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Molecular theory of elastic constants of liquid crystals: Application to uniaxial phases

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We use density-functional theory to derive an expression for the distortion free energy of molecular ordered phases and expand it in terms of the order parameters characterizing the structure of the phase and the molecular correlation function of an effective isotropic liquid. We derive expressions for the elastic constants of the uniaxial nematic and smectic-A phases of the liquid crystals and express the results in terms of the spherical-harmonic coefficients of the direct pair-correlation function of the effective isotropic liquid. These harmonic coefficients are obtained by solving the Ornstein-Zernike equation using the Percus-Yevick closure relation for a hard-core system and using a perturbation method for a model system interacting via a pair potential that has angle-dependent attractive parts in addition to hard-core repulsion. It is shown that the repulsive part of the pair interaction makes a dominant contribution to the elastic constants of the liquid crystals.

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I. INTRODUCTION

The understanding of the elastic constants of liquid crystals is important for a number of reasons. In the first place, they appear in the description of virtually all phenomena where the variation of the *director* is manipulated by external fields (display devices) [1,2]. Second, they provide unusually sensitive probes of the microscopic structure of the ordered state. Valuable information regarding the nature and importance of various anisotropies of the intermolecular potentials and of the spatial and angular correlation functions can be derived from the study of the elastic constants. Knowledge of the elasticity of the liquid crystals is also needed in the study of the order-parameter fluctuation and defect stability in them [3]. Because of these reasons the study of the elastic constants has drawn considerable interest in recent years [3,4]. Most of the theoretical efforts directed towards developing molecular theories for the elastic constants are, however, confined to the uniaxial nematic phase [5–13].

Starting with this paper we present a unified theory based on the density-functional formalism [14] and express the elastic constants of the ordered phases (liquid crystals, plastic crystals, and crystalline solids) in terms of the order parameters which characterize the nature and amount of ordering, and in terms of the molecular correlations which characterize the structure of the system. Note that the correlation functions of the ordered phases (or inhomogeneous systems) are, in general, not known and hence to be approximated. The integrals which involve these correlation functions can be approximated by the integrals involving the correlation functions of an *effective isotropic* liquid. The density of this liquid is determined by a criterion [15] to be discussed below (see Sec. II for details). The pair-correlation functions of the isotropic fluid are found by solving the Ornstein-Zernike equation using either the hypernetted chain or the Percus-Yevick (PY) closure relations [16–18]. In this paper, we confine ourselves to the uniaxial phases of the liquid crystals and report result for the nematic (N) and the smectic-A (SmA) phases. The other phases of the liquid crystals will be treated in subsequent papers.

For a nematic phase with uniaxial molecular order, an expression for the elastic energy in terms of the elastic constants was derived by Osean [19] ad Frank [20],

$$\Delta A_e = \tfrac{1}{2}\int d\mathbf{r}[K_1(\nabla\cdot\hat{\mathbf{n}})^2 + K_2(\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}})^2 + K_3(\hat{\mathbf{n}}\times\nabla\times\hat{\mathbf{n}})^2] , \quad (1.1)$$

where $\hat{\mathbf{n}}(r)$ is the director at point $\mathbf{r}$ and the subscript e stands for distortion. In the limit of long-wavelength elastic distortion, the elastic free-energy ΔA_e is proportional to q^2, where $\mathbf{q}$ is the wave vector of the distortion and the elastic moduli K_i are wave-vector independent, giving rise to the terminology Frank elastic constants. The first term in Eq. (1.1) gives energy associated with splay, the second that associated with twist or torsion, and the third that associated with flexion or bend. Thus the Frank elastic constants K_i characterize the free-energy increase associated with the three normal modes of deformation of the oriented nematic state. While for systems considering the long-elongated molecules, K_2 is found to be smallest and K_3 largest, i.e., $K_3 > K_1 > K_2$, for the discotic nematic, K_2 is largest and K_3 smallest, i.e., $K_2 > K_1 > K_3$. All the K_i are, however, found to be of the order of 10^{-6} dyn.

The SmA phase has a liquid character along the plane of the layer and responds like a solid to a force perpendicular to the layers [1,2]. Thus, two very different situations arise: One is where the thickness of the layers is strictly invariable, but they have curvature. The other is where their curvature is small and partly relaxed by the variation in thickness which describes small deformations of the fundamental planar state. The free energy of the distortion associated with these modes is thus written as

$$\Delta A_e=\int d\mathbf{r}\left[\frac{1}{2}K_1\left[\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}\right]^2+\frac{1}{2}B\left[\frac{\partial u}{\partial z}\right]^2\right], \tag{1.2}$$

where $u(x,y,z)$ represents a small displacement of the layers normal to their planes. In the SmA phase, twist and bend deformations are prohibited since $\nabla\times\hat{\mathbf{n}}=\mathbf{0}$. This is because at each point $\hat{\mathbf{n}}$ is normal to the layers. Owing to the variation of u along Z, the following additional term may appear in the distortion free-energy density:

$$\frac{1}{2}K'\left[\frac{\partial^2 u}{\partial z^2}\right]^2+\frac{1}{2}K''\frac{\partial^2 u}{\partial z^2}\left[\frac{\partial^2 u}{\partial x^2}+\frac{\partial^2 u}{\partial y^2}\right]. \tag{1.3}$$

The contribution of these terms is expected to be small in the limit of long-wavelength distortion and is generally neglected. In Eq. (1.2) B is the compressional elastic constant and has the dimension of an energy per unit volume. Since K_i has the dimension of an energy per unit length, a parameter λ defined as

$$\lambda=(K_1/B)^{1/2}$$

has a dimension of length; λ is expected to be of the order of molecular length [1].

A density-functional theory for the Frank elastic constants of the uniaxial N phase was developed by Singh [9–11] and others [8,12]. Their theory has been used to calculate K_i for a number of model systems using approximate forms for the pair-correlation functions of the medium [13,21–23]. We, however, find that none of these approximate forms of the pair-correlation function gives the structure of the medium correctly [17] and therefore the results reported by these authors are not accurate. In this paper we use the *weighted density-functional theory* [15] and express the elastic constants in terms of integrals which involve spherical harmonic coefficients of the direct pair-correlation function (DPCF) of an effective isotropic system.

The paper is organized as follows. In Sec. II we use the density-functional theory to derive a general expression for the distortion free energy in the limit of long-wavelength distortions. This is done by examining at a mean-field level the entropic and energetic differences between the deformed and undeformed states of the ordered phase. The entropic (usually referred to as the ideal gas) part of the free energy does not make any contribution to the distortion free energy. The energetic part is found by an expansion about the free energy of the undeformed state and replacing the DPCF of the ordered phase by that of an effective liquid. The density of the liquid is obtained by weighting the physical density over a physically relevant range about the given point using a suitable weight factor [14,15]. In Sec. III we express the distortion free energy in terms of the order parameters. The subsequent two sections are devoted to the derivation of the elastic constants of the uniaxial nematic and SmA phases. In Sec. VI we evaluate the integrals which involve the spherical harmonic coefficients of the DPCF as a function of density for a model system and discuss the relative contributions of different branches of the interactions. The paper ends with a brief discussion given in Sec. VII.

II. DISTORTION FREE ENERGY

The basic thermodynamic potential used to determine the isothermal elastic properties of a system consisting of N particles contained in volume V at temperature T, is the Helmholtz free energy A. Elasticity is concerned with the behavior of $A[\rho]$ with respect to a small deformation of the system away from its equilibrium state. Such a deformation in the liquid crystals is caused by limiting surfaces of the sample or by external fields acting on molecules. In a nonuniform or ordered phase the free energy is a functional of the singlet distribution $\rho(\mathbf{x})$ defined as

$$\rho(\mathbf{x})\equiv\rho(\mathbf{r},\boldsymbol{\Omega})=\langle N\delta(\mathbf{r}-\mathbf{r}')\delta(\boldsymbol{\Omega}-\boldsymbol{\Omega}')\rangle, \tag{2.1}$$

where $\delta(a-b)$ is the Dirac delta function and $\langle\ \rangle$ represents ensemble average over the positions $\mathbf{r}'$ and orientations $\boldsymbol{\Omega}'$ of the N molecules in the system. The vector $\mathbf{x}$ is taken here to indicate both the location $\mathbf{r}$ of the center of a molecule and its relative orientation $\boldsymbol{\Omega}$ described by the Euler angles θ,ϕ,ψ. For an isotropic system $\rho(\mathbf{x})$ is independent of positions and orientations and the free energy is a function of ρ. We use the notation $d\boldsymbol{\Omega}=(1/\hat{\Omega})\sin\theta\, d\theta\, d\phi\, d\psi$ where $\hat{\Omega}=8\pi^2$ for a molecule of arbitrary symmetry and 4π for a linear molecule.

In the density-functional formulation the free energy of a system is expressed in terms of the direct correlation function of the medium [14]. Taking a reference system characterized by the singlet distribution $\rho_r(\mathbf{x})$ we find for the excess free energy of a system of singlet distribution $\rho(\mathbf{x})$ as [14]

$$\beta\Delta A[\rho]=\beta A[\rho]-\beta A[\rho_r]=\beta\Delta A[\rho_r]-\int d\mathbf{x}_1\Delta\rho(\mathbf{x}_1)\int_0^1 ds\, c^{(1)}(\mathbf{x}_1;[s\rho_r])$$
$$-\int d\mathbf{x}_1\int d\mathbf{x}_2\rho(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2)\int_0^1 ds\, s\int_0^1 ds' c^{(2)}(\mathbf{x}_1,\mathbf{x}_2;[s\rho(\mathbf{x}_1 s')]), \tag{2.2}$$

where

$$\beta A[\rho]=\beta A_{\mathrm{id}}[\rho]+\beta\Delta A[\rho]$$

and

$$\beta A_{\mathrm{id}}[\rho]=\int d\mathbf{x}\,\rho(\mathbf{x})\{\ln[\rho(\mathbf{x})\Lambda]-1\}. \tag{2.3}$$

Here $\beta A_{\mathrm{id}}[\rho]$ is the free energy of an ideal gas of density distribution $\rho(\mathbf{x})$ and Λ is the cube of thermal wavelength associated with a molecule

$$\rho(\mathbf{x},s')=\rho_r(\mathbf{x})+s'\Delta\rho(\mathbf{x}), \tag{2.4a}$$

where

$$\Delta\rho(\mathbf{x})=\rho(\mathbf{x})-\rho_r(\mathbf{x}) \ . \tag{2.4b}$$

The functions $c^{(1)}$ and $c^{(2)}$ appearing in Eq. (2.2) are, respectively, the one- and two-particle direct correlation functions of the medium. For a nonuniform system they are functional of $\rho(\mathbf{x})$ which we, whenever essential, indicate by square brackets. The parameter s (and s') characterizes a path in the density space along which integration is performed. Because of the existence of functional $A[\rho]$, the result is independent of the path of integration [24].

If the reference density $\rho_r(\mathbf{x})$ is taken zero everywhere we find from Eq. (2.2)

$$\beta\Delta A[\rho]=-\tfrac{1}{2}\int d\mathbf{x}_1\int d\mathbf{x}_2\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\bar{c}(\mathbf{x}_1,\mathbf{x}_2) \ , \tag{2.5}$$

where

$$\bar{c}(\mathbf{x}_1,\mathbf{x}_2)=\int_0^1 ds\, s\int_0^1 ds' c^{(2)}(\mathbf{x}_1,\mathbf{x}_2;[ss'\rho_r]) \ . \tag{2.6}$$

Note that Eqs. (2.2) and (2.5) are exact but need the value of $c^{(2)}$. Assuming that one can calculate the values of $c^{(2)}$ for any density along the path of integration, Eq. (2.2) or (2.5) provides a useful way for calculating $\beta\Delta A[\rho]$. It is, however, only for a uniform fluid that $c^{(2)}$ is found either by solving the integral equation theories of the liquid state or by computer simulations. We, therefore, write (2.2) or (2.5) in terms of correlation functions of a uniform fluid. This is done in two ways: in one of the methods we choose $\rho_r(\mathbf{x})=\rho_f$, the density of an isotropic liquid which has chemical potential equal to that of the ordered phase and perform the functional Taylor expansion for $c^{(1)}$ and $c^{(2)}$ functions in the ascending powers of $\Delta\rho(\mathbf{x})=\rho(\mathbf{x})-\rho_f$. The expansion coefficients are the higher-order direct correlation functions of the isotropic fluid. Thus,

$$\begin{aligned}\beta(\Delta A[\rho]-\Delta A[\rho_r])=&-\int d\mathbf{x}_1\Delta\rho(\mathbf{x}_1)c^{(1)}(\rho_f)\\&-\tfrac{1}{2}\int d\mathbf{x}_1\int d\mathbf{x}_2[\Delta\rho(\mathbf{x}_1)\delta\rho_r(\mathbf{x}_2)+\delta\rho_r(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2)+\Delta\rho(\mathbf{x}_1)\Delta\rho(\mathbf{x}_2)]c^{(2)}(\rho_f)\\&-\tfrac{1}{6}\int d\mathbf{x}_1\int d\mathbf{x}_2\int d\mathbf{x}_3\{\,\delta\rho_r(\mathbf{x}_1)[2\delta\rho_r(\mathbf{x}_2)\Delta\rho(\mathbf{x}_3)+\Delta\rho(\mathbf{x}_2)\Delta\rho(\mathbf{x}_3)]\\&\qquad+\Delta\rho(\mathbf{x}_1)[2\delta\rho_r(\mathbf{x}_2)\Delta\rho(\mathbf{x}_3)+\delta\rho_r(\mathbf{x}_2)\delta\rho_r(\mathbf{x}_3)\\&\qquad+\Delta\rho(\mathbf{x}_2)\Delta\rho(\mathbf{x}_3)]\}c^{(3)}(\rho_f)+\cdots\end{aligned} \tag{2.7}$$

with

$$\delta\rho_r(\mathbf{x}_i)=\rho_r(\mathbf{x}_i)-\rho_f, \quad c^{(n)}(\rho_f)=c^{(n)}(\mathbf{x}_1,\mathbf{x}_2,\ldots,\rho_f) \ .$$

Note that for a uniform fluid, $c^{(1)}(\rho_f)$ is position independent and therefore, the first term on the right-hand side of Eq. (2.7) does not make any contribution to the distortion free energy. In what follows we neglect all terms which involve $c^{(n)}(\rho_f)$ with $n\geq 3$. Thus using the symmetry of the system we find for the deformation free energy,

$$\begin{aligned}\beta\Delta A_e[\rho]&=\beta(\Delta A[\rho]-\Delta A[\rho_0])\\&=-\tfrac{1}{2}\int d\mathbf{x}_1\int d\mathbf{x}_2[\rho_e(\mathbf{x}_1)\rho_e(\mathbf{x}_2)-\rho_0(\mathbf{x}_1)\rho_0(\mathbf{x}_2)]c^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\rho_f) \ ,\end{aligned} \tag{2.8}$$

where $\Delta A[\rho_0]$ and $\rho_0(\mathbf{x})$ are, respectively, the excess free energy and singlet distribution of the undistorted ordered phase. The subscript e stands for the deformed state. In most of the calculation ρ_f is taken equal to the density of coexisting isotropic fluid and, therefore, Eq. (2.8) holds near the isotropic-liquid crystal transition point.

In an alternative approach one uses Eq. (2.5) to calculate the excess free energy of a nonuniform system and replaces the unknown function $c^{(2)}$ by the DPCF of an *effective* isotropic reference fluid. For atomic systems a number of schemes have been proposed to calculate the *effective density* of the reference fluid. We find the scheme of Denton and Ashcroft [15] particularly simple to be extended to the molecular system. Thus,

$$\bar{\rho}[\rho]=\frac{1}{\rho_0 V}\int d\mathbf{x}_1\int d\mathbf{x}_2\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)\omega(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho}) \ , \tag{2.9}$$

where ρ_0 is the average density of the ordered phase and ω is a weight factor. $\bar{\rho}[\rho]$ is viewed here as a functional of $\rho(\mathbf{x})$. To ensure that the approximation becomes exact in the limit of a uniform system, the weight factor ω must satisfy the normalization condition

$$\int d\mathbf{x}_2\omega(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho})=1 \ .$$

Requiring that ω satisfy

$$-c^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\rho_u)=\lim_{\rho\to\rho_u}\frac{\delta^2(\beta\Delta A)}{\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)} \tag{2.10}$$

exactly, one finds

$$\omega(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho})=-\frac{1}{2\Delta a'(\bar{\rho})}\left[\beta^{-1}c^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho})+\frac{1}{V}\bar{\rho}\Delta a''(\bar{\rho})\right] , \tag{2.11}$$

where $\Delta a(\bar{\rho})$ is the excess free energy per particle and primes on it denote derivatives with respect to density. Thus we find from Eq. (2.5) the following expression for the free energy of the deformed state:

$$\beta\Delta A_e[\rho]=\beta(\Delta A[\rho]-\Delta A[\rho_0])$$
$$=-\tfrac{1}{2}\int d\mathbf{x}_1\int d\mathbf{x}_2[\rho_e(\mathbf{x}_1)\rho_e(\mathbf{x}_2)-\rho_0(\mathbf{x}_1)\rho_0(\mathbf{x}_2)]c^{(2)}(\mathbf{x}_1,\mathbf{x}_2;\bar{\rho}) \ . \tag{2.12}$$

The elastic constants are defined by the second-order term of the expansion of the free energy of the deformed state around the free energy of the equilibrium (undeformed) state in the ascending powers of a parameter, which measures the deformation. The first term of this expansion is balanced by the equilibrium "stresses" of the undeformed state. One defines the elastic free energy per unit volume as

$$E_e/V=\frac{1}{V}\{\Delta A_e[\rho]+P(V_e-V)\} \ , \tag{2.13}$$

where V_e is the volume of the deformed sample and P the isotropic pressure.

III. EXPANSION OF THE DISTORTION FREE ENERGY IN TERMS OF ORDER PARAMETERS

A complete set of order parameters which characterize the nature and magnitude of the ordering is found from Eq. (2.1) when Dirac delta functions are expanded in a complete set of basis functions. Thus using Fourier expansion for the spatial δ function and the generalized spherical harmonics for the angular δ function, we get [15]

$$\rho_0(\mathbf{x})=\rho_0\sum_{\mathbf{G}}\sum_{l,m,n}Q_{lmn}(G)\exp(i\mathbf{G}\cdot\mathbf{r})D^l_{mn}(\mathbf{\Omega}) \ , \tag{3.1}$$

where $\mathbf{G}$ are reciprocal lattice vectors (RLV's) of a periodic structure present in the ordered phase and

$$Q_{lmn}(G)=(2l+1)\langle\exp(-i\mathbf{G}\cdot\mathbf{r}')D^{l*}_{mn}(\mathbf{\Omega}')\rangle \tag{3.2}$$

are the order parameters. Equation (3.1) presents a general expansion and holds for crystalline solids, smectics, nematics, plastic solids, etc., as special cases. We note that [14]

$$Q_{000}(0)=1 \ , \tag{3.3a}$$

$$Q_{000}(G)=\mu_G=\frac{1}{N}\int\int d\mathbf{r}\,d\mathbf{\Omega}\,\rho(\mathbf{r},\mathbf{\Omega})\exp(-i\mathbf{G}\cdot\mathbf{r}) \ , \tag{3.3b}$$

$$Q_{l00}(G)=Q_{Gl}=(2l+1)\tau_{Gl}$$
$$=\frac{2l+1}{N}\int\int d\mathbf{r}\,d\mathbf{\Omega}\,\rho(\mathbf{r},\mathbf{\Omega})$$
$$\times\exp(-i\mathbf{G}\cdot\mathbf{r})P_l(\cos\theta) \ , \tag{3.3c}$$

$$Q_{lmn}(0)=\frac{2l+1}{N}\int\int d\mathbf{r}\,d\mathbf{\Omega}\,\rho(\mathbf{r},\mathbf{\Omega})D^{l*}_{mn}(\mathbf{\Omega}) \ , \tag{3.3d}$$

where μ_G, $Q_{lmn}(0)$, and τ_{Gl} are, respectively, the positional, orientational, and mixed order parameters. There can be up to $(2l+1)^2$ orientational order parameters of rank l, although this number can be drastically reduced by exploiting the symmetry of the ordered phase and its constituent molecules.

In the limit of long-wavelength distortion the magnitudes of the order parameters are assumed to remain unchanged. The changes occur in the direction of the directors making them position dependent and in the RLV's $\mathbf{G}$. The RLV's $\mathbf{G}_e$ of the strained structure are related to G of the unstrained structure as

$$\mathbf{G}_e=(\underline{I}+\underline{\epsilon})^{-1}\cdot\mathbf{G} \ , \tag{3.4}$$

where $\underline{\epsilon}$ is a strain matrix which governs the change in position. Thus for a deformed state

$$\rho_e(\mathbf{x})=\rho_0\sum_{\mathbf{G}}\sum_{l,m,n}Q_{lmn}(G)\exp(i\mathbf{G}_e\cdot\mathbf{r})D^l_{m,n}(\mathbf{\Omega}_e) \ . \tag{3.5}$$

All angles without subscript e refer to a space fixed (SF) frame whose origin is located at r_1. Let the molecule 1 be at the origin with principal director $\hat{\mathbf{n}}(\mathbf{r}_1)$ pointing in the direction of the SF Z axis and molecule 2 at distance $\mathbf{r}_{12}$ from the origin, where $\hat{\mathbf{n}}(\mathbf{r}_2)$ represents the direction of the local principal director (see Fig. 1). Substituting Eqs. (3.1) and (3.5) into Eq. (2.12) and performing integration over $\mathbf{r}_1$ we find

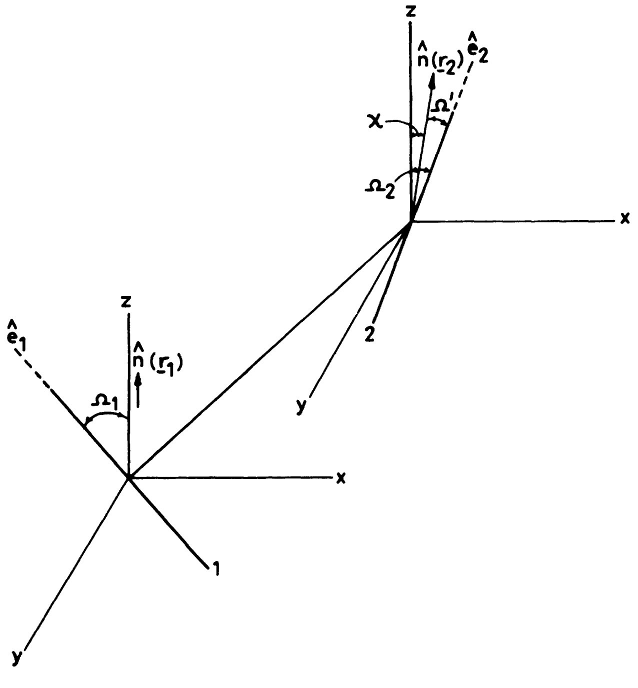

FIG. 1. Definition of angular variables for two linear molecules.

$$\frac{\beta\Delta A_e[\rho]}{V}=-\tfrac{1}{2}\rho_0^2\int d\mathbf{r}_{12}\int d\boldsymbol{\Omega}_1\int d\boldsymbol{\Omega}_2\sum_{l_1,l_2}\sum_{m_1,m_2}\sum_{n_1,n_2}\sum_{\mathbf{G}}Q_{l_1m_1n_1}(G)Q_{l_2m_2n_2}(-G)$$
$$\times[D^{l_1}_{m_1n_1}(\boldsymbol{\Omega}_1)D^{l_2}_{m_2n_2}(\boldsymbol{\Omega}_{2e})\exp(i\mathbf{G}_e\cdot\mathbf{r}_{12})$$
$$-\exp(i\mathbf{G}\cdot\mathbf{r}_{12})D^{l_1}_{m_1n_1}(\boldsymbol{\Omega}_1)D^{l_2}_{m_2n_2}(\boldsymbol{\Omega}_2)]c^{(2)}(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)\;. \tag{3.6}$$

Let $\chi(\mathbf{r}_{12})$ be the angle between the principal directors at $\mathbf{r}_1$ and $\mathbf{r}_2$. Using the rotational properties of the generalized spherical harmonic [26] we find

$$D^{l_2}_{m_2n_2}(\boldsymbol{\Omega}_{2e})=\sum_m D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}_{12}))D^{l_2}_{mn_2}(\boldsymbol{\Omega}_2)\;. \tag{3.7}$$

Since the isotropic fluid DPCF is an invariant pairwise function, it has an expansion in the SF frame of the form

$$c^{(2)}(\mathbf{r}_{12},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=\sum_{l'_1,l'_2,l}\sum_{m'_1,m'_2,m'}\sum_{n'_1,n'_2}c(l'_1l'_2l;n'_1n'_2;r_{12})c_g(l'_1l'_2l;m'_1m'_2m')D^{l'_1}_{m'_1n'_1}(\boldsymbol{\Omega}_1)^*D^{l'_2}_{m'_2n'_2}(\boldsymbol{\Omega}_2)^*Y_{lm'}(\hat{\mathbf{r}}_{12})^*\;, \tag{3.8}$$

where $c_g(l'_1l'_2l;m'_lm'_2m')$ are the Clebsch-Gordan coefficients, $c(l'_1l'_2l;n'_1n'_2;r_{12})$ the harmonic expansion coefficient of the DPCF, and $\hat{\mathbf{r}}_{12}=\mathbf{r}_{12}/|\mathbf{r}_{12}|$ is a unit vector along the intermolecular axis. When Eqs. (3.7) and (3.8) are substituted into Eq. (3.6) and the orthonormality condition for the generalized harmonics is used

$$\frac{\beta\Delta A_e[\rho]}{V}=-\frac{1}{2}\rho_0^2\sum_{l_1,l_2,l}\sum_{m_1,m_2,m,m'}\sum_{n_1,n_2}\sum_{\mathbf{G}}\frac{1}{(2l_1+1)(2l_2+1)}c_g(l_1l_2l;m_1mm')Q_{l_1m_1n_1}(G)Q_{l_2m_2n_2}(-G)$$
$$\times\int d\mathbf{r}_{12}[\exp(i\mathbf{G}_e\cdot\mathbf{r}_{12})D^{l_2}_{mm_2}(\Delta\chi(\mathbf{r}_{12}))-\exp(i\mathbf{G}\cdot\mathbf{r}_{12})]$$
$$\times Y^*_{lm'}(\hat{\mathbf{r}}_{12})c(l_1l_2l;n_1n_2;r_{12})\;. \tag{3.9}$$

This equation presents a general expression for the distortion free-energy density in the limit of long-wavelength distortion and is the principal result of this paper. We will make use of this equation to derive expressions for the elastic constants of the different ordered phases in this and subsequent publications.

IV. UNIAXIAL NEMATIC PHASE

In an uniaxial phase the singlet distribution must be invariant under rotation about the director (Z axis) which implies that $m_1=m_2=0$. In addition, if the phase has a symmetry plane perpendicular to the director, only terms with even l_1 and l_2 will contribute. Thus

$$\frac{1}{V}\beta\Delta A_e[\rho]=-\tfrac{1}{2}\rho_n^2\sum_{l_1,l_2,l}{}'\sum_m\sum_{n_1,n_2}\frac{Q_{l_10n_1}Q_{l_20n_2}}{(2l_1+1)(2l_2+1)}c_g(l_1l_2l;0mm)$$
$$\times\int d\mathbf{r}_{12}\left[\left[\frac{4\pi}{2l_2+1}\right]^{1/2}Y_{l_2m}(\Delta\chi(r_{12}))-1\right]c(l_1l_2l;n_1n_2;r_{12})Y^*_{lm}(\hat{\mathbf{r}}_{12})\;, \tag{4.1}$$

where ρ_n is the nematic number density and prime on the summation indicates that l_1,l_2 are even. If the system is composed of cylindrically symmetric molecules the rotation about the molecular symmetry axis should not modify the distribution, i.e., $n_1=n_2=0$. Since [26]

$$c(l_1l_2l;n_1n_2;r_{12})=\left[\frac{(2l_1+1)(2l_2+1)}{(4\pi)^2}\right]^{1/2}c_{l_1l_2l}(r_{12})\;, \tag{4.2}$$

we find that for a uniaxial phase composed of axially symmetric molecules, Eq. (4.1) reduces to

$$\frac{1}{V}\beta\Delta A_e[\rho]=-\tfrac{1}{2}\rho_n^2\sum_{l_1,l_2,l}{}'\sum_m\left[\frac{(2l_1+1)(2l_2+1)}{(4\pi)^2}\right]^{1/2}\bar{P}_{l_1}\bar{P}_{l_2}$$
$$\times c_g(l_1l_2l;0mm)\int d\mathbf{r}_{12}\left[\left[\frac{4\pi}{2l_1+1}\right]^{1/2}Y_{l_2m}(\Delta\chi(\mathbf{r}_{12}))-1\right]c_{l_1l_2l}(r_{12})Y^*_{lm}(\hat{\mathbf{r}}_{12})\;. \tag{4.3}$$

Note that $\Delta\chi(\mathbf{r}_{12})$ is the orientation of $\hat{\mathbf{n}}(\mathbf{r}_2)$ with respect to $\hat{\mathbf{n}}(\mathbf{r}_1)$ which is taken to be along the Z axis of a space fixed frame. Without any loss of generality, we can confine the variation of $\hat{\mathbf{n}}(\mathbf{r}_2)$ in a plane (say XZ). Thus

$$Y_{l_2 m}(\Delta\chi(\mathbf{r}_{12}))=Y_{l_2 m}(\Delta\theta(\mathbf{r}_{12}),0)\ . \tag{4.4}$$

For small $\Delta\theta$ we can expand the spherical harmonics in ascending power of $\Delta\theta$ leading to

$$Y_{l_2 m}(\Delta\theta(\mathbf{r}),0)=\left[\frac{2l_2+l}{4\pi}\right]^{1/2}\delta_{m,0}+\Delta\theta(\mathbf{r})b_{l_2 1}(\delta_{m,1}-\delta_{m,\underline{1}})+\tfrac{1}{2}\Delta\theta^2(\mathbf{r})[b_{l_2 0}\delta_{m,0}+b_{l_2 2}(\delta_{m,2}+\delta_{m,\underline{2}})]+\cdots\ , \tag{4.5}$$

where

$$b_{l_2 0}=-\tfrac{1}{2}l_2(l_2+1)\left[\frac{2l_2+1}{4\pi}\right]^{1/2}, \tag{4.6a}$$

$$b_{l_2 1}=-b_{l_2 \underline{1}}=-\tfrac{1}{2}l_2(l_2+1)\left[\frac{2l_2+1}{4\pi}\frac{(l_2-1)!}{(l_2+1)!}\right]^{1/2}, \tag{4.6b}$$

$$b_{l_2 2}=b_{l_2 \underline{2}}=\tfrac{1}{4}(l_2-1)l_2(l_2+1)(l_2+2)\left[\frac{2l_2+1}{4\pi}\frac{(l_2-2)!}{(l_2+2)!}\right]^{1/2}. \tag{4.6c}$$

For splay, twist, and bend deformations the deformation angle $\Delta\theta$ has been evaluated to order q^2 to give [5,7]

$$\Delta\theta(\mathbf{r})=r^2\begin{bmatrix}-(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}}) & (\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\\ & 0 & \\ (\hat{\mathbf{r}}\cdot\hat{\mathbf{x}}) & (\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})\end{bmatrix}\quad\text{and}\quad\Delta\theta^2(\mathbf{r})=r^2\begin{bmatrix}(\hat{\mathbf{r}}\cdot\hat{\mathbf{x}})^2\\(\hat{\mathbf{r}}\cdot\hat{\mathbf{y}})^2\\(\hat{\mathbf{r}}\cdot\hat{\mathbf{z}})^2\end{bmatrix}, \tag{4.7}$$

where $\hat{\mathbf{x}},\hat{\mathbf{y}},\hat{\mathbf{z}}$ are unit vectors along XYZ axes. The subscript 12 has been dropped from $\mathbf{r}_{12}$. Substituting Eqs. (4.5) and (4.7) into Eq. (4.3) and integrating over $\hat{\mathbf{r}}$ we get the following expressions for the Frank elastic constants [see Eq. (1.1)]:

$$\beta K_1=-\frac{1}{3\sqrt{5}}\rho_n^2\sum_{l_1,l_2}{}'(2l_1+1)^{1/2}\bar{P}_{l_1}\bar{P}_{l_2}\{\tfrac{1}{2}\sqrt{5}b_{l_2 0}c_g(l_1l_20;000)J_{l_1l_20}+[-\tfrac{1}{2}b_{l_2 0}c_g(l_1l_22;000)+\sqrt{6}b_{l_2 1}c_g(l_1l_22;011)$$
$$+\sqrt{3/2}b_{l_2 2}c_g(l_1l_22;022)]J_{l_1l_22}\}\ , \tag{4.8}$$

$$\beta K_2=-\tfrac{1}{6}\rho_n^2\sum_{l_1,l_2}{}'(2l_1+1)^{1/2}\bar{P}_{l_1}\bar{P}_{l_2}\{b_{l_2 0}c_g(l_1l_20;000)J_{l_1l_20}-\frac{1}{\sqrt{5}}[b_{l_2 0}c_g(l_1l_22;000)+\sqrt{6}b_{l_2 2}c_g(l_1l_22;022)]J_{l_1l_22}\}\ , \tag{4.9}$$

$$\beta K_3=-\frac{1}{3\sqrt{5}}\rho_n^2\sum_{l_1,l_2}{}'(2l_1+1)^{1/2}\bar{P}_{l_1}\bar{P}_{l_2}\{\tfrac{1}{2}\sqrt{5}b_{l_2 0}c_g(l_1l_20;000)J_{l_1l_20}+[b_{l_2 0}c_g(l_1l_22;000)-\sqrt{6}b_{l_2 1}c_g(l_1l_22;011)]J_{l_1l_22}\}\ , \tag{4.10}$$

where

$$J_{l_1l_2l}=\int dr\, r^4 c_{l_1l_2l}(r)\ . \tag{4.11}$$

In Appendix A we expand the above expressions for βK_i as

$$\beta K_i=\sum_{l_1,l_2}\beta K_i(l_1,l_2) \tag{4.12}$$

and give explicit results for $\beta K_i(l_1,l_2)$ for $2\le l_1,l_2\le 8$. They suggest the following general relations:

$$K_i(0,l_2)=K_i(l_1,0)=0\ , \tag{4.13a}$$

$$K_1(2,2)=K_3(2,2)\neq K_2(2,2)\ , \tag{4.13b}$$

$$\frac{K_2(2,4)}{K_1(2,4)}=\frac{K_2(4,6)}{K_1(4,6)}=\frac{K_2(6,8)}{K_1(6,8)}=\cdots=\frac{1}{3}\ , \tag{4.13c}$$

and

$$\frac{K_3(2,4)}{K_1(2,4)}=\frac{K_3(4,6)}{K_1(4,6)}=\frac{K_3(6,8)}{K_1(6,8)}=\cdots=-\frac{4}{3}\ . \tag{4.13d}$$

V. THE SMECTIC *A* PHASE

Since the Sm *A* phase has one-dimensional positional ordering in addition to orientational ordering, one has, from Eq. (3.9),

$$\frac{1}{V}\beta\Delta A_e[\rho]=-\frac{1}{8\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{m}\sum_{k}Q_{kl_1}Q_{-kl_2}c_g(l_1l_2l;0mm)[(2l_1+1)(2l_2+1)]^{-1/2}$$
$$\times\int d\mathbf{r}\left[\left[\frac{4\pi}{2l_2+1}\right]^{1/2}\exp(iG_ez_{12})Y_{lm}(\Delta\chi(\mathbf{r}_{12}))-\exp(iGz_{12})\right]c_{l_1l_2l}(r)Y^*_{lm}(\hat{\mathbf{r}})\ , \qquad (5.1)$$

where $G=2\pi k/d$ and $G_e=2\pi k/d_e$; d_e and d are the interlayer spacing of the distorted and undistorted Sm *A* phase and k is a positive or negative integer, z_{12} is the translational coordinate parallel to the layer normal, and $Q_{0l}=(2l+1)\bar{P}_l$, $Q_{k0}=\mu_Z$, and $Q_{kl}=(2l+1)\tau_{kl}$ are, respectively, orientational, positional, and mixed order parameters. In writing Eq. (5.1) we have assumed molecules of the system to be cylindrically symmetric. Neglecting the coupling between the distortions caused by the curvature in director orientation and dilation in layer thickness we find

$$\frac{1}{V}\beta\Delta A_e^{(s)}[\rho]=-\frac{1}{8\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{m}\sum_{k}Q_{kl_1}Q_{-kl_2}c_g(l_1l_2l;0mm)[(2l_1+1)(2l_2+1)]^{-1/2}$$
$$\times\int d\mathbf{r}\,e^{iGz_{12}}\left[\left[\frac{4\pi}{2l_2+1}\right]^{1/2}Y_{lm}(\Delta\chi(\mathbf{r}))-1\right]c_{l_1l_2l}(r)Y^*_{lm}(\hat{\mathbf{r}})\ , \qquad (5.2)$$

$$\frac{1}{V}\beta\Delta A^{(l)}[\rho]=-\frac{1}{8\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{m}\sum_{k}Q_{kl_1}Q_{-kl_2}c_g(l_1l_2l;0mm)\left[\frac{1}{(2l_1+1)(2l_2+1)}\right]^{1/2}$$
$$\times\int d\mathbf{r}[\exp(iG_ez_{12})-\exp(iGz_{12})]c_{l_1l_2l}(r)Y^*_{lm}(\hat{\mathbf{r}})\ . \qquad (5.3)$$

Equations (5.2) and (5.3) represent, respectively, the distortion free energy arising due to curvature in the director orientation and dilation in layer thickness.

Comparing Eq. (5.2) with Eq. (1.2) we obtain the following expression for K_1:

$$\beta K_1=-\frac{1}{4\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{k}\sum_{m}Q_{kl_1}Q_{-kl_2}c_g(l_1l_2l;0mm)\frac{1}{[(2l_1+1)(2l_2+1)]^{1/2}}$$
$$\times\int d\mathbf{r}\exp(iGz_{12})\left[\left[\frac{4\pi}{2l_2+1}\right]^{1/2}Y_{lm}(\Delta\chi(\mathbf{r}))-1\right]c_{l_1l_2l}(r)Y^*_{lm}(\hat{\mathbf{r}})\ . \qquad (5.4)$$

A plane wave traveling in the Z direction is symmetrical about the Z axis and can be expanded as a series of Legendre polynomials referred to this axis

$$e^{iGz_{12}}=\sum_{l'}(i)^{l'}(2l'+1)j_{l'}(Gr)P_{l'}(\cos\theta)\ , \qquad (5.5)$$

where $j_{l'}(Gr)$ are spherical Bessel functions and θ is angle between the Z axis and intermolecular axis r. Thus from Eqs. (4.5), (5.4), and (5.5) we get

$$\beta K_1=-\tfrac{1}{6}\rho_s^2\sum_{l_1,l_2}{}'\sum_{k}Q_{kl_1}Q_{-kl_2}(2l_1+1)^{-1/2}(2l_2+1)^{-1}$$
$$\times\sum_{l,l'}i^{l'}(2l'+1)^{1/2}J^{l'}_{l_1l_2l}\Bigg[b_{l_20}c_g(l_1l_2l;000)\delta_{ll'}$$
$$+\left[\frac{2l'+1}{2l+1}\right]^{1/2}c_g(2l'l,000)[-b_{l_20}c_g(l_1l_2l;000)c_g(2l'l;000)$$
$$+2\sqrt{6}b_{l_22}c_g(l_1l_2l;011)c_g(2l'l;101)$$
$$+\sqrt{6}b_{l_22}c_g(l_1l_2l;022)c_g(2l'l;202)]\Bigg]\ , \qquad (5.6)$$

where

$$J^{l'}_{l_1l_2l}=\int dr\,r^4j_{l'}(Gr)c_{l_1l_2l}(r)\ .$$

Using Eq. (3.4) we expand Eq. (5.3) in ascending powers of dilation parameter $\epsilon=(de/d-1)$. The term associated with $\frac{1}{2}\epsilon^2$ defines the bulk elastic constant B. Thus

$$\beta B=\frac{1}{16\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{k}\sum_{m}Q_{kl_1}Q_{-kl_2}c_g(l_1l_2l;0mm)[(2l_1+1)(2l_2+1)]^{-1/2}\int d\mathbf{r}\,r^2\int d\hat{\mathbf{r}}\,G^2z_{12}^2e^{iGz_{12}}c_{l_1l_2l}(r)Y_{lm}^*(\hat{\mathbf{r}})\,\cdot \tag{5.7}$$

Using Eq. (5.5) we simplify Eq. (5.7) to give

$$\beta B=\tfrac{1}{12}(4\pi)^{-1/2}\rho_s^2\sum_{l_1,l_2,l\,l',k}{}'\sum G^2Q_{kl_1}Q_{-kl_2}[(2l_1+1)(2l_2+1)]^{-1/2}J_{l_1l_2l}^{l'}i^{l'}(2l'+1)^{1/2}c_g(l_1l_2l;000)$$
$$\times\left[\delta_{ll'}+2\left[\frac{2l'+1}{2l+1}\right]^{1/2}c_g^2(2l'l;000)\right]\,. \tag{5.8}$$

The term proportional to ϵ in the free-energy expansion is found to be

$$-\frac{i}{8\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{k}Q_{kl_1}Q_{-kl_2}c_g(l_1l_2l;0mm)G[(2l_1+1)(2l_2+1)]^{-1/2}\int d\mathbf{r}\,z_{12}e^{iGz_{12}}c_{l_1l_2l}(r)Y_{lm}^*(\hat{\mathbf{r}})\,. \tag{5.9}$$

When this term is set equal to zero for each G, one finds a condition for equilibrium layer separation. To show this we consider the free-energy density of the undistorted smectic phase

$$\frac{1}{V}\beta\Delta A=\Delta f_d=-\frac{1}{8\pi}\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{m}\sum_{k}Q_{kl_2}Q_{-kl_2}c_g(l_1l_2l;0mm)[(2l_1+1)(2l_2+1)]^{-1/2}\int d\mathbf{r}c_{l_1l_2l}(r)\exp(iGz_{12})Y_{lm}^*(\hat{\mathbf{r}})\,. \tag{5.10}$$

The interlayer spacing d is determined by minimizing Δf_d with respect to G. Thus

$$\frac{\partial f_d}{\partial G}=f_d'=-\frac{1}{8\pi}i\rho_s^2\sum_{l_1,l_2,l}{}'\sum_{m}\sum_{k}Q_{kl_1}Q_{-kl_2}C_g(l_1l_2l;0mm)[(2l_1+1)(2l_2+1)]^{-1/2}\int d\mathbf{r}\,c_{l_1l_2l}(r)z_{12}Y_{lm}^*(\hat{\mathbf{r}})e^{iGz_{12}}=0\,, \tag{5.11}$$

which is identical to Eq. (5.9).

In Appendix B we write for the elastic constants of SmA as

$$\beta K=\sum_{l_1}{}'\sum_{l_2}{}'\beta K_1(l_1,l_2) \tag{5.12a}$$

and

$$\beta B=\sum_{l_1}{}'\sum_{l_2}{}'\beta B(l_2,l_2) \tag{5.12b}$$

and evaluate the terms of these series for $0\le l_1,l_2\le 4$.

VI. RESULTS FOR A MODEL SYSTEM

We consider a model system the molecules of which have prolate ellipsoid of revolution symmetry and interact via a pair potential:

$$u(\mathbf{r},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=(u^{(0)}+u^{(d-d)}+u^{(d-q)}+u^{(q-q)})(\mathbf{r},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2) \tag{6.1}$$

with

$$u^{(0)}(\mathbf{r},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=(u^{(\mathrm{HC})}+u^{(\mathrm{dis})})(\mathbf{r},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)\,. \tag{6.2}$$

Here $u^{(\mathrm{HC})}(\mathbf{r},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)$ represents the repulsion between hard ellipsoids of revolution (HER) parametrized by the length-to-width ratio $x_0=a/b$, where $2a$ and $2b$ denote, respectively, the length of the major (axis of revolution) and minor axes of the ellipsoids. For $u^{(\mathrm{HC})}$ we choose

$$u^{(\mathrm{HC})}(\mathbf{r},\boldsymbol{\Omega}_1,\boldsymbol{\Omega}_2)=\begin{cases}\infty & \text{for } r\le D(\hat{\mathbf{r}},\boldsymbol{\Omega}_{12})\\ 0 & \text{for } r>D(\hat{\mathbf{r}},\boldsymbol{\Omega}_{12})\,,\end{cases} \tag{6.3}$$

where $D(\hat{\mathbf{r}},\boldsymbol{\Omega}_{12})$ is the distance of closest approach of two molecules with relative orientation given by $\boldsymbol{\Omega}_{12}$ approaching in the direction of $\hat{\mathbf{r}}$ (which is the unit vector along the intermolecular axis). For $D(\hat{\mathbf{r}},\boldsymbol{\Omega}_{12})$ we choose the expression given by Berne and Puchukas [27],

$$D(\hat{\mathbf{r}},\boldsymbol{\Omega}_{12})=d_0\left[1-\frac{\chi}{2}\left\{\frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_1+\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_2)^2}{1+\chi(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}+\frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_1-\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_2)^2}{1-\chi(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}\right\}\right]^{-1/2}, \tag{6.4}$$

where

$$\chi=\frac{x_0^2-1}{x_0^2+1}\,.$$

$\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are unit vectors along the symmetry axes of the two interacting molecules.

For $u^{(\mathrm{dis})}$ we choose a form given by Gay and Berne [28],

$$u^{(\mathrm{dis})}(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=\begin{cases}0 \quad \text{for } r<D(\hat{\mathbf{r}},\mathbf{\Omega}_{12}) \\ -\epsilon(\hat{\mathbf{r}},\mathbf{\Omega}_{12})\left[\dfrac{d_0}{r-D(\hat{\mathbf{r}},\mathbf{\Omega}_{12})+d_0}\right]^6 \quad \text{for } r\geq D(\hat{\mathbf{r}},\mathbf{\Omega}_{12})\ ,\end{cases} \tag{6.5}$$

where

$$\epsilon(\hat{\mathbf{r}},\mathbf{\Omega}_{12})=\epsilon_1(\mathbf{\Omega}_{12})\epsilon_2^2(\hat{\mathbf{r}},\mathbf{\Omega}_{12}) \tag{6.6a}$$

with

$$\epsilon_1(\mathbf{\Omega}_{12})=\epsilon_0[1-\chi^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2]^{-1/2} \tag{6.6b}$$

and

$$\epsilon_2(\hat{\mathbf{r}},\mathbf{\Omega}_{12})=1-\frac{1}{2}\chi'\left[\frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_1+\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_2)^2}{1+\chi'(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}+\frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_1-\hat{\mathbf{r}}\cdot\hat{\mathbf{e}}_2)^2}{1-\chi'(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)}\right] . \tag{6.6c}$$

Here ϵ_0 is a constant with unit of energy and

$$\chi'=\frac{\epsilon_s^{1/2}-\epsilon_e^{1/2}}{\epsilon_s^{1/2}+\epsilon_e^{1/2}}\ ,$$

where ϵ_s is the value for the depth of the potential for a side-to-side configuration and ϵ_e the value for an end-to-end configuration. A good representation of the interaction is found by choosing $\epsilon_e/\epsilon_s\simeq 0.2$ for $x_0\simeq 3$. Note that the potential given by Eqs. (6.2)–(6.6) has a hard-core repulsion in contrast to the Gay-Berne potential which has a soft repulsion [like the Lennard-Jones (12-6) potential repulsion but with angle-dependent length and depth parameters given above]. This difference in the repulsive part of the potential will, however, not affect the basic features of the result as the softness of the repulsive core is treated in the hard-core model using the temperature- and density-dependent hard-core length parameter [21].

In Eq. (6.1) the terms with superscripts *d-d*, *d-q*, and *q-q* indicate the interactions arising due to the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The centers for the origin of these interactions are taken to be the center of molecules. Thus

$$u^{(d\text{-}d)}(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=-\frac{\mu^2}{r^3}f^{(d\text{-}d)}(\theta_1',\theta_2',\phi')\ , \tag{6.7}$$

$$u^{(d\text{-}q)}(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=\frac{3}{2}\frac{\mu Q}{r^4}f^{(d\text{-}q)}(\theta_1',\theta_2',\phi')\ , \tag{6.8}$$

$$u^{(q\text{-}q)}(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=\frac{3}{4}\frac{Q^2}{r^5}f^{(q\text{-}q)}(\theta_1',\theta_2',\phi')\ , \tag{6.9}$$

where

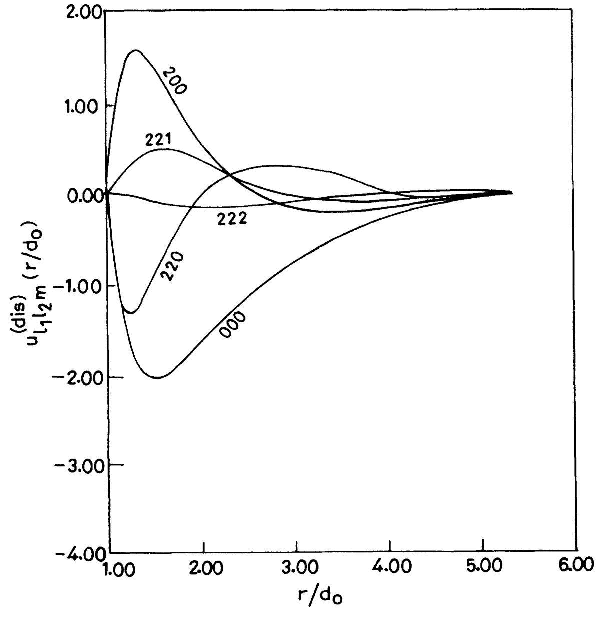

FIG. 2. The body-fixed potential harmonic coefficients $u_{l_1l_2m}^{(\mathrm{dis})}(r)$ for the dispersion interaction for $x_0=3$. The numbers on the curves represent the values of l_1l_2m.

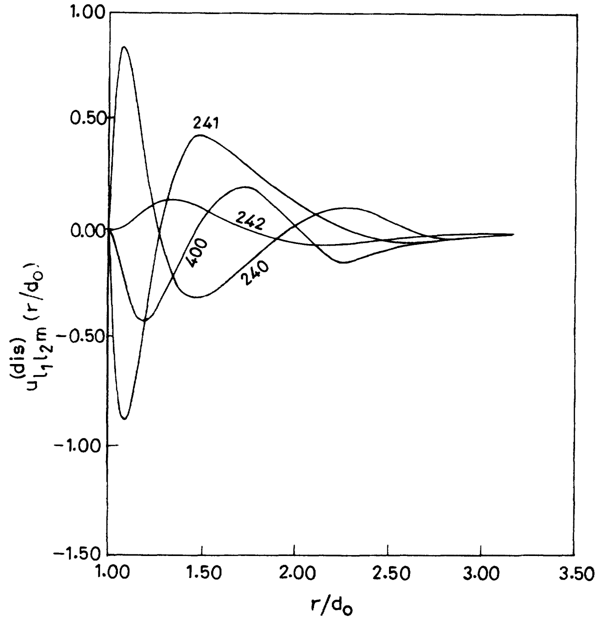

FIG. 3. The body-fixed potential harmonic coefficients $u_{l_1l_2m}^{(\mathrm{dis})}(r)$ for the dispersion interaction for $x_0=3$. The numbers on the curves represent the values of l_1l_2m.

$$f^{(d\text{-}d)}(\theta'_1,\theta'_2,\phi')=2\cos\theta'_1\cos\theta'_2-\sin\theta'_1\sin\theta'_2\cos\phi' \;, \tag{6.10}$$

$$f^{(d\text{-}q)}(\theta'_1,\theta'_2,\phi')= 3\cos\theta'_1(3\cos^2\theta'_2-1)-6\sin\theta'_1\sin\theta'_2\cos\theta'_2\cos\phi'+3\cos\theta'_2(3\cos^2\theta'_1-1)-6\sin\theta'_1\sin\theta'_2\cos\theta'_1\cos\phi' \;, \tag{6.11}$$

$$f^{(q\text{-}q)}(\theta'_1,\theta'_2,\phi')= 1-5\cos^2\theta'_1-5\cos^2\theta'_2+17\cos^2\theta'_1\cos^2\theta'_2+2\sin^2\theta'_1\sin^2\theta'_2\cos^2\phi'-16\sin\theta'_1\sin\theta'_2\cos\theta'_1\cos\theta'_2\cos\phi' \;. \tag{6.12}$$

All angles with a prime are measured in a body-fixed (BF) frame.

Since the structure of the isotropic liquid is primarily controlled by the harsh repulsive interaction, we use a first-order perturbation theory to calculate the DPCF of the system. Thus [21]

$$c(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=(c^{(\mathrm{HC})}+c^{(p)})(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2) \tag{6.13}$$

with

$$c^{(p)}(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=-\beta(u^{(p)}g^{(\mathrm{HC})})(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2) \;, \tag{6.14}$$

where

$$u^{(p)}(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2)=(u^{(\mathrm{dis})}+u^{(d\text{-}d)}+u^{(d\text{-}q)}+u^{(q\text{-}q)})(\mathbf{r},\mathbf{\Omega}_1,\mathbf{\Omega}_2) \;.$$

Here $c^{(\mathrm{HC})}$ and $g^{(\mathrm{HC})}$ are, respectively, the DPCF and the PCF of a system of the HER. Recently Ram and Singh [17] have solved the PY equation for the spherical-harmonic coefficients of these functions for a system of the HER. We take their results and calculate $c^{(p)}$ from Eq. (6.14). Thus in the BF frame for $\beta=1$,

$$\begin{aligned} c^{(p)}_{l_1 l_2 m}(r_{12}) = -\frac{1}{4\pi}\beta \sum_{l'_1,l'_2}\sum_{l''_1,l''_2} & \left[\frac{(2l'_1+1)(2l'_2+1)(2l''_1+1)(2l''_2+1)}{(2l_1+1)(2l_2+1)}\right]^{1/2} c_g(l'_1l''_1l_1;000)c_g(l'_2l''_2l_2;000) \\ & \times \sum_{m',m''} c_g(l'_1l''_1l_1;m'm''m)c_g(l'_2l''_2l_2;m'm''m)u^{(p)}_{l'_1l'_2m'}(r_{12})g^{(\mathrm{HC})}_{l''_1l''_2m''}(r_{12}) \;, \end{aligned} \tag{6.15}$$

where the summations are over all allowed values of l'_1, l'_2, l''_1, l''_2, m', and m''. The SF frame harmonic coefficients are found from the results of Eq. (6.15) by the linear transformation [26]

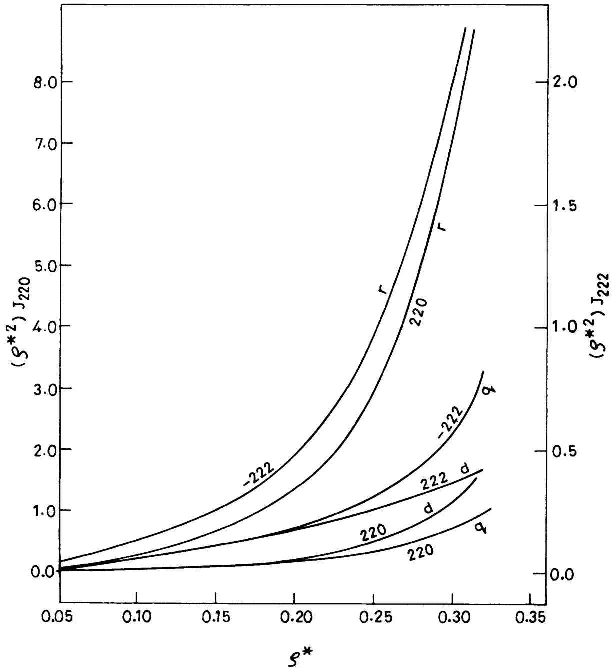

FIG. 4. Values of $\rho^{*2}J_{220}$ and $\rho^{*2}J_{222}$ are plotted as a function of density $\rho^*(=\rho d_0^3)$ for $x_0=3$. The numbers on the curves represent the values of l_1l_2l and the letters r, d, and q stand for the contribution of repulsion, dispersion, and quadrupole interactions. The minus sign signifies the negative value for corresponding integral.

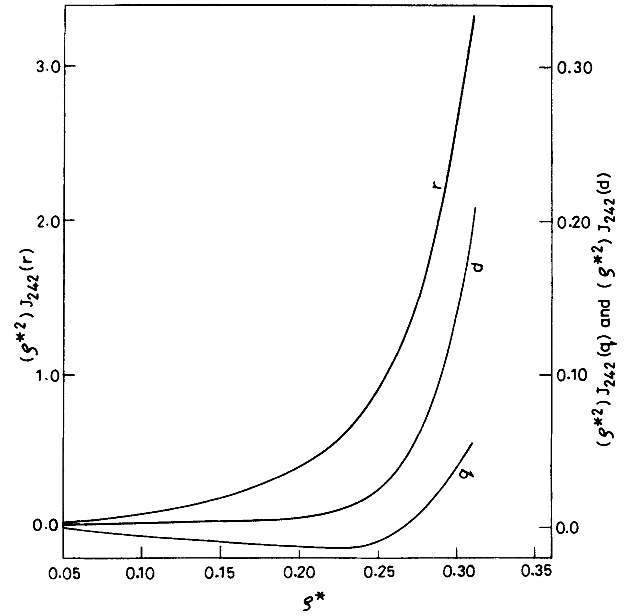

FIG. 5. Values of $\rho^{*2}J_{242}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

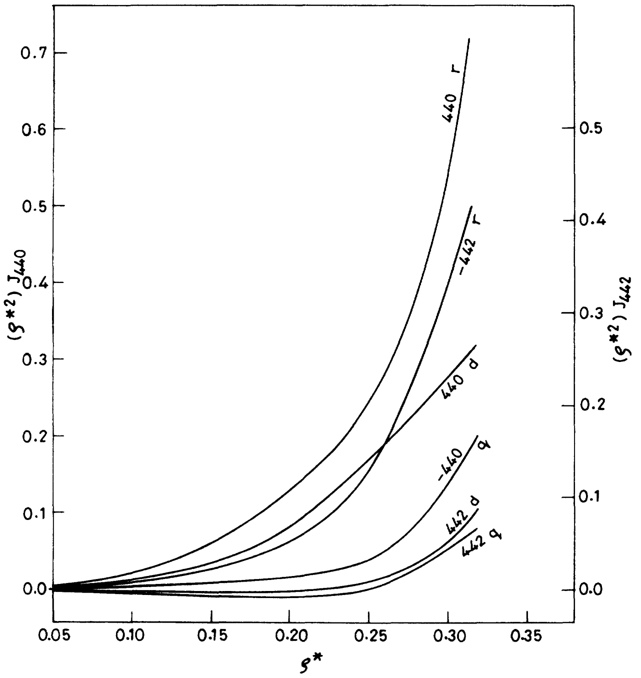

FIG. 6. Values of $\rho^{*2}J_{440}$ and $\rho^{*2}J_{442}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

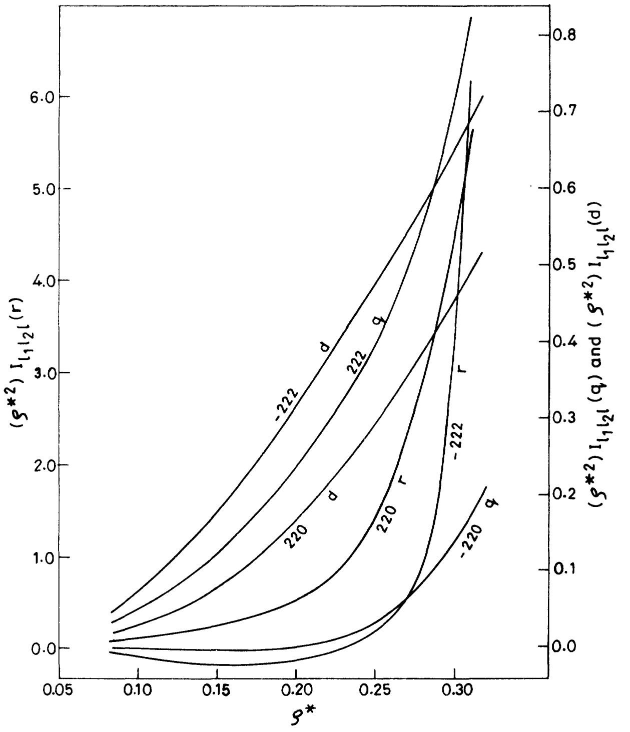

FIG. 7. Values of $\rho^{*2}I_{220}$ and $\rho^{*2}I_{222}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

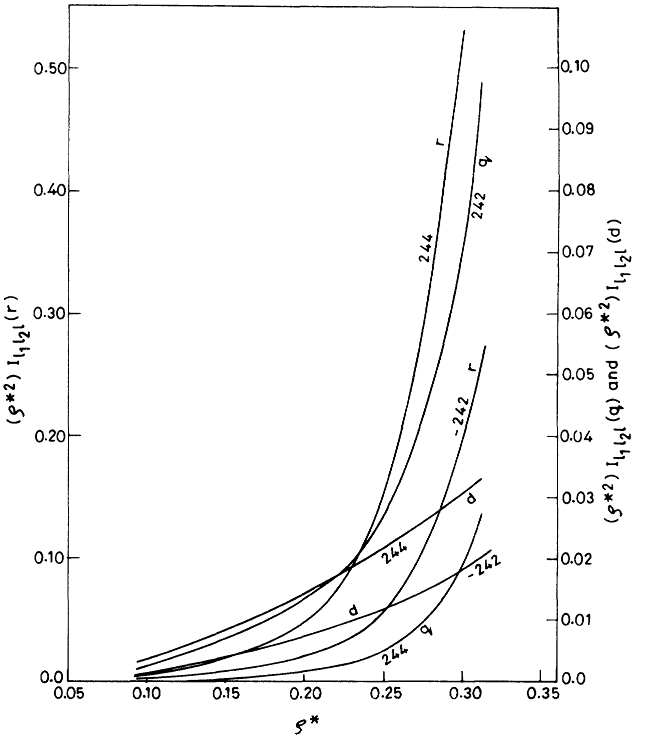

FIG. 8. Values of $\rho^{*2}I_{242}$ and $\rho^{*2}I_{244}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

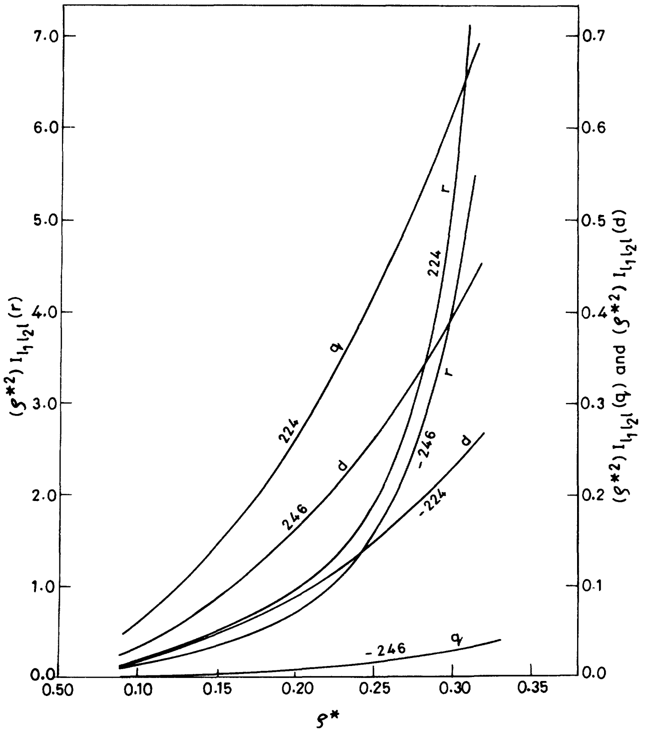

FIG. 9. Values of $\rho^{*2}I_{224}$ and $\rho^{*2}I_{246}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

$$c_{l_1 l_2 l}(r_{12})=\sum_m \left[\frac{4\pi}{2l+1}\right]^{1/2} c_g(l_1 l_2 l;m_1 m_2 m)c_{l_1 l_2 m}(r_{12}) \ . \tag{6.16}$$

From the fact that the c-harmonic coefficients which contribute to the free energy of uniaxial liquid crystal consisting of cylindrically symmetric molecules have even l_1, l_2 indices and that the c-harmonic coefficients of the HER system survive only for the even values of l_1'', l_2'' we note that only those interaction will contribute to Eqs. (6.15) and (6.16) which have nonvanishing u harmonics for the even values of l_1', l_2'. This leads us immediately to the following conclusions.

(i) Since in the case of the d-d and d-q interactions the nonvanishing u harmonics (in the BF frame) are $u_{110}^{(d\text{-}d)}(r)$, $u_{111}^{(d\text{-}d)}(r)$, $u_{120}^{(d\text{-}q)}(r)$, and $u_{121}^{(d\text{-}q)}(r)$, these interactions do not contribute to the free energy of the uniaxial phase.

(ii) The q-q interaction contributes to the free energy and to the elastic constants of the ordered phase because the nonvanishing u-harmonic coefficients (in the BF frame) for this interaction are $u_{220}^{(q\text{-}q)}(r)$, $u_{221}^{(q\text{-}q)}(r)$, and $u_{222}^{(q\text{-}q)}(r)$.

(iii) For the dispersion interaction of Eq. (6.5) the nonvanishing u-harmonic coefficients in the BF frame are

$$u_{000}^{(\text{dis})}(r),\quad u_{400}^{(\text{dis})}(r),\quad u_{200}^{(\text{dis})}(r)\ ,$$

$$u_{240}^{(\text{dis})}(r),\quad u_{220}^{(\text{dis})}(r),\quad u_{241}^{(\text{dis})}(r)\ ,$$

$$u_{221}^{(\text{dis})}(r),\quad u_{242}^{(\text{dis})}(r),\quad u_{222}^{(\text{dis})}(r)\ ,$$

$$u_{440}^{(\text{dis})}(r),\quad u_{441}^{(\text{dis})}(r),\quad u_{442}^{(\text{dis})}(r)\ ,$$

$$u_{443}^{(\text{dis})}(r),\quad u_{444}^{(\text{dis})}(r)\ .$$

These harmonics are evaluated numerically and in Figs. 2 and 3 we show results for some of the harmonics whose contributions are expected to be relatively important. With the known c harmonics we calculate values of $J_{l_1 l_2 l}$ and $J_{l_1 l_2 l}^{l'}$ as a function of density $\rho^*(=\rho d_0^3)$ for repulsion, dispersion, and quadrupolar branches of the interactions. For $x_0=3.0$ and $\beta=1$ we plot in Figs. 4–6 the function $J_{l_1 l_2 l}$ and compare the contributions arising from different branches of the interactions. We note that (i) the contribution of the hard-core interaction dominates and (ii) the series of Eq. (4.13) rapidly converges as l_1 and l_2 increase. In Figs. 7–9 we plot the values of

$$I_{220}=J_{220}^{0}+J_{220}^{2}\ , \tag{6.17a}$$

$$I_{222}=J_{222}^{0}-\tfrac{20}{7}J_{222}^{2}-\tfrac{27}{7}J_{222}^{4}\ , \tag{6.17b}$$

$$I_{224}=\tfrac{1}{14}J_{224}^{2}-\tfrac{82}{77}J_{224}^{4}-\tfrac{25}{22}J_{224}^{6}\ , \tag{6.17c}$$

$$I_{242}=\tfrac{1}{2}J_{242}^{0}+\tfrac{4}{7}J_{242}^{2}+\tfrac{1}{14}J_{242}^{4}\ , \tag{6.17d}$$

$$I_{244}=-\tfrac{1}{7}J_{244}^{2}+\tfrac{6}{7}J_{244}^{4}+J_{244}^{6}\ , \tag{6.17e}$$

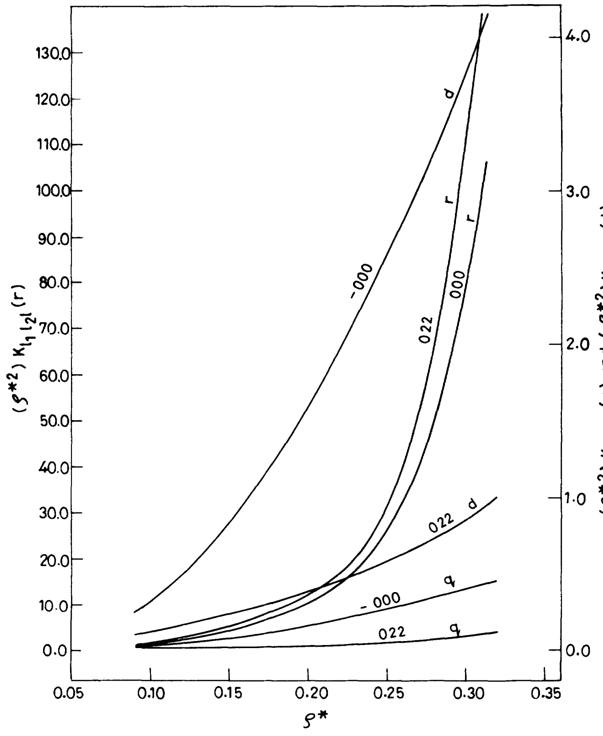

FIG. 10. Values of $\rho^{*2}K_{000}$ and $\rho^{*2}K_{022}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

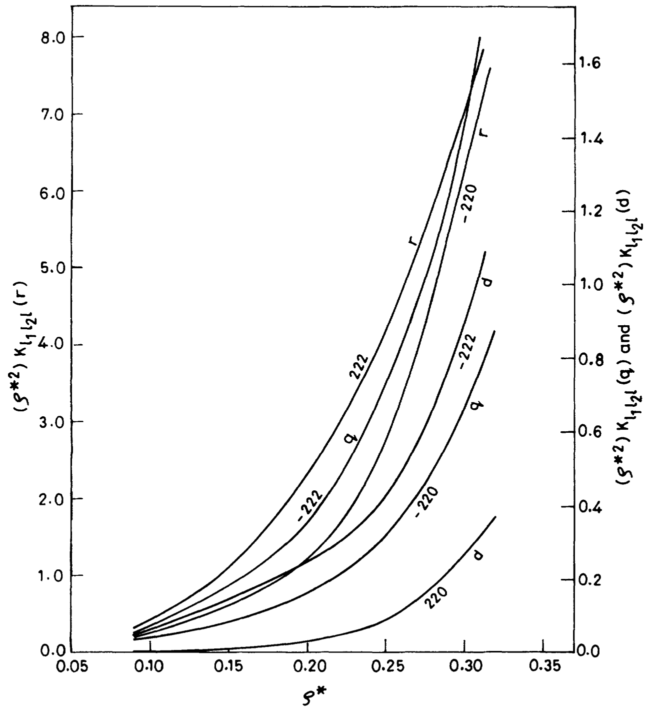

FIG. 11. Values of $\rho^{*2}K_{220}$ and $\rho^{*2}K_{222}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

$$I_{246}=-J^{4}_{246}+13J^{6}_{246}+14J^{8}_{246} \qquad (6.17\text{f})$$

as a function of density. The βK_1 of the SmA phase is expressed in terms of these quantities (see Appendix B). From these figures it is clear that at low densities all interactions contribute almost equally but at higher densities ($\rho^* \geq 0.28$) the contribution of repulsive interaction increases steeply and dominates over contributions of other interactions. Note that the density $\rho^* \simeq 0.28$ is close to the isotropic-nematic transition density in a system of HER of $x_0=3.0$ [17].

In Figs. 10–13 we plot the values of

$$M_{000}=J^{0}_{000}-2J^{2}_{000}\ , \qquad (6.18\text{a})$$

$$M_{022}=2J^{0}_{022}-\tfrac{55}{7}J^{2}_{022}+\tfrac{36}{7}J^{4}_{022}\ , \qquad (6.18\text{b})$$

$$M_{220}=J^{0}_{220}-2J^{2}_{220}\ , \qquad (6.18\text{c})$$

$$M_{222}=2J^{0}_{222}-\tfrac{55}{7}J^{2}_{222}+\tfrac{36}{7}J^{4}_{222}\ , \qquad (6.18\text{d})$$

$$M_{224}=-\tfrac{4}{7}J^{2}_{224}+\tfrac{117}{77}J^{4}_{224}-\tfrac{10}{11}J^{6}_{224}\ , \qquad (6.18\text{e})$$

$$M_{044}=-\tfrac{4}{7}J^{2}_{044}+\tfrac{117}{77}J^{4}_{044}-\tfrac{10}{11}J^{6}_{044}\ , \qquad (6.18\text{f})$$

$$M_{242}=2J^{6}_{242}-\tfrac{55}{7}J^{2}_{242}+\tfrac{36}{7}J^{4}_{242}\ , \qquad (6.18\text{g})$$

$$M_{244}=\tfrac{4}{7}J^{2}_{244}-\tfrac{117}{77}J^{4}_{244}+\tfrac{10}{11}J^{6}_{244}\ , \qquad (6.18\text{h})$$

$$M_{246}=\tfrac{90}{11}J^{4}_{246}-\tfrac{1079}{55}J^{6}_{246}+\tfrac{56}{5}J^{8}_{246} \qquad (6.18\text{i})$$

as a function of density. The βB of the SmA phase is written in terms of $M_{l_1 l_2 l}$ (see Appendix B). From these figures it is obvious that the dominant contribution to the compressional elastic constants comes from the repulsive interaction. The terms which contribute most for all interactions are those which involve M_{000} and M_{022}.

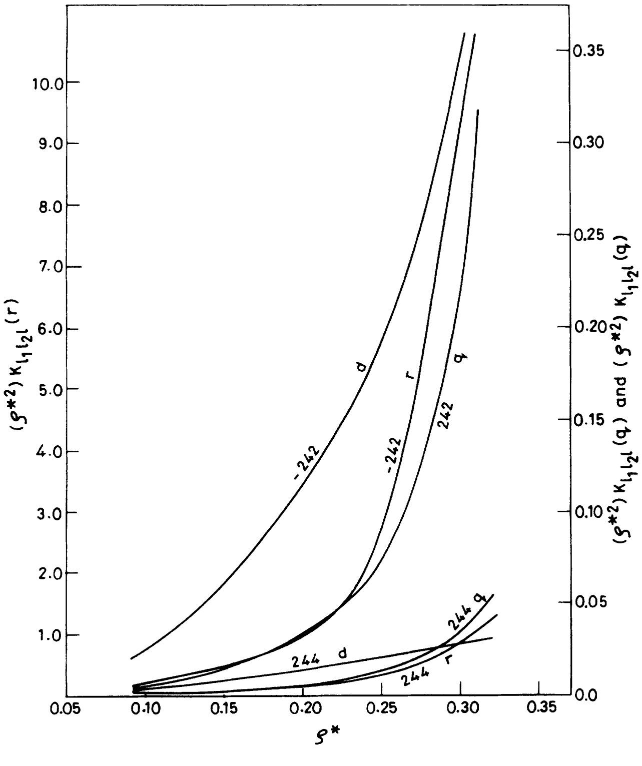

FIG. 12. Values of $\rho^{*2}K_{242}$ and $\rho^{*2}K_{244}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

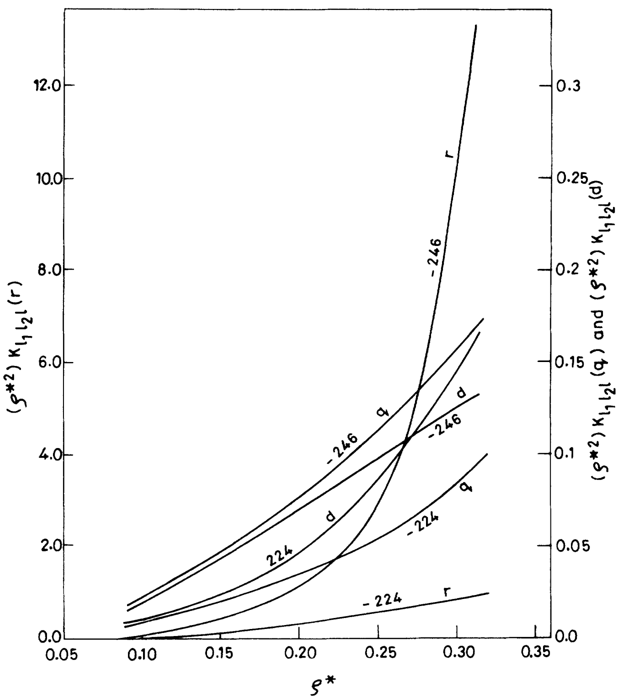

FIG. 13. Values of $\rho^{*2}K_{224}$ and $\rho^{*2}K_{246}$ are plotted as a function of ρ^*. Other details are the same as in Fig. 4.

VII. DISCUSSIONS

We have used the density-functional theory to express the distortion free energy of an ordered molecular system (plastic crystals, liquid crystals, and crystalline solids) in terms of the order parameters characterizing the phase and the correlation functions of an effective liquid. The density of the effective liquid can be found by any versions of the weighted density-functional formalism [14]. We found it easy to extend the formulation of Denton and Ashcroft [15] developed for the atomic liquids to the molecular systems [17,25]. The expression of the distortion free energy given by Eq. (2.12) or (3.9) is general and is applicable to crystalline solids, plastic crystals, and liquid crystals. In this paper we have considered the uniaxial nematic and SmA phases and have derived expressions for the relevant elastic constants in the long-wavelength limit. Note that when the size of molecules and/or molecular correlation functions become of the size of the wavelength of distortion, the elastic moduli may depend on the wave vector [29].

The theory developed in this paper needs the value of order parameters, spherical-harmonic coefficients of the DPCF of an effective fluid as a function of temperature and density and the information about the constituent molecules, viz., electric multipole moments, length-to-width ratio, etc., as input information. In the limit of long-wavelength distortion it is assumed that the magnitude of the order parameters does not get affected due to the distortion; it is only the direction of the directors which becomes position dependent. Thus, one uses the value of the order parameters determined either experimentally or calculated from the theory. The c harmonics for a given system are found either by solving the OZ equation with suitable closure relations or by adopting a perturbation scheme which is based on the fact that the fluid structures at high densities are primarily controlled by the repulsive part of the interactions.

Instead of calculating the elastic constants and comparing them with experiments we preferred to show the nature of contributions of different branches of interactions for a model system. This we do because of (i) the inherent inability to mimic the complicated molecular shape of real systems by simple models and (ii) the poor information available about the input data. We have, however, shown elsewhere [21] that the elastic constants of the nematic phase are adequately represented by the simple models. This is because of the fact that the main contribution to the elastic constants comes from the repulsive part of the interactions. The dipole-dipole and dipole-quadrupole interactions do not contribute. Though the dispersion and the quadrupole-quadrupole interactions contribute, their contributions in the density range of the liquid crystals are small.

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APPENDIX A

In this appendix we evaluate the terms of series of Eq. (4.13) for $2 \le l_1 l_2 \le 8$. For the uniaxial nematic phase we find

$$\beta K_1(2,2) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_n^2 \bar{P}_2^2 \left[\frac{1}{2}J_{220} - \frac{1}{\sqrt{14}}J_{222}\right], \tag{A1}$$

$$\beta K_1(2,4) = -\frac{3}{4}\left[\frac{5}{\sqrt{14\pi}}\right] \rho_n^2 \bar{P}_2 \bar{P}_4 J_{242}, \tag{A2}$$

$$\beta K_1(4,4) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_n^2 \bar{P}_4^2 \left[\sqrt{5}J_{440} - \frac{13}{2\sqrt{77}}J_{442}\right], \tag{A3}$$

$$\beta K_1(4,6) = -\frac{3}{4}\left[7\left[\frac{5}{11\pi}\right]^{1/2}\right] \rho_n^2 \bar{P}_4 \bar{P}_6 J_{462}, \tag{A4}$$

$$\beta K_1(6,6) = \frac{7}{2}\left[\frac{13}{\pi}\right]^{1/2} \rho_n^2 \bar{P}_6^2 [\tfrac{1}{2}J_{660} - \tfrac{4}{25}(\tfrac{5}{154})^{1/2} J_{662}], \tag{A5}$$

$$\beta K_1(6,8) = -\frac{3}{4}\left[9\left[\frac{7}{5\pi}\right]^{1/2}\right] \rho_n^2 \bar{P}_6 \bar{P}_8 J_{682}, \tag{A6}$$

$$\beta K_2(2,2) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_n^2 \bar{P}_2^2 [\tfrac{1}{2}J_{220} + (\tfrac{2}{7})^{1/2} J_{222}], \tag{A7}$$

$$\beta K_2(2,4) = -\frac{1}{4}\left[\frac{5}{\sqrt{14\pi}}\right] \rho_n^2 \bar{P}_2 \bar{P}_4 J_{242}, \tag{A8}$$

$$\beta K_2(4,4) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_n^2 \bar{P}_4^2 \left[\sqrt{5}J_{440} + \frac{47}{2\sqrt{77}}J_{442}\right], \tag{A9}$$

$$\beta K_2(4,6) = -\frac{1}{4}\left[7\left[\frac{5}{11\pi}\right]^{1/2}\right] \rho_n^2 \bar{P}_4 \bar{P}_6 J_{462}, \tag{A10}$$

$$\beta K_2(6,6) = \frac{1}{4}\left[\frac{13}{\pi}\right]^{1/2} \rho_n^2 \bar{P}_6^2 [7J_{660} + 17(\tfrac{14}{55})^{1/2} J_{662}], \tag{A11}$$

$$\beta K_2(6,8) = -\frac{1}{4}\left[9\left[\frac{7}{5\pi}\right]^{1/2}\right] \rho_n^2 \bar{P}_6 \bar{P}_8 J_{682}, \tag{A12}$$

$$\beta K_3(2,2) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_n^2 \bar{P}_2^2 \left[\frac{1}{2}J_{220} - \frac{1}{\sqrt{14}}J_{222}\right], \tag{A13}$$

$$\beta K_3(2,4) = \frac{5}{\sqrt{14\pi}} \rho_n^2 \bar{P}_2 \bar{P}_4 J_{242}, \tag{A14}$$

$$\beta K_3(4,4) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_n^2 \bar{P}_4^2 \left[\sqrt{5}J_{440} + \frac{17}{\sqrt{77}}J_{442}\right], \tag{A15}$$

$$\beta K_3(4,6) = 7\left[\frac{5}{11\pi}\right]^{1/2} \rho_n^2 \bar{P}_4 \bar{P}_6 J_{462}, \tag{A16}$$

$$\beta K_3(6,6) = \frac{7}{2}\left[\frac{13}{\pi}\right]^{1/2} \rho_n^2 \bar{P}_6^2 [\tfrac{1}{2}J_{660} + 13(\tfrac{1}{770})^{1/2} J_{662}], \tag{A17}$$

$$\beta K_3(6,8) = 9\left[\frac{7}{5\pi}\right]^{1/2} \rho_n^2 \bar{P}_6 \bar{P}_8 J_{682}. \tag{A18}$$

APPENDIX B

We give explicit expressions for a few terms of the series of Eq. (5.12).

$$\beta K_1(2,2) = \left[\frac{5}{4\pi}\right]^{1/2} \rho_s^2 \sum_k \tau_{k2}^2 [I_{220} - \tfrac{2}{7}I_{222} - 9(\tfrac{2}{7})^{1/2} I_{224}], \tag{B1}$$

$$\beta K_1(2,4) = -\frac{15}{2\sqrt{\pi}} \rho_s^2 \sum_K \tau_{k2}\tau_{k4} \left[(\tfrac{2}{7})^{1/2} I_{242} + \frac{3}{\sqrt{77}} I_{244} + (\tfrac{1}{143})^{1/2} I_{246}\right], \tag{B2}$$

$$\beta B(0,0)=\frac{1}{12\sqrt{\pi}}\rho_s^2\sum_k k^2\mu_k^2 M_{000}\ , \tag{B3}$$

$$\beta B(0,2)=\frac{1}{12\sqrt{\pi}}\rho_s^2\sum_{k^2}\mu_k\tau_{k2}M_{022}\ , \tag{B4}$$

$$\beta B(2,2)=\frac{1}{6}\left[\frac{5}{4\pi}\right]^{1/2}\rho_s^2\sum_k k^2\tau_{k2}^2[M_{220}-(\tfrac{2}{7})^{1/2}M_{222}+9(\tfrac{2}{7})^{1/2}M_{224}]\ , \tag{B5}$$

$$\beta B(0,4)=\frac{3}{4\sqrt{\pi}}\rho_s^2\sum_k k^2\mu_k\tau_{k4}M_{044}\ , \tag{B6}$$

$$\beta B(2,4)=\frac{1}{2}\left[\frac{5}{4\pi}\right]^{1/2}\rho_s^2\sum_k k^2\tau_{k2}\tau_{k4}[M_{242}+6(\tfrac{5}{77})^{1/2}M_{244}+(\tfrac{5}{143})^{1/2}M_{246}]\ . \tag{B7}$$

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