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Molecular theory of liquid crystals: Application to the nematic phase

Y. Singh
School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801
*and Department of Physics, Banaras Hindu University, Varanasi 221005, Uttar Pradesh, India**

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A density-functional description of liquid crystals is developed. Formally exact expansions for thermodynamic functions in terms of a direct-correlation function are given. Approximations to the direct-correlation function lead to different versions of the molecular-field theories of liquid crystals. The properties of the uniform nematic phase including the isotropic-nematic phase transition at constant pressure are discussed. Expressions are given for the change in density and order parameters at the transition in terms of the direct-correlation function of the isotropic phase. Methods for calculating the direct-correlation functions of the isotropic phase are also discussed. A formal theory for the statistical mechanics of a nonuniform liquid crystal is developed and used to derive expressions for the Frank elastic constants. This approach provides a starting point for the investigation of the phase transitions in the liquid crystals and the properties of inhomogeneous systems. A microscopic description of the Landau—de Gennes theory is also given.

I. INTRODUCTION

Liquid crystals constitute a state of matter occurring on the phase diagram between the ordered solid phase where the mobility of individual molecules is restricted and the isotropic phase where molecular mobility and general lack of molecular order exist. As such, it is an unusually fascinating state because it combines properties of both phases. Liquid crystals, with which we are concerned here, may be of the nematic, cholesteric, or smectic type. In the nematic phase, the molecular centers of gravity are disordered as in a liquid, but we have a statistically parallel orientation of the long axes of the molecules along an axis (the director $\vec{n}$). In all known cases, there appears to be complete rotational symmetry around the preferred axis. Nematic phase usually occurs only with materials which do not distinguish between right and left and the molecules of which have rodlike shape. The cholesteric phase is simply a helically ordered nematic phase.

Smectic liquid crystals have stratified structure with the long axes of the rodlike or lathlike molecules parallel to each other in the layers. Since a variety of molecular arrangements are possible within each stratification, a number of (eight are known so far) smectic phases are possible. In smectic A the molecules are upright in each layer with their centers irregularly specified in a liquidlike fashion. Smectic B differs from A in that the molecular centers in each layer are hexagonal close packed. Smectic C is a tilted form of smectic A. If in addition to the tilt there is an ordered arrangement within each layer, it is labeled B_C. Other smectic modifications have more complex structure.[1]

The theory of liquid crystals has been developing in two major directions. One, using the phenomenological theory of Landau and de Gennes,[2] in which the Helmholtz free energy is expanded in powers of the *order parameter* and its gradient, requiring in the process five or more adjustable parameters to be determined by experiments. While this theory is physically appealing and mathematically convenient, it has many drawbacks, including lack of quantitative predictive power about the phase diagram.[3] In the *molecular-field* theories[4,5] one begins with a model, be it in the form of rods or interparticle potentials, and proceeds to calculate *solvent mediated anisotropic external potential* (effective one-body potential or pseudopotential) acting on each individual molecule. Such calculation needs full knowledge of pair-correlation functions.[6] For a potential which mimics all the important features of molecular structure this approach includes lengthy and complicated mathematical derivation and numerical computation. As a consequence, too many simplifying approximations are made—in the choice of models, in the statistical mechanical approximation schemes, and in the evaluation of the correlation functions and thermodynamic properties.[1,6]

In the view of many workers[7,8] orientational order in liquid crystals results primarily from the short-range highly anisotropic repulsive forces between rodlike molecules. The high density of the liquid is achieved by the intermolecular attractions which are assumed to be isotropic. On the other hand, the Maier-Saupe theory[4] and its modifications[9–12] and extensions[5,13] attribute the formation of the ordered phase to the anisotropic attractive interactions, the repulsive interactions are assumed to be isotropic, at least to a first approximation, and serve to provide a positive pressure. The mean-field averaging of the long-range attraction is obtained in a phenomenological way neglecting the coupling between radial and orientational correlations.[14]

There have been a number of attempts[11,15–18] in the past to study the nematic-isotropic phase transition by incorporating both anisotropic intermolecular repulsions and attractions. Some of these theories are successful in predicting certain thermodynamic properties of common nematogens, for example, the phase diagram of homologous series, qualitative correct temperature dependence of order parameter, etc., but very poor in predicting volume changes at transitions, latent heats, maximum supercooling temperatures, etc. The reason for at least some of their shortcomings is quite obvious. As none of them take full account of the orientational and spatial correlations between particles and treat both attractive and repulsive branches of intermolecular interactions accurately, they cannot be expected to be quantitative.

In a recent publication Singh and Singh[6] have developed a statistical mechanical perturbation theory to describe the equilibrium properties of the nematic phase. In this theory the reference potential is nonspherical and consists of the short-range rapidly varying repulsive part of the pair potential. It was shown that the coupling between the angular pair correlation and isotropic dispersion interaction which does not play any role in the Maier-Saupe-type theory, is very important in controlling the properties of the ordered phase. The theory was applied to study the isotropic-nematic transition for model potentials.[6,19]

In this paper we first describe (Sec. II) a density-functional theory which allows us to construct formally exact expansions for thermodynamic functions in terms of the direct-correlation functions and single-particle density distribution. The direct-correlation function which appears in these expressions is a *functional* of the single-particle density distribution and the pair interactions. Functional Taylor expansion is used in Sec. III to derive the expressions for the single-particle density distribution and free energy for a nonuniform classical system subjected to an external potential. The density distribution is expressed in terms of order parameters to characterize crystalline solids, different phases of liquid crystals, and isotropic liquids.

In Sec. IV we describe the equilibrium properties of the nematic phase and isotropic-nematic transition at constant pressure. Section V is devoted to the derivation of expressions for the Frank elastic constants using the formalism of Sec. III. In the Appendix we discuss some of the approximations made in Sec. IV and give a microscopic derivation of the Landau—de Gennes theory.

II. FORMAL THEORY OF THE LIQUID-CRYSTALLINE PHASE

We consider a system of nonspherical molecules of arbitrary symmetry contained in a volume V at temperature T. When there are N particles in the system, the configurational energy U is approximated by

$$U(\bar{x}_1,\ldots,\bar{x}_N)=\sum_{i=1}^{N} U^e(\bar{x}_i)+\sum_{i>j=1}^{N} U(\bar{x}_i,\bar{x}_j)\ , \qquad (2.1)$$

where, for economy of notation, we use vector $\bar{x}_i$ to indicate both the location $\bar{r}_i$ of the center of the ith molecule and its relative orientation Ω_i described by Euler angles θ_i, ϕ_i, and χ_i. The volume element $d\bar{x}_i$ is equivalent to $d^3r_i d\Omega_i$ where $d^3r = dx\,dy\,dz$ and

$$d\Omega=(1/8\pi^2)\sin\theta\, d\theta\, d\phi\, d\chi\ .$$

$U^e(\bar{x}_i)$ is the potential energy of a molecule at position r_i with relative orientation Ω_i due to external forces, and $U(\bar{x}_i,\bar{x}_j)$ is the intermolecular pair potential for molecules i and j.

The grand partition function of the system is

$$\Xi=e^W=\sum_{N=0}^{\infty}\frac{1}{N!}\int\cdots\int\left[\prod_{i=1}^{N} z(\bar{x}_i)\right]\times\left[\prod_{\substack{i>j=1\\ i<j}}^{N}[1+f(\bar{x}_i,\bar{x}_j)]\right]\times\prod_{i=1}^{N} d\bar{x}_i\ , \qquad (2.2)$$

where

$$z(\bar{x}_i)=\frac{1}{\Lambda}\exp[\beta\mu-\beta U^e(\bar{x}_i)]=\frac{1}{\Lambda}\exp[\psi(\bar{x}_i)]\ ,$$

$$f(x_i,x_j)=\exp[-\beta U(x_i,x_j)]-1\ ,$$

and

$$\beta=(kT)^{-1}\ ,$$

μ is the chemical potential and

$$\Lambda=\int\exp(-\beta E_k)dp_1\cdots dp_s/h^s\ ,$$

where s is the number of degrees of freedom of a molecule and E_k is its kinetic energy. Each integration in (2.2) is extended to the sample volume V for positions and to the usual domains of $0\le\theta\le\pi$, $0\le\phi\le2\pi$, and $0\le\chi\le2\pi$ for angles.

From (2.2) one obtains

$$\frac{\delta W}{\delta\psi(\bar{x}_i)}=\langle\rho(\bar{x}_i)\rangle\equiv\rho(\bar{x}_i) \qquad (2.3)$$

and

$$\frac{\delta^2 W}{\delta\psi(\bar{x}_i)\delta\psi(\bar{x}_j)}=\langle\delta\rho(\bar{x}_i)\delta\rho(\bar{x}_j)\rangle=\rho(\bar{x}_i)\delta(\bar{x}_i-\bar{x}_j)+\rho(\bar{x}_i)\rho(\bar{x}_j)h(\bar{x}_i\bar{x}_j)\ , \qquad (2.4)$$

where $\langle\ \rangle$ represents the ensemble average, $\delta\rho(\bar{x}_i)$ represents the fluctuation in the single-particle density distribution at $\bar{x}_i$, and $h(\bar{x}_i,\bar{x}_j)$ is the total pair-correlation function.

We define a reduced Helmholtz free energy by

$$\beta F=\int\rho(\bar{x})\psi(\bar{x})d\bar{x}-W\ . \qquad (2.5)$$

The functional derivative of βF with respect to $\rho(\bar{x})$ is[20]

$$\frac{\delta(\beta F)}{\delta\rho(\bar{x})}=\psi(\bar{x})\ . \qquad (2.6)$$

Thus βF is the natural functional of $\rho(\bar{x})$. In fact (2.5) is the Legendre transform which transforms from the potential $\psi(\bar{x})$ as a variable to the density $\rho(\bar{x})$ as a variable.

In general, one writes for single-particle density distribution[20]

$$\rho(\bar{x})=\frac{e^{\psi(\bar{x})+c_1(\bar{x})}}{\Lambda} , \tag{2.7}$$

where $-kTc_1(\bar{x})$ can be thought of as a *solvent-mediated effective potential field* acting at x. Let

$$H=\beta F-\beta F^0 , \tag{2.8}$$

where βF^0 is the reduced Helmholtz free energy for the system without intermolecular interactions,

$$\beta F^0=\int d\bar{x}\rho(\bar{x})[\ln\rho(\bar{x})\Lambda+\beta U^e(\bar{x})-1] . \tag{2.9}$$

H is the excess reduced Helmholtz free energy arising from the intermolecular interactions and is in general functional of single-particle density distribution $\rho(\bar{x})$ and the pair potential U.

In terms of Mayer graphs,[21] H is the sum of all distinct connected irreducible graphs with no labeled points and with a factor of the single-particle density distribution $\rho(x_i)$ for every field point i. The Mayer function $f(\bar{x}_i\bar{x}_j)$ specified in the definition of the grand-canonical partition function (2.2) connects the points. The function H can be used as a generating functional for the correlation functions[21,22]

$$\begin{aligned}\frac{\delta H}{\delta\rho(\bar{x}_1)}&=-c_1(\bar{x}_1;\{\rho,U\})\\ &=-\ln\rho(\bar{x}_1)+\ln z(\bar{x}_1) ,\end{aligned} \tag{2.10}$$

$$\begin{aligned}\frac{\delta^2 H}{\delta\rho(\bar{x}_1)\delta\rho(\bar{x}_2)}&=-c_2(\bar{x}_1,\bar{x}_2;\{\rho,U\})\\ &\equiv-c_2\{\rho\} ,\end{aligned} \tag{2.11}$$

$$\begin{aligned}\frac{\delta^n H}{\prod_{i=1}^{n}\delta\rho(\bar{x}_i)}&=-c_n(\bar{x}_1,\ldots,\bar{x}_n;\{\rho,U\})\\ &\equiv-c_n\{\rho\} ,\end{aligned} \tag{2.12}$$

and

$$\begin{aligned}\frac{\delta H}{\delta U(\bar{x}_1,\bar{x}_2)}&=-\tfrac{1}{2}n_2(\bar{x}_1,\bar{x}_2;\{\rho,U\})\\ &\equiv-\tfrac{1}{2}n_2\{\rho\} ,\end{aligned} \tag{2.13}$$

where the two-particle density-distribution function n_2 gives the probability of finding simultaneously a molecule in a volume element $d\bar{r}_i d\Omega_i$ centered at $\bar{r}_i,\Omega_i$ and a second one in a volume element $d\bar{r}_j d\Omega_j$ centered at $\bar{r}_j,\Omega_j$. We can write

$$n_2(\bar{x}_i,\bar{x}_j;\{\rho,U\})=\rho(\bar{x}_1)\rho(\bar{x}_1)g(\bar{x}_1,\bar{x}_2;\{\rho,U\}) , \tag{2.14}$$

where $g(\bar{x}_1,\bar{x}_2;\{\rho,U\})=1+h(\bar{x}_1\bar{x}_2;\{\rho,U\})$ is the pair-correlation function. The functional dependence of the above-defined quantities on ρ and U is indicated by curly brackets.

The function $c_2(\bar{x}_1,\bar{x}_2;\{\rho,U\})$ appearing in (2.11) is the Ornstein-Zernike direct pair-correlation function and is related to the pair correlation as follows:

$$\begin{aligned}h(\bar{x}_1,\bar{x}_2)=c(\bar{x}_1,\bar{x}_2)+\int\rho(\bar{x}_3)h(\bar{x}_1,\bar{x}_3)&\\ \times c(\bar{x}_2,\bar{x}_3)d\bar{x}_3 .&\end{aligned} \tag{2.15}$$

If we start from zero density and want to build up a system in which density at $\bar{x}_1$ is $\rho(\bar{x}_1)$ and at $\bar{x}_2$, $\rho(\bar{x}_2)$, etc., then the $H\{\rho,U\}$ of the resulting system is obtained by the functional integration of (2.11) which leads to

$$H\{\rho,U\}=\int d\bar{x}_1\int d\bar{x}_2\rho(\bar{x}_1)\rho(\bar{x}_2)\bar{c}_2\{\rho\} , \tag{2.16}$$

where

$$\bar{c}_2\{\rho\}=\int_0^1 dy\int_0^y dx\, c_2\{x\rho\} . \tag{2.17}$$

It is important to realize that the existence of functional βF guarantees that the above result is independent of path of integration.

Combining Eqs. (2.8), (2.9), and (2.16) we get

$$\begin{aligned}\beta F=\int d\bar{x}\rho(\bar{x})[\beta U^e(\bar{x})+\ln\rho(\bar{x})\Lambda-1]&\\ -\int d\bar{x}_1 d\bar{x}_2\rho(\bar{x}_1)\rho(\bar{x}_2)\bar{c}_2\{\rho\} .&\end{aligned} \tag{2.18}$$

Sometimes it is convenient to work with the grand thermodynamic potential $-W$. First we note from Eq. (2.7) that

$$\psi(\bar{x}_1)=\ln\rho(\bar{x})\Lambda-c_1(\bar{x},\{\rho\}) . \tag{2.19}$$

Now we combine Eqs. (2.5), (2.18), and (2.19) which in the absence of an external field leads to

$$\begin{aligned}-W=-\int d\bar{x}\,\rho(\bar{x})+\int c_1(\bar{x},\{\rho\})\rho(\bar{x})d\bar{x}&\\ -\int d\bar{x}_1 d\bar{x}_2\rho(\bar{x}_1)\rho(\bar{x}_2)\bar{c}_2(\bar{x}_1,\bar{x}_2,\{\rho\}) .&\end{aligned} \tag{2.20}$$

From Eqs. (2.1) and (2.5) we have

$$\begin{aligned}\beta F&=\beta\mu\langle N\rangle-\beta PV-\beta\int\rho(\bar{x})U^e(\bar{x})d\bar{x}\\ &=\beta A-\beta\int\rho(\bar{x})U^e(\bar{x})d\bar{x}\end{aligned}$$

or

$$\beta A=\beta F+\beta\int\rho(\bar{x})U^e(\bar{x})d\bar{x} . \tag{2.21}$$

Here βA is the reduced Helmholtz free energy of the system in the absence of an external field. From (2.21), (2.6), and (2.2) we get

$$\left.\frac{\delta(\beta A)}{\delta\rho(\bar{x})}\right|_{\rho(\bar{x})=\langle\rho(\bar{x})\rangle;\,U^e(x)\text{ fixed}}=\psi(\bar{x})+\beta U^e(\bar{x})=\beta\mu , \tag{2.22}$$

where $\langle\rho(x)\rangle$ represents the equilibrium density distribution. Thus if $\int\rho(\bar{x})dx=N$ is held fixed,

$$\delta(\beta A)=\int d\bar{x}\,\frac{\delta(\beta A)}{\delta\rho(\bar{x})}\bigg|_{\rho(\bar{x})=\langle\rho(\bar{x})\rangle;\,U^e(\bar{x})\text{ fixed}}\delta\rho(\bar{x})$$

$$=\beta\int d\bar{x}\,\mu\delta\rho(\bar{x})$$

$$=0\;. \tag{2.23}$$

This is a stationary principle which is a consequence of

$$\frac{\delta(\beta A)}{\delta\rho(x)}\bigg|_{\text{equil}}=\text{const}\;,\quad\text{independent of }\bar{x}\;.$$

Thus for any system in equilibrium the chemical potential must be the same throughout the sample.

The equilibrium single-particle density distribution is determined by minimizing the free energy βA or βF for a given external field subject to the constraint

$$\int\rho(x)d\bar{x}=\langle N\rangle\;. \tag{2.24}$$

III. NONUNIFORM SYSTEM

In a nonuniform system $\rho(\bar{x})$ is a function of position and orientation and c_2 is functional of $\rho(\bar{x})$. Performing a functional Taylor expansion of c_2 about the local-density distribution $\rho(\bar{x}_1)$ we obtain

$$c_2\{\rho\}=c_2(\rho(\bar{x}_1))+\int d\bar{x}_3[\rho(\bar{x}_3)-\rho(\bar{x}_1)]c_3(\rho(\bar{x}_1))+\tfrac{1}{2}\int d\bar{x}_3d\bar{x}_4[\rho(\bar{x}_3)-\rho(\bar{x}_1)][\rho(\bar{x}_4)-\rho(\bar{x}_1)]c_4(\rho(\bar{x}_1))+\cdots\;, \tag{3.1}$$

the $c_n(\rho(\bar{x}_1))\equiv c_n(\bar{x}_1,\ldots,\bar{x}_n;\rho(\bar{x}_1))$ are "local," i.e., they are the correlation functions of a uniform fluid with constant density $\rho(\bar{x}_1)$.

When (3.1) is substituted in (2.18), one obtains after some mathematical manipulations

$$\beta F=\int d\bar{x}\,\rho(\bar{x})[\beta U^e(\bar{x})+\ln\rho(\bar{x})\Lambda-1]+\beta\Delta F^u(\rho(\bar{x}_1))$$
$$+\beta\Delta F^l+\beta\Delta F_1^n+\beta\Delta F_2^n+\cdots\;, \tag{3.2}$$

where

$$\beta\Delta F^u(\rho(\bar{x}))=-\int d\bar{x}_1d\bar{x}_2[\rho(\bar{x}_1)]^2\bar{c}_2(\rho(\bar{x}_1))\;, \tag{3.3}$$

$$\beta\Delta F^l=-\int d\bar{x}_1d\bar{x}_2\rho(\bar{x}_1)[\rho(\bar{x}_2)-\rho(\bar{x}_1)]\bar{c}_2(\rho(\bar{x}_1))\;, \tag{3.4}$$

$$\beta\Delta F_1^n=-\int d\bar{x}_1d\bar{x}_2[\rho(\bar{x}_1)]^2[\rho(\bar{x}_2)-\rho(\bar{x}_1)]\times\frac{\delta\bar{c}_2(\rho(\bar{x}_1))}{\delta\rho(\bar{x}_1)}\;, \tag{3.5}$$

$$\beta\Delta F_2^n=-\tfrac{1}{2}\int d\bar{x}_1d\bar{x}_2\rho(\bar{x}_1)[\rho(\bar{x}_2)-\rho(\bar{x}_1)]^2\times\left[\frac{\delta\bar{c}_2(\rho(\bar{x}_1))}{\delta\rho(\bar{x}_1)}+\tfrac{1}{2}\rho(\bar{x}_1)\frac{\delta^2\bar{c}_2(\rho(\bar{x}_1))}{\delta\rho(\bar{x}_1)^2}\right]. \tag{3.6}$$

The quantity $\beta\Delta F^u(\rho(\bar{x}_1))$ is the Helmholtz free energy of a system of uniform density equal to the local density $\rho(\bar{x}_1)$. The superscript l denotes free energy correction $\beta\Delta F^l$ due to the nonuniformity of the system assuming the direct-correlation function is local [i.e., it depends only on the local density $\rho(\bar{x}_1)$]. The superscript n denotes free energy corrections $\beta\Delta F_1^n,\beta\Delta F_2^n$ (to first and second order) due to the system nonuniformity when "nonlocal" corrections to the direct-correlation function c_2 are made.

If the change in the density is small over the range of $\bar{c}_2$ we can use the Taylor expansion truncated after second order,

$$\rho(\bar{x}_2)-\rho(\bar{x}_1)=(\bar{x}_2-\bar{x}_1)\cdot\nabla\rho(\bar{x}_1)$$
$$+\tfrac{1}{2}[(\bar{x}_2-\bar{x}_1)\cdot\nabla]^2\rho(\bar{x}_1)\;. \tag{3.7}$$

For a system of N particles, the equilibrium density distribution for a given $U^e(\bar{x})$ is determined by minimizing the total free energy F subject to the constraint

$$\int\rho(\bar{x}_1)d\bar{x}_1=N\;,$$

i.e.,

$$\delta\left\{F-\mu_0\int\rho(\bar{x}_1)d\bar{x}_1\right\}=0\;, \tag{3.8}$$

where μ_0 is the chemical potential of the system. From (3.2)–(3.6) we get

$$\beta U^e(\bar{x}_1)+\beta[\mu(\rho(\bar{x}_1))-\mu_0]-\int d\bar{x}_2[\rho(\bar{x}_2)-\rho(\bar{x}_1)]c_2(\rho(\bar{x}_1))-\tfrac{1}{4}\int d\bar{x}_2[\rho(\bar{x}_2)-\rho(\bar{x}_1)]^2\frac{\partial c_2(\rho(\bar{x}_1))}{\partial\rho(\bar{x}_1)}=0\;, \tag{3.9}$$

where

$$\beta\mu(\rho(\bar{x}_1))=\frac{\partial\beta f^u(\rho(\bar{x}_1))}{\partial\rho(\bar{x}_1)} \tag{3.10}$$

with

$$\beta f^u(\rho(\bar{x}_1))=\rho(\bar{x}_1)[\ln\rho(\bar{x}_1)\Lambda-1]$$
$$-\rho(x_1)^2\int d\bar{x}_2\bar{c}_2(\rho(\bar{x}_1))\;. \tag{3.11}$$

The formalism given in this section is a generalization of the Singh-Abraham[23] theory of nonuniform atomic fluid to a system of molecules of arbitrary symmetry. The theory discussed so far is quite general and can be used to describe the properties of crystalline solids, liquid crystals, isotropic liquids, transition from one phase to the other, and the properties of interfaces. To characterize these phases we introduce order parameters in the following way:

$$\rho(\bar{x})=\rho(\bar{r},\Omega)$$
$$=\rho_0\left[1+\sum P_{Lmn}(q)\exp(i\vec{k}_q\cdot\vec{r})D_{m,n}^L(\Omega)\right]\;, \tag{3.12}$$

where ρ_0 is the average number density, $\vec{k}_q$ are reciprocal lattice vectors of the crystalline phase, and ρ_0 is the mean density. The $P_{Lmn}(q)$ are the order parameters and the D_{mn}^L are the Wigner rotation matrices.

For a monatomic crystalline lattice, $L=m=n=0$. Thus

$$\rho(\bar{r},\Omega)=\rho(\bar{r})=\rho_0\left[1+\sum P_{000}(q)e^{i\vec{k}_q\cdot\vec{r}}\right] . \tag{3.13}$$

For uniform nematics (3.12) reduces to

$$\rho(\bar{r},\Omega)=\rho_0\left[1+\sum P_{Lmn}(0)D_{m,n}^L(\Omega)\right] . \tag{3.14}$$

In isotropic fluid, $P_{Lmn}=0$ for all values of L, m, and n. For smectic phase with positional order in one dimension only (e.g., a smectic-A or -C phase) we can restrict the series (3.12) to

$$\rho(\bar{r},\Omega)=\rho_0\left[1+\sum P_{Lmn}(q)e^{ik_q z}D_{m,n}^L(\Omega)\right] , \tag{3.15}$$

where $k_q=k_{qz}$ and z is parallel to the layer normal.

The expressions given above for $\rho(r,\Omega)$ can be simplified by using the symmetry of the molecules and mesophase. For example, in a uniaxial nematic phase with cylindrically symmetric molecules, (3.14) reduces to

$$\rho(\bar{r},\Omega)=\rho_0\left[1+\sum_{\substack{L\geq 2\\ L\text{ even}}}(2L+1)\bar{P}_L P_L(\cos\theta)\right] , \tag{3.16}$$

where

$$\bar{P}_L=\frac{1}{2\rho_0}\int\rho(\bar{r},\Omega)P_L(\cos\theta)\sin\theta\, d\theta$$

is the orientational order parameter of the nematic phase and θ is the angle between the director and the symmetry axis of the molecule.

IV. UNIFORM NEMATIC PHASE

A. Equilibrium properties

Since the homogeneous nematic phase is translationally invariant, we can write

$$\rho(\bar{r},\Omega)=\rho_0 f(\Omega) , \tag{4.1a}$$

$$n_2(\bar{x}_1,\bar{x}_2)=\rho_0^2 f(\Omega_1)f(\Omega_2)g(\bar{r}_{12},\Omega_1,\Omega_2) . \tag{4.1b}$$

With $f(\Omega)=1+\sum P_{Lmn}(0)D_{m,n}^L(\Omega)$ for molecules of arbitrary symmetry or

$$f(\Omega)=1+\sum_{\substack{L\geq 2\\ L\text{ even}}}(2I+1)\bar{P}_L P_L(\cos\theta) \tag{4.1c}$$

for cylindrically symmetric molecules. $f(\Omega)$ is an orientational singlet distribution normalized to unity,

$$\int f(\Omega)d\Omega=1 , \tag{4.2}$$

and θ is the angle between the director and the symmetry axis. ρ_0 is the mean number density.

For uniform nematic phase it is convenient to rewrite Eq. (2.18) in the following way:

$$\begin{aligned}\frac{\beta F}{N}=\frac{\beta F_0}{N}&+\int d\Omega f(\Omega)\ln f(\Omega)\\ &-\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-][f(\Omega_2)-1]\\ &\times\bar{c}_2\{\rho_0 f(\Omega)\} ,\end{aligned} \tag{4.3}$$

where

$$\bar{c}_2\{\rho_0 f(\Omega)\}=\int_0^1 dx\int_0^x dy\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\{y\rho_0 f(\Omega)\}) \tag{4.4}$$

and $\beta F_0/N$ is the free energy per particle of an isotropic system at density ρ_0. Equation (4.3) is obtained by functional integration of (2.11) from initial density ρ_0 (corresponding to isotropic phase) to a final density $\rho_0 f(\Omega)$ (corresponding to the nematic phase). It may, however, be noted that the direct-correlation function is still a functional of the single-particle density distribution. We use functional Taylor expansion to write it in terms of the correlation function of the isotropic system. Thus

$$\begin{aligned}c_2\{\rho_0 f(\Omega)\}=c_2(\rho_0)&+\rho_0\int d\bar{r}_3 d\Omega_3[f(\Omega_3)-1]c_3(\rho_0)\\ &+\tfrac{1}{2}\rho_0^2\int d\bar{r}_3 d\Omega_3 d\bar{r}_4 d\Omega_4[f(\Omega_3)-1]\\ &\times[f(\Omega_4)-1]c_4(\rho_0) .\end{aligned} \tag{4.5}$$

From (4.3)—(4.5) we get

$$\begin{aligned}\frac{\beta\Delta F}{N}=\int d\Omega f(\Omega)\ln f(\Omega)&-\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-1][f(\Omega_2)-1]\bar{c}_2(\rho_0)\\ &-\rho_0^2\int d\bar{r}_{12}d\Omega_1 d\Omega_2 d\bar{r}_3 d\Omega_3[f(\Omega_1)-1][f(\Omega_2)-1][f(\Omega_3)-1]\bar{c}_3(\Omega_0)\cdots .\end{aligned} \tag{4.6}$$

Equation (4.6) is not suitable for computation since it includes the three-body direct-correlation function about which little is known. However, in a uniform system $f(\Omega)$ is expected to be constant throughout the sample, we may approximate Eq. (4.6) as (see the Appendix)

$$\begin{aligned}\frac{\beta\Delta F}{N}\simeq\int f(\Omega)\ln f(\Omega)d\Omega&-\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-1][f(\Omega_2)-1]\bar{c}_2(\rho_0)\\ &-\tfrac{1}{2}\rho_0^2\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-1][f(\Omega_2)-1]^2\frac{\delta\bar{c}_2}{\delta\rho_0}+\cdots .\end{aligned} \tag{4.7}$$

This expression can be used to obtain the Landau–de Gennes expansion (see the Appendix). The orientational singlet distribution function $f(\Omega)$ is determined by minimizing the free energy subject to the normalization condition (4.2). This leads to

$$f(\Omega)=\frac{1}{z}\exp\left[2\rho_0\int d\bar{r}_{12}d\Omega_2[f(\Omega_2)-1]\bar{c}_2+\tfrac{3}{2}\rho_0^2\int d\bar{r}_{12}d\Omega_2[f(\Omega_2)-1]^2\frac{\delta\bar{c}_2}{\delta\rho_0}\right], \tag{4.8}$$

where z is the normalization constant.

Equations (4.7) and (4.8) are suitable to study the equilibrium properties of the nematic phase as well as the properties of the isotropic-nematic transition at constant density.

B. Isotropic-nematic transition at constant pressure

The isotropic-nematic transition at constant pressure is accompanied by change in density. We therefore rewrite (4.1a) as

$$\rho(\bar{r},\Omega)=\rho_l[\Delta\rho^*+f(\Omega)]\ , \tag{4.9}$$

where $\Delta\rho^*=(\rho_0-\rho_l)/\rho_l$ is the fractional change in density due to transition, ρ_0 is the mean number density of the nematic phase, ρ_l is the density of the liquid phase, and $f(\Omega)$ is given by (4.1c). In order to locate the transition and its properties we consider the grand thermodynamic potential $-W$ [Eq. (2.20)] which we now rewrite as

$$\begin{aligned}-W=&-\int d\bar{r}\,d\Omega\,\rho(\bar{r},\Omega)+\int d\bar{r}\,d\Omega\,\rho(\bar{r},\Omega)c_1\{\rho(\bar{r},\Omega)\}+H(\rho_l)\\&-\int d\bar{r}_1d\Omega_1d\bar{r}_2d\Omega_2[\rho(\bar{r}_1,\Omega_1)-\rho_l][\rho(\bar{r}_2,\Omega_2)-\rho_l]\tilde{c}_2\{\rho(\bar{r},\Omega)\}\ ,\end{aligned} \tag{4.10}$$

where $H(\rho_l)$ is the excess Helmholtz free energy of the liquid phase. $c_1\{\rho(\bar{r},\Omega)\}$ can be obtained by functional integration of (2.11) from initial density ρ_l (corresponding to isotropic liquid) to the final density of the liquid crystal. This leads to

$$c_1\{\rho(\bar{r},\Omega)=c_1(\rho_l)+\int d\bar{r}_2d\Omega_2[\rho(\bar{r}_2\Omega_2)-\rho_l]\tilde{c}_2\{\rho(\bar{r},\Omega)\}\ , \tag{4.11}$$

where

$$\tilde{c}\{\rho(\bar{r},\Omega)\}=\int_0^1 d\alpha c_2\{\alpha\rho(\bar{r},\Omega)\}$$

combining (4.10) and (4.11) we get

$$\begin{aligned}-\Delta W=W-W_l=&-\int d\bar{r}[\rho(\bar{r},\Omega)-\rho_l]-\int d\bar{r}_1d\Omega_1d\bar{r}_2d\Omega_2[\rho(\bar{r}_1,\Omega_1)-\rho_l]\\&\times\{[\rho(\bar{r}_2,\Omega_2)-\rho_l]\bar{c}_2(\rho_l)-[\rho(\bar{r}_2,\Omega_2)+\rho_l]\tilde{c}_2(\rho_l)\}\\&-\int d\bar{r}_1d\Omega_1d\bar{r}_2d\Omega_2[\rho(\bar{r}_2,\Omega_2)-\rho_l]^2\left[[\rho(\bar{r}_1,\Omega_1)-\rho_l]\frac{\delta\bar{c}_2(\rho_l)}{\delta\rho_l}-\rho(\bar{r}_1,\Omega_1)\frac{\delta\tilde{c}_2(\rho_l)}{\delta\rho_l}\right]\cdots\ .\end{aligned} \tag{4.12}$$

It is expected that at the transition in which we are primarily interested here, the direct-correlation function of the isotropic liquid and nematic phase are essentially the same. Thus the terms written explicitly in (4.12) should be sufficient.

Substituting (4.9) in (4.12) one gets

$$\begin{aligned}-\frac{\Delta W}{N}=&-\Delta\rho^*-\rho_l\int d\bar{r}_{12}d\Omega_1d\Omega_2\{\Delta\rho^*+[f(\Omega_2)-1]\}\{[\Delta\rho^*+f(\Omega_1)-1]\bar{c}_2(\rho_l)-[1+\Delta\rho^*+f(\Omega_1)]\tilde{c}_2(\rho_l)\}\\&-\rho_l^2\int d\bar{r}_{12}d\Omega_1d\Omega_2[\Delta\rho^*+f(\Omega_2)-1]^2\left[[\Delta\rho^*+f(\Omega_1)-1]\frac{\delta\bar{c}_2(\bar{\rho}_l)}{\delta\rho_l}-[\Delta\rho^*+f(\Omega_1)]\frac{\delta\tilde{c}_2(\rho_l)}{\delta\rho_l}\right].\end{aligned} \tag{4.13}$$

It may also be noted that by combining Eqs. (2.19), (4.9), and (4.11) the following relation can be obtained:

$$\ln[\Delta\rho^*+f(\Omega_1)]=\rho_l\int d\bar{r}_2d\Omega_2\left[[\Delta\rho^*+f(\Omega_2)-1]\tilde{c}_2(\rho_l)+\tfrac{1}{2}\rho_l\{\Delta\rho^*+[f(\Omega_2)-1]\}^2\frac{\delta\tilde{c}_2(\rho_l)}{\delta\rho_l}\right]. \tag{4.14}$$

Equation (4.14) leads to the following two relations

$$1+\Delta\rho^*=\int d\Omega_1\exp\left[\rho_l\int d\bar{r}_2d\Omega_2\{\Delta\rho^*+[f(\Omega_1)-1]\}\left[\tilde{c}_2(\rho_l)+\tfrac{1}{2}\rho_l\{\Delta\rho^*+[f(\Omega_2)-1]\}\frac{\delta\tilde{c}_2}{\delta\rho_l}\right]\right] \tag{4.15}$$

and

$$\bar{P}_L = \int f(\Omega) P_L(\cos\theta) d\Omega$$

$$= \int d\Omega_1 P_L(\cos\theta) \exp\left[\rho_l \int d\bar{r}_2 d\Omega_2 [\Delta\rho^* + f(\Omega_1) - 1] \left[\tilde{c}_2(\rho_l) + \tfrac{1}{2}\rho_l \{\Delta\rho^* + [f(\Omega_2) - 1]\} \frac{\delta \tilde{c}_2(\rho_l)}{\delta \rho_l}\right]\right] . \quad (4.16)$$

Transition properties such as change in density, values of order parameters, etc., will be obtained by solving Eqs. (4.13), (4.15), and (4.16) self-consistently. The transition will be located by finding $-\Delta W/N = 0$. The theory presented in this subsection is a generalization of the Ramakrishna-Yussuff[24] theory of freezing to the nematic-isotropic transition. Numerical results for some model systems will be reported in a future communication.

It may, however, be noted that the theory described here is a *mean-field* theory which does not take into account properly the effect of molecular orientational fluctuations. Nelson and Toner[25] have shown that it is only for d-dimensional systems with $d > 6$ that a mean-field theory of the nematic-isotropic transition becomes correct.

The problem of calculating the equilibrium properties of nematic phase has thus reduced to getting a suitable scheme for the evaluation of the direct-correlation function. The solutions of integral equations such as the hypernetted-chain (HNC) equation, the Percus-Yeuick (PY) equation, the mean-spherical approximation (MSA), or the optimized random-phase approximation (ORPA) are difficult to obtain. This is because the solution of these equations involves, even for axially symmetric rigid molecules, repetitive sixfold, numerical integration and requires the calculation of the full anisotropic pair-correlation function, a procedure that is numerically very complicated but that can be accomplished by spherical harmonic expansion.[26] Another method that can be applied to anisotropic fluids with relative ease is a case of a perturbation scheme.

In developing a perturbation scheme, one begins by writing the potential energy of interaction $U(\bar{r}_1\Omega_1, \bar{r}_2\Omega_2)$ as a sum of two parts—one part of this division is known as the reference potential $U_0(\bar{r}_1, \Omega_1; \bar{r}_2, \Omega_2)$ and the other is the perturbation potential $U_p(\bar{r}_1, \Omega_1; \bar{r}_2, \Omega_2)$, i.e.,

$$U(\bar{r}_1, \Omega_1; \bar{r}_2, \Omega_2) = U_0(\bar{r}_1, \Omega_1; \bar{r}_2, \Omega_2) + U_p(\bar{r}_1, \Omega_1; \bar{r}_2, \Omega_2) .$$

For example, a commonly used division is the one suggested by Weeks, Chandler, and Andersen[27] (WCA) in which the reference potential represents that part of the pair potential which describes the repulsive force and vanishes when the force vanishes. The remainder of the potential is treated as the perturbation. In the case of the uniform atomic fluid at liquid densities, it has been found that first-order perturbation theory gives good convergence. We may hope that the same may be true in the case of fluids of long elongated molecules which exhibit a liquid-crystalline phase under suitable conditions.

We noted earlier that H is functional of pair potential. We now expand H about $U = U_0$ and use (2.13) and (2.14) to obtain

$$H\{\rho, u\} = H\{\rho, u_0\} + \int d\bar{x}_1 \int d\bar{x}_2 \left.\frac{\delta H}{\delta U(\bar{x}_1, \bar{x}_2)}\right|_{U=U_0} U_p(\bar{x}_1, \bar{x}_2) + \cdots$$

$$= H\{\rho, U_0\} - \tfrac{1}{2}\beta \int d\bar{x}_1 \rho(\bar{x}_1) \int d\bar{x}_2 \rho(\bar{x}_2) g_0(\bar{x}_1, \bar{x}_2) U_p(\bar{x}_1, \bar{x}_2) . \quad (4.17)$$

In Eq. (4.17), $H\{\rho, U_0\}$ represents the excess free energy of the reference system as a functional of single-particle density distribution and the pair reference potential.

From relation (2.11) we have

$$c_2(\bar{x}_1, \bar{x}_2) = c_2^{(0)}(\bar{x}_1, \bar{x}_2) - \frac{\delta^2}{\delta\rho(\bar{x}_1)\delta\rho(\bar{x}_2)} \times \left[\frac{\beta}{2} \int d\bar{x}_1 d\bar{x}_2 \rho(\bar{x}_1) \rho(\bar{x}_2) g^0(\bar{x}_1, \bar{x}_2)\right]$$

which leads to[23]

$$c_2(\bar{x}_1, \bar{x}_2) = c^{(0)}(\bar{x}_1, \bar{x}_2) - \beta U_p(\bar{x}_1, \bar{x}_2) \times \left[g^0(\bar{x}_1, \bar{x}_2) + 2\rho(\bar{x}_1) \frac{\delta g^0(\bar{x}_1, \bar{x}_2)}{\delta\rho(\bar{x}_1)} + \tfrac{1}{2}\rho(\bar{x}_1)^2 \frac{\delta^2 g^0(\bar{x}_1, \bar{x}_2)}{\delta\rho^2(\bar{x}_1)}\right] . \quad (4.18)$$

Using the above expression of the direct-correlation function in the compressibility equation gives the first-order perturbation theory which is equivalent to the WCA perturbation theory of atomic fluid as formulated in Ref. 27. We also make note of the fact that from Eq. (4.18), we may write

$$\bar{c}_2(\bar{x}_1, \bar{x}_2) = \bar{c}_2^{(0)}(\bar{x}_1, \bar{x}_2) - \tfrac{1}{2}\beta U_p(\bar{x}_1, \bar{x}_2) g^{(0)}(\bar{x}_1, \bar{x}_2) . \quad (4.19)$$

Substitution of this in (4.7) leads to a perturbation theory recently developed by Singh and Singh.[6] Values of $c_2^{(0)}$ and $g^{(0)}$ can be obtained either from computer simulations or from approximate schemes.[28]

It may be interesting to note that when Eq. (4.19) is substituted in Eq. (2.18) one gets (in the absence of an external field)

$$\frac{\beta F}{N}=\frac{\beta F_r}{N}+\int d\bar{r}\,d\Omega_1 f(\Omega_1)\psi(\Omega_1)\ ,$$

where

$$\frac{\beta F_r}{N}=\int d\Omega\, f(\Omega)[\ln f(\Omega)-1]+\ln\rho_0\Lambda$$

$$-\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2 f(\Omega_1)f(\Omega_2)$$

$$\times\bar{c}_2^{(0)}(\bar{r}_{12},\Omega_1,\Omega_2;\{\rho f(\Omega)\})$$

and

$$\psi(\Omega_1)=\tfrac{1}{2}\rho_0\beta\int d\Omega_2 g^{(0)}(\bar{r},\Omega_1,\Omega_2;\{\rho_0 f(\Omega)\})$$

$$\times U_p(\bar{r},\Omega_1,\Omega_2)\ ,$$

$\psi(\Omega_1)$ is referred to as in the literature as the *effective one-body orientation perturbation potential* or pseudopotential.

It must be realized that the intermolecular attraction which is usually taken as a perturbation does not give rise merely to a uniform background as many authors have assumed,[29] but rather to a configuration dependent potential energy. Such erroneous assumption leads to an unrealistic restriction on the density dependence of the pseudopotential.

V. FRANK ELASTIC CONSTANTS OF NEMATIC LIQUID CRYSTALS

The Frank elastic constants are a measure of the free energy associated with long-wavelength distortions of the nematic state in which the local preferred direction of molecular orientation varies in space. If the local preferred direction at the point R is parallel to the director $\hat{n}(R)$, the free energy associated with the distortion may be written as[2,30]

$$\Delta F=\tfrac{1}{2}\int d\bar{R}[K_1(\vec{\nabla}\cdot\hat{n})^2+K_2(\hat{n}\cdot\vec{\nabla}\times\hat{n})^2$$

$$+K_3(\hat{n}\times\vec{\nabla}\times\hat{n})^2]\ . \tag{5.1}$$

The distortions corresponding to K_1, K_2, and K_3 are called splay, twist, and bend, respectively. The Frank elastic constants K_i characterize the free energy increase associated with the three normal modes of deformation of the ordered nematic state.

In order to derive molecular expressions for the K_i's, we first choose an arbitrary point $R=0$ in the deformed liquid crystal as the origin of a space-fixed coordinate system. The z axis of this system is taken parallel to the director at the origin, i.e., $\hat{z}=\hat{n}(R=0)$. For pure splay, twist, and bend deformations, the variations in $\hat{n}(R)$ are always confined to a plane. If the x axis is chosen such that (x,z) is the plane containing $n(R)$,[31]

$$\hat{n}(R)=\hat{x}\sin\mathcal{X}(R)+\hat{z}\cos\mathcal{X}(R)\ .$$

$\mathcal{X}(R)$ is the angle between the director at R, and the director at the origin, i.e., $\cos\mathcal{X}(R)=\hat{z}\cdot\hat{n}(R)$.

With any distortion we may associate a wave number q. The increase in the free energy due to a long-wavelength distortion will be proportional to q^2, because the symmetry of the system ensures that the distortions corresponding to q and $-q$ are equivalent. The long-wavelength distortion corresponds to the change in the director over some characteristic length of the system being small, i.e., $\mathcal{X}\sim qd\ll 1$, d may be taken to be the range of the direct-correlation function. In this limit one finds for $\mathcal{X}(R)$

$$\mathcal{X}(R)=\begin{cases} qx-q^2xz+0(q^3) & \text{splay}\\ qy & \text{twist}\\ qz+q^2xz+0(q^3) & \text{bend}\end{cases} \tag{5.2}$$

and for distortion-free energy density around the origin,

$$\Delta a(0)=\begin{cases} \tfrac{1}{2}K_1q^2+O(q^4) & \text{splay}\\ \tfrac{1}{2}K_2q^2+O(q^4) & \text{twist}\\ \tfrac{1}{2}K_3q^2+O(q^4) & \text{bend}\ .\end{cases} \tag{5.3}$$

Since in pure splay, bend, and twist, the deformed nematic has the same local structure everywhere, the above results do not depend on the choice of the origin.

In a deformed nematic phase the orientational distribution function is a function of position in space. We therefore write it as $f(\Omega,R)$ for the distribution at point R. Taking the undeformed nematic phase as our reference system we rewrite Eqs. (3.2)—(3.6) in a form more appropriate to our present problem. Thus

$$\beta F=\int d\bar{R}\,\beta a(R)$$

$$=\int d\,\bar{R}[\beta a_u(R)+\beta\Delta a(R)]\ ,$$

where

$$\beta a_u(R)=\rho_0\int d\Omega_1 f(\Omega_1,R)[\ln f(\Omega_1,R)+\ln\rho_0+\ln\Lambda-1]$$

$$-\rho_0^2\int d\bar{r}\,d\Omega_1 d\Omega_2 f(\Omega_1,\bar{R})f(\Omega_2,\bar{R})\bar{c}_2(\rho(\bar{r}_1\Omega)) \tag{5.4}$$

and

$$\beta\Delta a(R)=-\rho_0^2\int d\bar{r}\,d\Omega_1 d\Omega_2 f(\Omega_1,\bar{R})[f(\Omega_2,\bar{R}+\bar{r})-f(\Omega_2,\bar{R})]\bar{c}_2(\rho_0)$$

$$-\rho_0^3\int d\bar{r}\,d\Omega_1 d\Omega_2 f(\Omega_1,\bar{R})[f(\Omega_2,\bar{R}+\bar{r})-f(\Omega_2,R)]\frac{\delta\bar{c}_2(\rho_0)}{\delta\rho_0}$$

$$-\tfrac{1}{2}\rho_0^3\int d\bar{r}\,d\Omega_1 d\Omega_2[f(\Omega_2,\bar{R}+r)-f(\Omega_2,\bar{R})]^2\left[\frac{\delta\bar{c}_2(\rho_0)}{\delta\rho_0}+\tfrac{1}{2}\rho_0\frac{\delta^2\bar{c}_2(\rho_0)}{\delta\rho_0^2}\right]\ . \tag{5.5}$$

Here $\beta a_u(R)$ is the free energy density at position R of an undeformed nematic liquid crystal and $\beta\Delta a(R)$ is the free energy density of deformation. In writing (5.5) we have assumed that the direct-correlation function in the undeformed liquid-crystal phase is very similar to the isotropic liquid at the same mean density.

Since $\mathcal{X}(R)$ is the angle between the director at $\vec{R}$ and the director at the origin, we write $f(\Omega,R)=f(\Omega,\mathcal{X}(R)$. For an undeformed system $\mathcal{X}(r)=0$. Thus the distortion free energy density at $R=0$ is

$$\beta\Delta a(0)=-\rho_0^2\int d\bar{r}\int d\Omega_1 d\Omega_2 f(\Omega_1,0)[f(\Omega_2,\mathcal{X}(\bar{r}))-f(\Omega_2,0)]\left[\bar{c}_2(\rho_0)+\rho_0\frac{\partial\bar{c}_2(\rho_0)}{\partial\rho_0}\right]$$
$$-\tfrac{1}{2}\rho_0^3\int d\bar{r}\,d\Omega_1 d\Omega_2[f(\Omega_2,\mathcal{X}(\bar{r}))-f(\Omega_2,0)]^2\left[\frac{\partial\bar{c}_2(\rho_0)}{\partial\rho_0}+\tfrac{1}{2}\rho_0\frac{\partial^2\bar{c}_2(\rho_0)}{\partial\rho_0^2}\right]. \tag{5.6}$$

If the distortion angle is small, i.e., $\mathcal{X}(r)\ll 1$, we can expand $f(\Omega,\mathcal{X}(\bar{r}))$ as a power series in $\mathcal{X}$. Keeping terms to order q^2, one gets

$$f(\Omega_2,\mathcal{X}(r))-f(\Omega_2,0)=f'(\Omega_2,0)\begin{bmatrix} qz-q^2xz \\ qy \\ qz+q^2xz \end{bmatrix}+\tfrac{1}{2}f''(\Omega_2,0)\begin{bmatrix} q^2x^2 \\ q^2y^2 \\ q^2z^2 \end{bmatrix}, \tag{5.7}$$

where x, y, and z are the Cartesian components of $\bar{r}$ in the space-fixed system.

From Eqs. (5.5) and (5.7), we get

$$\beta\Delta a(0)=-\rho_0^2\int d\bar{r}\int d\Omega_1 d\Omega_2 f(\Omega_1,0)\left[f'(\Omega_2,0)\begin{bmatrix} qx+q^2xz \\ qy \\ qz+q^2xz \end{bmatrix}+\tfrac{1}{2}f''(\Omega_2,0)\begin{bmatrix} q^2x^2 \\ q^2y^2 \\ q^2z^2 \end{bmatrix}\right]$$
$$\times\left[\bar{c}_2(\rho_0)+\rho_0\frac{\partial\bar{c}_2(\rho_0)}{\partial\rho_0}\right]-\tfrac{1}{2}\rho_0^3\int d\bar{r}\,d\Omega_1 d\Omega_2[f'(\Omega_2,0)]^2\begin{bmatrix} q^2x^2 \\ q^2y^2 \\ q^2z^2 \end{bmatrix}$$
$$\times\left[\frac{\partial\bar{c}_2(\rho_0)}{\partial\rho_0}+\tfrac{1}{2}\rho_0\frac{\partial^2\bar{c}_2(\rho_0)}{\partial\rho_0^2}\right]. \tag{5.8}$$

Thus we have

$$\begin{bmatrix} K_1 \\ K_2 \\ K_3 \end{bmatrix}=-2\rho_0^2kT\int d\bar{r}\,d\Omega_1 d\Omega_2 f(\Omega_1,0)\left[f'(\Omega_2,0)\begin{bmatrix} -xz \\ 0 \\ xz \end{bmatrix}+\tfrac{1}{2}f''(\Omega_2,0)\begin{bmatrix} x^2 \\ y^2 \\ z^2 \end{bmatrix}\right]\left[\bar{c}_2(\rho_0)+\rho_0\frac{\partial\bar{c}_2(\rho_0)}{\partial\rho_0}\right]$$
$$-\rho_0^3kT\int d\bar{r}\,d\Omega_1 d\Omega_2 f'(\Omega_2,0)^2\begin{bmatrix} x^2 \\ y^2 \\ z^2 \end{bmatrix}\left[\frac{\partial\bar{c}_2(\rho_0)}{\partial\rho_0}+\tfrac{1}{2}\rho_0\frac{\partial^2\bar{c}_2(\rho_0)}{\partial\rho_0^2}\right]. \tag{5.9}$$

In deriving the above expressions for the Frank elastic constants, we assumed that the direct-correlation function of an ordered nematic phase can be approximated by the direct-correlation function of the isotropic liquid at the same mean number density ρ_0. We can improve upon this approximation by functional Taylor expansion of the direct-correlation function of the nematic phase about the direct-correlation function of the isotropic phase as has been done in Sec. IV.

Using the method described in Sec. IV for the calculation of the direct-correlation function we can evaluate K_i from Eq. (5.9). The results for certain model potentials will be reported in a future communication. It may, however, be noted that the expression for K_i given here is more complete and rigorous than reported by earlier workers.[31,32]

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APPENDIX

In this appendix we discuss the approximation used in deriving Eq. (4.7) and give a microscopic derivation for the Landau-de Gennes theory.

Equation (4.6) can be rewritten as

$$\begin{aligned}\frac{B\Delta F}{N}=&\int f(\Omega)\ln f(\Omega)d\Omega-\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-1][f(\Omega_2)-1]\bar{c}_2(\rho_0)\\&-\rho_0^2\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-1][f(\Omega_2)-1]^2\frac{\delta\bar{c}_2(\rho_0)}{\delta\rho_0}\\&-\tfrac{1}{2}\rho_0^3\int d\bar{r}_{12}d\Omega_1 d\Omega_2[f(\Omega_1)-1]^2[f(\Omega_2)-1]^2\frac{\delta^2\bar{c}_2(\rho_0)}{\delta\rho_0^2}+A+B\ ,\end{aligned}\tag{A1}$$

where

$$\begin{aligned}A&=-\rho_0^2\int d\bar{r}_{12}d\Omega_1 d\Omega_2\int d\bar{r}_3 d\Omega_3[f(\Omega_1)-1][f(\Omega_2)-1][f(\Omega_3)-f(\Omega_2)]\bar{c}_3(\rho_0)\\&=+\tfrac{1}{2}\rho_0^2\int d\bar{r}_{12}d\Omega_1[f(\Omega_1)-1]\int d\bar{r}_3 d\Omega_2 d\Omega_3[f(\Omega_2)-f(\Omega_3)]^2\bar{c}_3(\rho_0)\ ,\end{aligned}\tag{A2}$$

$$\begin{aligned}B=&-\tfrac{1}{2}\rho_0^3\int d\bar{r}_{12}d\Omega_1 d\Omega_2\int d\bar{r}_3 d\bar{r}_4 d\Omega_3 d\Omega_4\{[f(\Omega_1)-1]^2[f(\Omega_2)-1][f(\Omega_3)-f(\Omega_2)]\\&\qquad+[f(\Omega_1)-1][f(\Omega_2)-1][f(\Omega_3)-1][f(\Omega_4)-f(\Omega_1)]\}\bar{c}_4(\rho_0)\\=&\tfrac{1}{4}\rho_0^3\int d\bar{r}_{12}d\Omega_1 d\Omega_2\int d\bar{r}_3 d\Omega_3 d\bar{r}_4 d\Omega_4\{[f(\Omega_1)-1]^2[f(\Omega_3)-f(\Omega_2)]^2+[f(\Omega_2)-1]\\&\qquad\times[f(\Omega_3)-1][f(\Omega_4)-f(\Omega_1)]^2\}\bar{c}_4(\rho_0)\ .\end{aligned}\tag{A3}$$

In writing the above equations we have made use of the following relations:

$$\frac{\delta\bar{c}_2(\rho_0)}{\delta\rho_0}=\int d\bar{r}_3 d\Omega_3\bar{c}_3(\rho_0)\ ,\tag{A4}$$

$$\frac{\delta^2\bar{c}_2}{\delta\rho_0^2}=\frac{\delta\bar{c}_3}{\delta\rho_0}=\int d\bar{r}_3 d\Omega\bar{c}_4(\rho_0)\ .\tag{A5}$$

In a homogeneous ordered phase, the orientation distribution $f(\Omega)$ is constant throughout the sample. Thus the magnitude of A and B is expected to be negligibly small compared to other terms in (A1) provided the fluctuations about the most probable value of $f(\Omega)$ is small. Neglecting A and B from (A1), we obtain Eq. (4.7). Equation (A1) can be used to derive the Landau—de Gennes expansion of free energy which we describe below.

In the Landau—de Gennes theory of the isotropic-nematic transition[2,30] the Gibbs free energy is written as a power-law expansion around the isotropic equilibrium position. We prefer to use the Helmholtz free energy per particle; with this slight alteration we have

$$\frac{\beta\Delta E}{N}-a\bar{P}_2^2+b\bar{P}_2^3+c\bar{P}_2^4+d\bar{P}_2\bar{P}_4+f\bar{P}_2^2\bar{P}_4\ .\tag{A6}$$

When we substitute (4.1c) into (A1), and retain terms involving $\bar{P}_2$ and $\bar{P}_4$ only, we get

$$a=\tfrac{5}{2}-25\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2 P_2(\cos\theta_1)P_2(\cos\theta_2)\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\rho_0)\ ,$$

$$b=-\tfrac{25}{21}-125\rho_0^2\int d\bar{r}_{12}d\Omega_1 d\Omega_2 P_2(\cos\theta_1)P_2^2(\cos\theta_2)\frac{\delta\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\rho_0)}{\delta\rho_0}\ ,$$

$$c=\tfrac{125}{28}-\tfrac{625}{2}\rho_0^3\int d\bar{r}_{12}d\Omega_1 d\Omega_2 P_2^2(\cos\theta_1)P_2^2(\cos\theta_2)\frac{\delta^2\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\rho_0)}{\delta\rho_0^2}\ ,$$

$$d=\tfrac{9}{2}-81\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2 P_4(\cos\theta_1)P_4(\cos\theta_2)\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\rho_0)\ ,$$

$$e=-\rho_0\int d\bar{r}_{12}d\Omega_1 d\Omega_2 P_2(\cos\theta_1)P_4(\cos\theta_2)\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\rho_0)\ ,$$

and

$$f=-\tfrac{135}{7}-225\rho_0^2\int d\bar{r}_{12}d\Omega_1 d\Omega_2 P_2^2(\cos\theta_1)P_4(\cos\theta_2)\frac{\delta\bar{c}_2(\bar{r}_{12},\Omega_1,\Omega_2;\rho_0)}{\delta\rho_0}\ .$$

It may be noted that the power-law expansion for full one-particle orientational distribution entropic contribution converges slowly. This may limit the range of applicability of this kind of expansion. In the treatment of pretransitional effects where terms of higher order than quadratic are usually small, (A6) is very useful.[2]

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*Permanent address.

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