Evans 1979), and in what we believe to be the best current theory of freezing (Ramakrishnan and Yussouff 1979, Haymet and Oxtoby 1981). In a recent paper we have discussed the application of density functional theories to simple molecular fluids (Sluckin 1981), and there are close parallels between the present work, and both our previous work, and the Ramakrishnan–Yussouff melting theory mentioned above. We shall also be concerned with functional derivatives of the free energy with respect to the local density, and this causes the Ornstein–Zernike direct correlation function of the isotropic fluid to play a prominent role in the theory. As hinted above, it is in the study of inhomogeneous fluids that the density functional approach has proved particularly useful, and in subsequent papers we shall apply the formalism developed in this paper to inhomogeneous situations. In particular we shall be interested in the nematic–isotropic interface, the nematic–vapour interface, and nematic effects in fluids near walls.

We may regard the theory expounded in this paper as a *mesoscopic* theory of the isotropic–nematic transition. In spirit it lies between a fully *microscopic* theory—in which the liquid partition function is evaluated, and a *macroscopic* theory—which depends totally on a number of phenomenological parameters. The mesoscopic theory provides a link between the macroscopic theory, for instance Landau–de Gennes theory (Stephen and Straley 1974, de Gennes 1969), and the microscopic input, which in this case is the intermolecular potential of the molecules making up the nematogen. This link is provided through moments of the Ornstein–Zernike direct correlation function. One may obtain information about the direct correlation function either by solving the integral equations of classical liquid theory (Hansen and McDonald 1976), or by interpretation of experimental scattering data; alternatively one may merely parametrise the direct correlation function. The eventual aim of a microscopic theory of nematics is to understand the dependence of liquid crystal properties upon molecular chemical structure. We hope that this work will be a stage along this road. However, real intermolecular interactions are complicated; our idealisation will be to treat

molecules as cylindrically symmetric point centres of potential. This idealisation is rather major, and precludes quantitative understanding of major chemically important features of liquid crystal behaviour.

It is also important to emphasise a major drawback in our theory. All mean-field theories are at best incomplete descriptions of phase transition behaviour. In the case of the nematic–isotropic transition it seems that the effect of molecular orientational fluctuations is not correctly taken into account whichever mean-field theory is used (Nelson and Toner 1981). Indeed, it is only for d-dimensional systems for $d > 6$ that a mean field theory of the nematic–isotopic transition becomes correct. However, it is difficult to make a link between the gross features of the transition and the fluid microscopic properties. It is also useful to optimise the information which may be obtained from mean-field theories, and to discuss the nature of the assumptions which underly them, assumptions which may be different from the explicit assumptions of the authors.

The material in the paper is arranged as follows. In § 2 we briefly summarise the density functional theory as applied to simple molecular fluids. In § 3 we use this material to make a functional expansion of the free energy around the isotropic state. It is at this stage that it becomes clear how important is the spherical harmonic expansion of the direct correlation function. We solve the resulting equations in order to describe the nematic state at the nematic–isotropic transition. In § 4 we examine closely the theory of the nematic state in our language, and its relationship to the phenomenologies of Onsager (1949) and Maier and Saupe (1958, 1959, 1960). We show that in the limit of zero compressibility our theory reduces to that of Maier and Saupe, and provides a microscopic formula for the Maier–Saupe pseudopotential U. We discuss the relationship between our formula for U and some expressions derived by other authors. We also derive a simple formula for the density change at the first order nematic–isotropic transition. Finally in § 5 we make some concluding remarks.

2. The molecular density functional theory

2.1. Preparatory comments

We shall be concerned throughout this article with a fluid of axially symmetric rigid molecules, each of which is at a position defined by r, and has an orientation defined by a solid angle ω, which needs only two Euler angles θ, φ to specify it. Two molecules (r_1, ω_1), (r_2, ω_2) interact with a potential energy $U(r_{12}, \omega_1, \omega_2)$, where $r_{12} = r_2 - r_1$, and there exists a spherical harmonic expansion

$$U(r, \omega_1, \omega_2) = \sum_{l_1, l_2, l} \sum_{m_1, m_2, m} U(l_1, l_2, l, r) C(l_1, l_2, l; m_1, m_2, m)$$

$$\times Y_{l_1 m_1}(\omega_1) Y_{l_2 m_2}(\omega_2) Y_{lm}(\omega_r) \tag{2.1}$$

where $C(l_1, l_2, l; m_1, m_2, m)$ are Clebsch–Gordan coefficients and $Y_{lm}(\omega)$ are the usual normalised spherical harmonics. The vector r is defined by magnitude r and direction ω_r.

The mean density of the fluid $\rho(r, \omega)$ may be expressed as a spherical harmonic expansion:

$$\rho(r, \omega) = \sum_{l,m} \rho_{lm}(r) Y_{lm}(\omega). \tag{2.2}$$

In nematic liquid crystals the molecules at a point r are predominantly lined up in a particular direction, known as the *director*. A unit vector in this direction, designated here $\hat{l}(r)$, is a local axis of symmetry, and the angular distribution function $\rho(r, \omega)$ is symmetric with respect to rotations around this axis; more formally.

$$\rho(r, \omega) = \rho(r, \hat{n}(\omega) \cdot \hat{l})$$

where $\hat{n}(\omega)$ is a unit vector in the direction ω. In the particular case when the director lies along the z axis,

$$\rho(r, \omega) = \sum_l \rho_l(r) Y_{l0}(\omega) = \sum_l \left(\frac{2l+1}{4\pi}\right) n_l(r) P_l(\cos\theta), \tag{2.3}$$

where

$$n_l(r) = \int d\omega \rho(r, \omega) P_l(\cos\theta) \tag{2.4}$$

and $P_l(\cos\theta)$ is the Legendre polynomial of order l.

It will be convenient for some purposes to describe $\rho(r, \omega)$ in terms of a cartesian tensor expansion. In this case

$$\rho(r, \omega) = (1/4\pi)[\rho(r) + 5\hat{n}_i(\omega)\hat{n}_j(\omega)q_{ij}(r) + \ldots] \tag{2.5}$$

where

$$q_{ij} = \tfrac{1}{2}q[3\hat{l}_i\hat{l}_j - \delta_{ij}] \tag{2.6}$$

and l is the nematic director, supposed along the z axis. Comparing (2.4) and (2.6) one may easily verify that

$$\rho(r) = n_0(r) \tag{2.7a}$$

$$q(r) = n_2(r). \tag{2.7b}$$

The cartesian tensor expansion is useful when dealing with the statistical mechanics of non-uniform fluids.

We may also define the angular distribution function $f(r, \omega)$ where

$$\rho(r)f(r, \omega) = \rho(r, \omega) \tag{2.8}$$

and

$$\int f(r, \omega) \, d\omega = 1. \tag{2.9}$$

The nematic order parameters $\bar{P}_l$ are then

$$P_l(r) = \int P_l(\cos\theta) f(r, \omega) \, d\omega \tag{2.10}$$

and

$$\rho\bar{P}_l = n_l. \tag{2.11}$$

2.2. The density functional theory

The state of the molecular fluid is defined by the density distribution function $\rho(r, \omega)$. There exists a unique free energy functional $\mathscr{F}[\rho(r, \omega)]$, such that in the presence of

external fields $V_{\text{ext}}(r, \omega)$ the total Helmholtz free energy is given by

$$F = \mathscr{F}[\rho(r, \omega)] + \int dr \, d\omega \, V_{\text{ext}}(r, \omega)\rho(r, \omega). \tag{2.12}$$

The grand thermodynamic potential is given by

$$\Omega = F - \mu \int \rho(r, \omega) \, dr \, d\omega \tag{2.13}$$

where μ is the chemical potential.

The functional $\mathscr{F}[\rho(r, \omega)]$ may be further subdivided as follows:

$$\mathscr{F}[\rho(r, \omega)] = \mathscr{F}_{\text{ideal}}[\rho(r, \omega)] - \Phi[\rho(r, \omega)] \tag{2.14}$$

where $\mathscr{F}$ reduces to $\mathscr{F}_{\text{ideal}}$ when there is no molecular interaction. $\mathscr{F}_{\text{ideal}}[\rho(r, \omega)]$ and $\Phi[\rho(r, \omega)]$ are also unique functionals of $\rho(r, \omega)$.

$$\mathscr{F}_{\text{ideal}}[\rho(r, \omega)] = k_B T \int dr \, d\omega \, \rho(r, \omega)[\ln(\Lambda\rho(r, \omega)) - 1] \tag{2.15}$$

where Λ is a quantum parameter.

The Ornstein–Zernike direct correlation function is defined by

$c(r_1, \omega_1; r_2, \omega_2)$

$$= \frac{1}{\rho(r_1, \omega_1)} \delta(r_1 - r_2)\delta(\omega_1 - \omega_2) - \frac{1}{k_B T} \frac{\delta^2 \mathscr{F}}{\delta\rho(r_1, \omega_1)\delta\rho(r_2, \omega_2)} \tag{2.16a}$$

$$= \frac{1}{k_B T} \frac{\delta^2 \Phi}{\delta\rho(r_1, \omega_1)\delta\rho(r_2, \omega_2)}. \tag{2.16b}$$

In an homogeneous liquid we may write

$$c(r_1, \omega_1; r_2, \omega_2) = c(r_{12}, \omega_1, \omega_2). \tag{2.17}$$

Finally the grand thermodynamic potential obeys a minimum principle:

$$(\delta\Omega/\delta\rho(r, \omega)) = (\delta\mathscr{F}/\delta\rho(r, \omega)) + V_{\text{ext}}(r, \omega) - \mu = 0 \tag{2.18}$$

and the one-particle direct correlation function is defined by $C(r, \omega)$:

$$k_B T C(r, \omega) = \delta\Phi/\delta\rho(r, \omega). \tag{2.19}$$

$-k_B T C(r, \omega)$ plays the role of an effective external potential.

For a more extensive discussion of the points in this section we refer the reader to other works (Evans 1979, Haymet and Oxtoby 1981, Sluckin 1981). We note, however, that a spherical harmonic expansion of $c(r_{12}, \omega_1, \omega_2)$ may be made, in the same vein as equation (2.1).

3. The nematic state

We consider the free energy of a fluid with constrained density $\rho(r, \omega)$, in an external potential $V(r, \omega)$, such that this state may be regarded as close to a locally stable

isotropic state with density $\rho_0(\omega) = n_I/4\pi$. Then the Helmholtz free energy is

$$F = \mathscr{F}_{\text{ideal}}[\rho(r,\omega)] - \Phi[\rho(r,\omega)] + \int V(r,\omega)\rho(r,\omega)\,dr\,d\omega. \qquad (3.1)$$

We make a functional expansion of $\Phi[\rho(r,\omega)]$ around $\Phi[\rho_0(\omega)]$, in powers of $\delta\rho(r,\omega) = \rho(r,\omega) - \rho_0(\omega)$, as far as second order in $\delta\rho(r,\omega)$. Then, using equations (2.16) and (2.19)

$$\Phi[\rho(r,\omega)] = \Phi[\rho_0(\omega)] + k_B T C_I \int \delta\rho(r,\omega)\,dr\,d\omega$$

$$+ \tfrac{1}{2} k_B T \int dr\,dr'\,d\omega\,d\omega'\,c_I(r'-r,\omega,\omega')\delta\rho(r,\omega)\delta\rho(r',\omega') + O(\delta\rho^3) \qquad (3.2)$$

where $C_I = C_0(\omega)$, the value of $C(r,\omega)$ in the isotropic state, and $c_I(r'-r,\omega,\omega')$ is defined in the isotropic state at density n_I.

We thus obtain, using equations (3.1), (3.2), (2.13) and (2.15) an approximation for the grand thermodynamic potential Ω, in the vicinity of the isotropic state:

$$\Omega = k_B T \int dr\,d\omega\,\{\rho(r,\omega)[\ln(\Lambda\rho(r,\omega)) - 1] - \Phi[\rho_0(\omega)]$$

$$+ \int dr\,d\omega\{\rho(r,\omega)[V(r,\omega) - \mu] - k_B T C_I\,\delta\rho(r,\omega)\}$$

$$- \tfrac{1}{2} k_B T \int dr\,dr'\,d\omega\,d\omega'\,c_I(r'-r,\omega,\omega')\,\delta\rho(r,\omega)\,\delta\rho(r',\omega'). \qquad (3.3)$$

The stable states obey the variational condition (2.18) on Ω. For these states

$$k_B T(\ln(\Lambda\rho(r,\omega)) - C_I - \int c_I(r'-r)\delta\rho(r',\omega')\,dr'\,d\omega' + V(r,\omega) - \mu = 0. \qquad (3.4)$$

The stability of the isotropic state demands that

$$k_B T[\ln(\Lambda\rho_0(\omega)) - C_I]\mu = 0. \qquad (3.5)$$

Substituting from equation (3.5) into (3.4) yields, for the anisotropic state with the same chemical potential μ as the isotropic state

$$\ln\left(\frac{\rho(r,\omega)}{\rho_0(\omega)}\right) = -\frac{1}{k_B T}\,V(r,\omega) + \int c_I(r'-r,\omega,\omega')\delta\rho(r',\omega')\,dr'\,d\omega' \qquad (3.6)$$

or

$$\rho(r,\omega) = \frac{n_I}{4\pi}\exp\left(-\frac{V(r,\omega)}{k_B T} + \int c_I(r'-r,\omega,\omega')\delta\rho(r',\omega')\,dr'\,d\omega'\right). \qquad (3.7)$$

This general formulation applies to uniform as well as non-uniform states. If we now specialise to the case when the anisotropic state is a uniform nematic, such that $V(r,\omega) = 0$, and

$$\rho(r,\omega) = \rho_N(\omega) = n_N f(\omega) \qquad (3.8)$$

we obtain

$$\rho_N(\omega) = \rho_0 \exp\left(\int d\mathbf{r} \, d\omega' \, c_I(\mathbf{r}, \omega, \omega')(\rho_N(\omega') - \rho_0)\right). \tag{3.9}$$

This is a self-consistent equation for $\rho_N(\omega)$. In order to locate the nematic–isotropic transition, it is necessary to combine equation (3.9) with the condition that the grand thermodynamic potentials in the isotropic and nematic phases are equal. From equation (3.3) we obtain

$$\Delta\Omega[\rho(\omega)] = \Omega[\rho(\omega)] - \Omega[\rho_0]$$

$$= k_B T \int d\mathbf{r} \, d\omega \left[\rho(\omega) \ln(\Lambda\rho(\omega)) - \rho_0 \ln(\Lambda\rho_0) - \delta\rho(\omega)\left(1 + C_I - \frac{\mu}{k_B T}\right)\right] \tag{3.10}$$

$$-\tfrac{1}{2} k_B T \int d\mathbf{r} \, d\mathbf{r}' \, d\omega \, d\omega' \, c_I(\mathbf{r}' - \mathbf{r}, \omega, \omega')\delta\rho(\omega)\delta\rho(\omega').$$

If $\rho(\omega) = \rho_N(\omega)$, we may apply equations (3.5) and (3.6) to yield

$$\frac{\Delta\Omega}{V}[\rho_N(\omega)] = k_B T \int d\omega [\rho_N(\omega) \ln(\rho_N(\omega)/\rho_0) - \delta\rho_N(\omega)]$$

$$-\tfrac{1}{2} k_B T \int c_I(\mathbf{r}, \omega, \omega')\delta\rho_N(\omega)\delta\rho_N(\omega') \, d\mathbf{r} \, d\omega \, d\omega' \tag{3.11}$$

where V is the volume of the system.

In order to locate the isotropic-nematic phase transition, (3.9) and (3.11) must be solved self-consistently; the Ornstein–Zernike direct correlation function must somehow be determined for the isotropic molecular fluid as a function of density and temperature.

Equation (3.9) and (3.11) may be combined to produce the *exact* result that

$$\frac{\Delta\Omega[\rho_N(\omega)]}{Vk_B T} = \int \delta\rho_N(\omega) \, d\omega \left(\int d\mathbf{r} \, d\omega' c_I(\mathbf{r}, \omega, \omega')\rho_0 - 1\right.$$

$$\left. +\tfrac{1}{2} \int \delta\rho_N(\omega')c_I(\mathbf{r}, \omega, \omega') \, d\mathbf{r} \, d\omega'\right). \tag{3.12}$$

This formula holds for the difference of grand thermodynamic potential between two locally stable states, one isotropic and one nematic, at the *same* chemical potential.

We note that in a more sophisticated theory the functional expansion (3.2) of $\Phi[\rho(\mathbf{r}, \omega)]$ could be taken to higher order in $\delta\rho(\mathbf{r}, \omega)$. The next term in this expansion is

$$\tfrac{1}{6} k_B T \int d\mathbf{r}_1 \, d\mathbf{r}_2 \, d\mathbf{r}_3 \, d\omega_1 \, d\omega_2 \, d\omega_3 \, \delta\rho(\mathbf{r}_1, \omega_1)\delta\rho(\mathbf{r}_2, \omega_2)\delta\rho(\mathbf{r}_3, \omega_3)c_3(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \mathbf{r}_3, \omega_3)$$

where $c_3(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2; \mathbf{r}_3, \omega_3)$ is the three-particle direct correlation, and is the functional derivative

$$\delta c(\mathbf{r}_1, \omega_1; \mathbf{r}_2, \omega_2)/\delta\rho(\mathbf{r}_3, \omega_3).$$

However, it seems likely that this term is not important for many physical purposes although in quantitative applications it may well be necessary to evaluate it.

3.2. *Mean field theory in spherical harmonic language*

We now re-express the functional $\Delta\Omega[\rho_N(\omega)]$ in equation (3.11) in the conventional spherical harmonic language. The theory will then be identical to conventional mean-field theories, but with a new identification of the mean-field parameters.

We define, analogously with equation (2.1)

$$c_I(r, \omega, \omega') = \sum_{l_1, l_2, l; \, m_1, m_2, m} c_I(l_1, l_2, l; r) Y_{lm}(\omega_r) C(l_1, l_2 \, l; m_1 m_2 m)$$

$$\times Y_{l_1 m_1}(\omega) Y_{l_2 m_2}(\omega'). \tag{3.14}$$

We use the expansion (2.4)

$$\rho_N(\omega) - \rho_0 = \frac{1}{4\pi} \delta n_0 + \sum_{\text{even } l > 0} \left(\frac{2l+1}{4\pi}\right) n_l P_l(\cos\theta) \tag{3.15}$$

where δn_0 is the change in density between the isotropic and nematic phases and define

$$c_I(l_1, l_2, l) = \int \mathrm{d}r \, c_I(l_1, l_2, l; r). \tag{3.16}$$

The functional (3.11) may now be shown to be equal to

$$\frac{\Delta\Omega}{V k_B T} = \int \mathrm{d}\omega \, \rho_N(\omega) \ln\left(\frac{\rho_N(\omega)}{\rho_0}\right) - k_B T \delta n_0$$

$$- \frac{k_B T}{2} \sum_{\text{even } l > 0} c_I(l, l, 0) n_l^2 \left(\frac{2l+1}{4\pi}\right)^{1/2} - \frac{k_B T}{2} \left(\frac{1}{4\pi}\right)^{1/2} c_I(0, 0, 0) \delta n_0^2. \tag{3.17}$$

This may now be expressed in terms of the fractional density change

$$\eta = (n_N - n_I)/n_I \tag{3.18}$$

the angular distribution functions $f_N(\omega)$ defined in equation (2.8), and the order parameters $\bar{P}_l$ defined in equation (2.11). We obtain

$$\Delta\Omega/n_I V k_B T = \int \mathrm{d}\omega \, (1+\eta) f_N(\omega) \ln[(1+\eta) 4\pi f_N(\omega)] - \eta - \frac{1}{2}\left(\frac{1}{4\pi}\right)^{1/2} n_I c_I(0, 0, 0) \eta^2$$

$$- \frac{1}{2}\left(\frac{1}{4\pi}\right)^{1/2} n_I (1+\eta)^2 \sum_{\text{even } l > 0} (2l+1)^{1/2} c_I(l, l, 0) \bar{P}_l^2. \tag{3.19}$$

This may be cast in familiar form in the following way.

(i) We define the potential parameters U_l by

$$U_l[n_I, T] = k_B T[(2l+1)/4\pi]^{1/2} n_I c_I(l, l, 0; n_I, T). \tag{3.20}$$

(ii) We separate the ideal gas contribution to the free energy into orientational and density components:

$$\int \mathrm{d}\omega \, (1+\eta) f_N(\omega) \ln[(1+\eta) 4\pi f_N(\omega)]$$

$$= (1+\eta) \ln(1+\eta) + (1+\eta) \int f_N \ln(4\pi f_N(\omega)) \, \mathrm{d}\omega. \tag{3.21}$$

(iii) We make a small η harmonic expansion of the density contribution to the free energy $\Delta\Omega$ (Evans 1979, Sluckin 1981)

$$k_B T[(1+\eta)\ln(1+\eta) - \eta - \tfrac{1}{2}(4\pi)^{-1/2} n_I c_I(0,0,0)\eta^2]$$

$$= \tfrac{1}{2}\eta^2 k_B T[1 - (4\pi)^{-1/2} n_I c_I(0,0,0)] + o(\eta^3) \tag{3.22}$$

$$= \tfrac{1}{2} n_I \chi^{-1} \eta^2 + o(\eta^3) \tag{3.23}$$

where χ is the isothermal compressibility of the isotropic liquid at density n_I and temperature T.

We thus obtain from equation (3.19) a functional form for the change in grand thermodynamic potential, as a functional of the angular distribution function $f_N(\omega)$, the order parameters $\bar{P}_l$, and the fractional density change η

$$\frac{\Delta\Omega}{n_I V} = \frac{1}{2n_I}\chi^{-1}\eta^2 + k_B T(1+\eta)\int d\omega\, f_N(\omega)\ln 4\pi f_N(\omega) - \tfrac{1}{2}(1+\eta)^2 \sum_{\text{even } l\geq 2} U_l \bar{P}_l^2. \tag{3.24}$$

The functional (3.24) is stationary for equilibrium or meta-equilibrium. In such a situation

$$f_N(\omega) = \frac{1}{4\pi Z}\exp\left(\sum_l (1+\eta)\bar{P}_l P_l(\cos\theta) U_l / k_B T\right) \tag{3.25}$$

$$Z = \frac{1}{4\pi}\int \exp\left(\sum_l (1+\eta)\bar{P}_l P_l(\cos\theta) U_l / k_B T\right) d\omega \tag{3.26}$$

$$\eta = n_I k_B T \chi \ln Z. \tag{3.27}$$

One may also derive an analogue to equation (3.12), giving an exact result for $\Delta\Omega$ in terms of $\bar{P}_l$ and η

$$\frac{\Delta\Omega}{n_I V}[\eta, \bar{P}_l] = -\frac{1}{n_I}\eta\chi^{-1}(1+\eta/2) + \tfrac{1}{2}\sum_{\text{even } l > 0}(1+\eta)^2 U_l \bar{P}_l^2. \tag{3.28}$$

4. Applications of the density functional theory

4.1. Relationship to other mean field theories

4.1.1. Maier–Saupe theory. This follows immediately from equation (3.24), assuming that the isothermal compressibility χ in the isotropic phase is zero, and hence that the fractional density change at the nematic–isotropic transition η is zero. The $\{U_l\}$ may now be treated as phenomenological parameters. In particular, if all $U_l = 0$ apart from U_2, it is known that $k_B T_{N-I} = 0.2203 U_2$. This is of course an idealised assumption, though in practise we expect that $\lim_{l\to\infty} U_l = 0$. A further discussion is given in the book edited by Luckhurst and Gray (1979).

4.2.2. Onsager theory. Modern theories of liquids provide a diagrammatic expansion for $c(r, \omega, \omega')$ (Hansen and McDonald 1976). The leading, density independent term in this expansion is the Mayer f function

$$f(r, \omega, \omega') = \exp[-U(r, \omega, \omega')/k_B T] - 1. \tag{4.1}$$

In the Onsager approximation, we approximate $c(r, \omega, \omega')$ by $f(r, \omega, \omega')$, and assume the only intermolecular interactions to be volume exclusion effects. Thus in this approximation

$$c(r_{12}, \omega_1, \omega_2) = -1 \quad \begin{array}{l} \text{if a configuration } (0, \omega_1), (r_{12}, \omega_2) \text{ is} \\ \text{forbidden on volume exclusion grounds.} \end{array}$$

$$= 0 \quad \text{otherwise.}$$

If we also assume $\chi = 0$, we may rewrite equations (3.11) and (3.25) as

$$\frac{\Delta\Omega}{n_I V} = k_B T\left(\int f_N(\omega) \ln 4\pi f_N(\omega) \, d\omega + \tfrac{1}{2} n_I \int f_N(\omega) f_N(\omega') v_{excl}(\omega, \omega') \, d\omega \, d\omega' \right) \tag{4.3}$$

where

$$v_{excl}(\omega, \omega') = \int_{\substack{\text{forbidden} \\ \text{configurations}}} d r.$$

This is precisely the Onsager formulation. It is immediately clear that in this approximation there are no temperature effects, and that any transition is dependent only on n_I, and molecular shape.

Poniewerski and Stecki (1979) have derived expressions for the Frank elastic constants in terms of $c(r, \omega, \omega')$; they have labelled the approximation $c(1, 2) = -1$ for volume excluded configurations as the Onsager approximation. Priest (1973) has effectively used this approximation to calculate the Frank elastic constants.

4.1.3. Generalised mean field theory. We now discuss approximation methods which may be useful in computing the spherical harmonics $C_I(l_1, l_2, l; r)$. Under some circumstances (Hansen and McDonald 1976) one may divide the intermolecular interaction into a reference and a perturbation component:

$$U(r_{12}, \omega_1, \omega_2) = U_0(r_{12}, \omega_2) + \lambda U_1(r_{12}, \omega_1, \omega_2) \tag{4.4}$$

The parameter λ is a perturbation parameter. Thermodynamic functions of the real liquid may then be expressed in terms of thermodynamic functions of the reference liquid interacting with the potential U_0, in a perturbation series in λ. The following exact formula is obtained (Evans and Schirmacher 1978) for the direct correlation function

$$c(r_{12}, \omega_1, \omega_2) - c_0(r_{12}, \omega_1, \omega_2)$$

$$= -\frac{1}{2k_B T} \frac{\delta^2}{\delta\rho(r_1\omega_1)\delta\rho(r_2\omega_2)} \int_0^1 d\lambda \int d r_1' \, d r_2' \, d\omega_1' \, d\omega_2'$$

$$\times \rho_\lambda^{(2)}(r_1', \omega_1'; r_2', \omega_2') U_1(r_{12}', \omega_1', \omega_2') \tag{4.5}$$

where the real liquid has $\lambda = 1$, the subscripts $0, \lambda$ represent properties of the reference system and the system with potential $U_0 + \lambda U_1$ respectively, and

$$\rho^{(2)}(r_1, \omega_1; r_2, \omega_2) = \rho(r_1, \omega_1)\delta(r_{12})\delta(\omega_{12}) + \rho(r_1, \omega_1)\rho(r_2, \omega_2)g(r_{12}, \omega_1, \omega_2) \tag{4.6}$$

is the two-particle density distribution function, and $g(r_{12}, \omega_1, \omega_2)$ is the usual pair distribution function.

If we suppose that the binding energy of the liquid is due to isotropic forces, and the anisotropic forces are 'weak' and long ranged in character, we may suppose that

U_0 and hence c_0, g_0 are isotropic

$$U_0(\boldsymbol{r}_{12}, \omega_1, \omega_2) = U_0(\boldsymbol{r}_{12}) \qquad g_0(\boldsymbol{r}_{12}, \omega_1, \omega_2) = g_0(\boldsymbol{r}_{12}) \qquad (4.7)$$
$$c_0(\boldsymbol{r}_{12}, \omega_1, \omega_2) = c_0(\boldsymbol{r}_{12})$$

whereas U_1 only has anisotropic components. If we further make the approximations in (4.5) that $\rho_\lambda^{(2)} = \rho_0^{(2)}$ and ignore the density dependence of the pair distribution function in the functional differentiation in equation (4.5), we obtain

$$c(\boldsymbol{r}_{12}, \omega_1, \omega_2) = c_0(\boldsymbol{r}_{12}) - (1/k_B T)\, U_1(\boldsymbol{r}_{12}, \omega_1, \omega_2) g_0(\boldsymbol{r}_{12}). \qquad (4.8)$$

One may easily see, comparing the harmonic expansions (2.1) and (3.14), that (4.8) implies ($l \neq 0$)

$$c(l_1, l_2, l, r) = -(1/k_B T) U_1(l_1, l_2, l, r) g_0(r) \qquad (4.9)$$

and hence the effective potential, from equation (3.20), is approximated by

$$U_l = -\left(\frac{2l+1}{4\pi}\right)^{1/2} n_I \int g_0(r) U_1(l, l, 0, r)\, \mathrm{d}r. \qquad (4.10)$$

This result has previously been obtained, by a different method, by Luckhurst and Gray (1979).

The very simplest approximation, often called the random phase approximation (RPA), consists of putting $g_0(r) = 1$ in equation (4.10); this corresponds to the earliest efforts of liquid crystal mean-field theory (Maier and Saupe 1958, 1959, 1960). A more sophisticated approximation consists of replacing $\rho_\lambda^{(2)}(\boldsymbol{r}_{12}, \omega_1, \omega_2)$ by $\rho_0^{(2)}(\boldsymbol{r}_{12}, \omega_1, \omega_2)$ in equation (4.5), but then *not* ignoring the density dependence of the pair distribution function. In atomic fluids this approximation has been labelled the mean density approximation (MDA) (Henderson and Ashcroft 1976). Work on structure factors for low q in atomic liquids, which uses essentially equation (4.5), has shown that there can be significant differences between the MDA and the RPA (McLaughlin and Young 1982).

We note, however, that the result (4.10) or variations thereof is only likely to give even approximate results if the separation of the potential into an isotropic portion U_0 and a weak anisotropic portion U_1 gives a good description of the liquid structure. The crucial approximation is that $\rho_\lambda^{(2)}(\boldsymbol{r}_{12}, \omega_1, \omega_2) = \rho_0^{(2)}(\boldsymbol{r}_{12}, \omega_1, \omega_2)$ over the range of r_{12} in which $U_1(l, l, 0; r_{12})$ is large; in this case the liquid structure is well described by a liquid interacting with potential U_0. This is certainly true for some model systems, but in real liquid crystals there are likely to be significant steric effects. As yet, however, there has not been much work on the determination of the direct correlation function of molecular fluids of strongly anisotropic molecules (Blum and Torruella 1972).

4.1.4. Generalised van der Waals theory.

In this approach (Gelbart and Ben Shaul 1982) a nematogen with distribution function $\rho(\boldsymbol{r}, \omega)$, at uniform density n, is thought of as consisting of a reference system of hard anisotropic molecules with volume v_0, while in addition these molecules have an attractive interaction $U_1(r, \omega, \omega')$. The Helmholtz free energy of the nematogen may then be written, in the spirit of perturbation theory,

$$F = F_{\text{reference}} + F_{\text{perturbation}}. \qquad (4.11)$$

The free energy of the reference system of anisotropic hard molecules is

$$F_{\text{reference}} = \mathscr{F}_{\text{ideal}}[\rho(r, \omega)] - \tfrac{1}{2} k_B T (1 - \eta_0)^{-1}$$

$$\times \int \rho(r, \omega)\rho(r', \omega')M(r' - r, \omega, \omega') \, dr \, dr' \, d\omega \, d\omega' \qquad (4.12)$$

where $\eta_0 = nv_0$ is the packing fraction and

$$M(r' - r, \omega, \omega') = -1 \qquad \text{if molecules at } (r, \omega), (r'\omega') \text{ overlap}$$

$$= 0 \qquad \text{otherwise.}$$

We note that $\int M(r, \omega, \omega') \, dr = v_{\text{excl}}(\omega, \omega')$ and that apart from the factor of $(1 - \eta_0)^{-1}$ equation (4.12) resembles equation (4.3).

$$F_{\text{perturbation}} = \tfrac{1}{2} \int \rho(r, \omega)\rho(r', \omega')U_1(r' - r, \omega, \omega')g_{\text{HC}}(r' - r, \omega, \omega') \, dr' \, d\omega \, d\omega'. \qquad (4.13)$$

Here $g_{\text{HC}}(r, \omega, \omega')$ is the pair distribution function of the reference system, which for many purposes may be approximated by

$$g_{\text{HC}}^{\text{app}}(r, \omega, \omega') = M(r, \omega, \omega') + 1. \qquad (4.14)$$

This formulation may now be compared with the general formulation (3.11). From the point of understanding the fluid nematic properties, it is equivalent to making the approximation

$$c(r, \omega, \omega') = c_{\text{HC}}(r, \omega, \omega') - \frac{1}{k_B T} U_1(r, \omega, \omega') \qquad (4.15a)$$

$$c_{\text{HC}}(r, \omega, \omega') = -(1 - \eta_0)^{-1}M(r, \omega, \omega'). \qquad (4.15b)$$

Equation (4.15a) has been written down as equation (4.8) above; the only difference is that here $c_0(r, \omega, \omega') = c_{\text{HC}}(r, \omega, \omega')$ is obtained using the recipe (4.15b).

4.1.5. Landau-de Gennes theory.

In the Landau–de Gennes theory of the isotropic-nematic transition (de Gennes 1969, Stephen and Straley 1974) the Gibbs free energy is written as a power-law expansion around the isotropic equilibrium position. We have preferred to use the grand thermodynamic potential per particle; with this slight alteration we have

$$\Delta\Omega/n_1 V = a\bar{P}_2^2 + b\bar{P}_2^3 + c\bar{P}_2^4. \qquad (4.16)$$

An association is traditionally made between this expansion and terms in the Maier–Saupe expansion; in that expansion as in ours the full one-particle orientational distribution entropic contribution to the free energy is kept (a power-law expansion of this term shows very slow convergence). We may make a similar association of terms between our functional expansion in $\delta\rho(r, \omega)$ and the expansion (4.16), thus assigning a microscopic value to a, b, c in (4.16). We are not optimistic that correct evaluation will in fact explain the properties of the nematic–isotropic transition; we expect (a), that in the mean field regime the convergence will be sufficiently slow that higher order terms must be considered, and (b), that orientational fluctuations not included in (4.16) as it stands will be important and depress $T_{\text{N-I}}$.

For simplicity we ignore all terms in the functional expansion of $\Delta\Omega$ except those in $\bar{P}_2$. We now consider the expansion of $\Delta\Omega$ (3.11), using the expansion of $\delta\rho(r, \omega)$

given by equation (2.3). It is also necessary to consider the expansion to $O(\delta\rho^4)$, and this involves terms in $c_3(r_1, \omega_1; r_2, \omega_2; r_3, \omega_3)$ and

$$c_4(r_1, \omega_1; r_2, \omega_2; r_3, \omega_3; r_4, \omega_4) = [\delta/\delta\rho\,(r_4, \omega_4)][c_3(r_1, \omega_1; r_2, \omega_2; r_3, \omega_3)]. \tag{4.17}$$

Straightforward though tedious analysis yields the results

$$a = \tfrac{1}{2}(5k_BT - U_2) \qquad b = -\tfrac{25}{21}k_BT - \tfrac{1}{6}U_3 \qquad c = \tfrac{125}{28}k_BT - \tfrac{1}{24}U_4 \tag{4.18a, b, c}$$

where

$$U_3 = \frac{125n^2}{(4\pi)^3}k_BT\int c_3(r, \omega_1; r_2, \omega_2; r_3, \omega_3)P_2(\cos\theta_1)P_2(\cos\theta_2)$$

$$\times P_2(\cos\theta_3)\,dr_2\,dr_3\,d\omega_1\,d\omega_2\,d\omega_3 \tag{4.19a}$$

$$U_4 = \frac{625n^3}{(4\pi)^4}k_BT\int c_4(r_1, \omega_1; r_2, \omega_2; r_3, \omega_3; r_4, \omega_4)P_2(\cos\theta_1)P_2(\cos\theta_2)P_2(\cos\theta_3)$$

$$\times P_2(\cos\theta_4)\,dr_2\,dr_3\,dr_4\,d\omega_1\,d\omega_2\,d\omega_3\,d\omega_4. \tag{4.19b}$$

In the usual formulation

$$a = a'(T - T^*). \tag{4.20}$$

Using (4.15) and the general formula (4.10) for U_2, we may derive

$$U_2 \simeq k_BTc_{2HC} + U_{2att} \tag{4.21}$$

where k_BTc_{2HC} is the contribution of steric effects to u_2, and u_{2att} is the contribution of longer-range attractive forces. We thus obtain

$$a = \tfrac{1}{2}[k_BT(5 - c_{2HC}) - U_{2att}] \tag{4.22}$$

$$= \tfrac{1}{2}k_B(5 - c_{2HC})(T - T^*) \tag{4.23}$$

where

$$T^* = u_{2att}(5 - c_{2HC})^{-1}. \tag{4.24}$$

4.2. Density change at the isotropic–nematic transition

Given the approximate functional (3.25) the nematic–isotropic transition takes place when

$$\Delta\Omega = 0$$

where $\Delta\Omega$ is described by the 'exact' result (3.29). Hence at T_{N-I}

$$\eta\chi^{-1}(1 + \tfrac{1}{2}\eta) = \tfrac{1}{2}n_I(1 + \eta)^2\sum_l U_l\bar{P}_l^2 \tag{4.25}$$

or to lowest order in the 'small' parameter χ

$$\eta = \tfrac{1}{2}n_I\chi\sum_l U_l\bar{P}_l^2. \tag{4.26}$$

If we regard this result as a perturbation expansion in χ, $\bar{P}_l(T_{N-I})$ can be calculated from (3.11), (3.26) and (3.27) assuming $\eta = 0$.

Thus for the Maier–Saupe fluid, in which $\bar{P}_2(T_{N-I}) = 0.44$,

$$U_2 = 4.54k_BT_{N-I} \qquad \text{and} \qquad \eta = 0.44n_I\chi k_BT_{N-I}. \tag{4.27}$$

We note that $n_1 k_B T \chi = S_d(0)$, the contribution of density fluctuations to the structure factor in the forward direction. Typically (Evans and Schirmacher 1978) this has a value in the range 0.025–0.05. Substituting this into (4.13) yields typical values of η of around 1–2%, which is in qualitative agreement with experiment.

5. Discussion

The distribution function $\rho(r, \omega)$ obeys the (exact) first BBGKY equation, which may be written either in terms of the direct correlation function

$$D \ln \rho(r, \omega) = \int c(r' - r; \omega, \omega') D' \rho(r', \omega') \, dr' \, d\omega' \tag{5.1}$$

or in terms of the pair-distribution function

$$D \ln \rho(r, \omega) = -\frac{1}{k_B T} \int \rho(r', \omega') g(r' - r, \omega, \omega') D' U(r' - r, \omega, \omega') \, dr' \, d\omega' \tag{5.2}$$

where D is a differential operator, and the differentiation may be taken covariantly with respect to angle or space. Molecular field theory assumes that short-range correlations are the same in the isotropic and nematic phases. The mathematical articulation of this assumption in our case is the validity of the functional expansion (3.2). Variational solution of the Euler–Lagrange equations of this expansion yields the solution for $\rho(r, \omega)$ given in (3.6). One may compare (3.6) and (5.1); it is apparent that the molecular field theory is equivalent to replacing the true (nematic) direct correlation function $c_N(r^1 - r, \omega, \omega')$ in (5.1) by its value in the isotropic phase. On the other hand, it is possible to consider (5.2) instead of (5.1) and replace the true $g(r, \omega, \omega')$ by $g_I(r, \omega, \omega')$. This approach has been explored by Woo and co-workers (Shih *et al* 1976, Lee and Woo 1977 and Chakravarty and Woo 1975a, b).

Clearly this approach is closely related to ours. We prefer our approach for a number of reasons. Firstly, the direct correlation function is a shorter range function than the pair distribution function, and experience in the theory of non-uniform fluids shows that approximation of $c(r)$ is more reliable than approximation of $g(r)$. Secondly, (5.2) is a rather unstable equation from a computing point of view. In particular, the derivative $DU(r, \omega, \omega')$ is likely to be large just where the pair distribution function is small, and errors are likely to be magnified. Similar problems bedevil the evaluation of the pressure through the virial theorem. Thirdly, use of equation (5.2) obscures the crucial role played in molecular field theory by the direct correlation function; (5.1) is a variational equation derived from the exact expression for the free energy, whereas (5.2) is a force balance equation and is not derivable from a variational approach.

Because of the crucial role played by the direct correlation function, our approach emphasises the importance of studying this quantity in isotropic molecular fluids with strongly anisotropic components. For atomic fluids, perturbation theories are now reasonably successful in approximating the direct correlation function. The Percus–Yevick and HNC equations have been solved for molecular fluids with spherical cores but anisotropic long-range interactions (Gray and Gubbins 1982); however, when the hard-core interactions are themselves non-spherical there has been little work, partly because of mathematical difficulties—a formal approach has been studied by Wertheim

(1980, 1981)—and partly because simple molecular fluids can often be treated more fruitfully by considering site–site pair correlation functions (Gray and Gubbins 1982).

In future papers in this series we shall extend the present work to deal with inhomogeneous liquid-crystal-like materials, and we shall study from a microscopic viewpoint, the surface tensions, surface widths and excess properties at the isotropic liquid–vapour, nematic–vapour, and isotropic–nematic interfaces. The free energy functional will be that used in equations (3.1) and (3.2) and expansions will be made in gradients of the density n_0 and the order parameters $\bar{P}_l$, following the method outlined by us previously (Sluckin 1981).

Acknowledgments

References

Blum L and Torruella A J 1972 *J. Chem. Phys.* **56** 303
Chakravarty S and Woo C W 1975a *Phys. Rev.* A **11** 713
—— 1975b *Phys. Rev.* A **12** 245
Chandrasekhar S 1977 *Liquid Crystals* (Cambridge: CUP)
De Gennes P G 1969 *Phys. Lett.* A **30** 454
—— 1974 *The Physics of Liquid Crystals* (London: Oxford University Press)
Evans R 1979 *Adv. Phys.* **28** 143–200
Evans R and Schirmacher W 1978 *J. Phys. C: Solid State Phys.* **11** 2437.
Gelbart W M and Ben Shaul A 1982 *J. Chem. Phys.* **77** 916 and references therein
Gray C G and Gubbins K E 1982 *Theory of Molecular Fluids* (London: OUP) in press
Hansen J P and McDonald I R 1976 *Theory of Simple Liquids* (New York: Academic)
Haymet A D J and Oxtoby D W 1981 *J. Chem. Phys.* **74** 2559
Henderson R L and Ashcroft N W 1976 *Phys. Rev.* A **13** 859
Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
Lee M A and Woo C W 1977 *Phys. Rev.* A **16** 750
Luckhurst G R and Gray G W (eds) 1979 *The Molecular Physics of Liquid Crystals* (New York: Academic)
McLaughlin I L and Young W H 1982 *J. Phys. C: Solid State Phys* **15** 1121
Maier W and Saupe A 1958 *Z. Naturf.* **13** 564
—— 1959, *Z. Naturf.* **14** 882
—— 1960 *Z. Naturf.* **15** 287
Nelson D R and Toner J 1981 *Phys. Rev.* B **24** 363
Onsager L 1949 *Ann. NY Acad. Sci.* **51** 627
Poniewierski A and Stecki J 1979 *Mol. Phys.* **38** 1931
Priest R G 1973 *Phys. Rev.* A **7** 720
Ramakrishnan T V and Yussouff M 1979 *Phys. Rev.* B **19** 2775
Shih Y M, Lin-Liu Y R and Woo C W 1976 *Phys. Rev.* A **14** 1895
Sluckin T J 1981 *Mol. Phys.* **43** 817
Stecki J and Kloczkowski A 1979 *J. Physique* **40** C3-360
Stephen M J and Straley J P 1974 *Rev. Mod. Phys.* **46** 617
Wertheim M S 1980 *J. Chem. Phys.* **73** 1398
—— 1981 *J. Chem. Phys.* **74** 2466