

Molecular theory of elastic constants of liquid crystals. III. Application to smectic phases with tilted orientational order

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Using the density-functional formalism we derive an expression for the distortion free energy of systems with continuous broken symmetry and use it to derive an expression for the elastic constants of smectic phases in which the director is tilted with respect to the smectic layer normal. As in the previous papers of this series [Y. Singh, S. Singh, and K. Rajesh, *Phys. Rev. A* **45**, 974 (1992); Y. Singh, K. Rajesh, V. J. Menon, and S. Singh, *Phys. Rev. E* **49**, 501 (1994)], the expressions for the elastic constants are written in terms of order and structural parameters. The structural parameters involve the generalized spherical harmonic coefficients of the direct pair correlation function of an effective isotropic liquid. The density of this effective isotropic liquid depends on the nature and amount of ordering present in the system and is evaluated self-consistently. We estimate the value of elastic constants using reasonable guesses for the order and structural parameters.

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I. INTRODUCTION

In a previous paper [1] of this series (hereafter referred to as I) we developed a theory based on the density-functional formalism [2] for the deformation free energy of any system with continuous broken symmetry, and applied the theory to derive expressions for the elastic constants of uniaxial nematic and smectic-A (Sm-A) phases. In the second paper [3] (hereafter referred to as II), the theory was applied to derive expressions for all the 12 bulk elastic constants of biaxial nematic phase of orthorhombic symmetry. These expressions of elastic constants are written in terms of order parameters that characterize the nature and amount of ordering in the phase and the structural parameters that involve the generalized spherical harmonic coefficients of the direct pair correlation function of an effective isotropic liquid, the density of which is determined using a criterion of the weighted density-functional formalism. The purpose of this paper is to expand upon the theory given in I and apply it to those smectic phases in which the director is tilted with respect to the smectic-layer normal. This class of smectics includes, Sm-C, Sm-I, Sm-F, and Sm-K phases and their chiral versions.

In general, smectic liquid crystals have a stratified structure with the long axes of the rodlike or lathlike molecules parallel to each other in the layers. This situation corresponds to partial breakdown of translational invariance. Since a variety of molecular arrangements are possible within each layer, a number of smectic phases are possible. Thus a smectic is defined by its periodicity in one direction of space and by its point group symmetry, which is a continuous or discrete subgroup of $D_{\infty h}$. In this article we are confined to those smectic phases where point group symmetries are C_{2h} and C_2 . The most important phases of this class of smectics, as far as elasticity is concerned, are Sm-C and Sm-C* phases.

In Sm-C the molecules are arranged as shown in Fig. 1. Each smectic layer is a two-dimensional liquid. The director $\hat{\mathbf{n}}$ makes a finite angle with the normal to the layer. The tilted

orientational order is described by a two-dimensional unit vector, which is along the projection of $\hat{\mathbf{n}}$ on the layer and is denoted as $\hat{\mathbf{c}}$ (see Fig. 1). The direction of $\hat{\mathbf{c}}$ is defined relative to a chosen axis in the plane and simultaneously with the sign of projection of $\hat{\mathbf{n}}$ on the normal to the layer. The correlation of the tilt direction of different layers implies that $\hat{\mathbf{c}}$ must be uniform over macroscopic distances. Though Sm-C is $\hat{\mathbf{n}} \leftrightarrow -\hat{\mathbf{n}}$ symmetric, such a symmetry operation does not hold for the $\hat{\mathbf{c}}$ director. The states described by $\hat{\mathbf{c}}$ and $-\hat{\mathbf{c}}$ are not equivalent and hence $\hat{\mathbf{c}}$ is a two-dimensional polar vector. The tilted structure introduces biaxiality within the layers and Sm-C is optically biaxial with point symmetry C_{2h} .

The other nonchiral smectic phases of this class, namely, Sm-I, Sm-F, and Sm-K all possess more order than the Sm-C phase. In these, each smectic layer is an independent two-dimensional bond-orientational ordered system. The coupling between neighboring hexatic layers drives the quasi-long-range, hexatic bond-orientational ordering of a layer into a truly long range ordered hexatic state. Therefore these phases have long ranged bond-orientational order but short ranged positional order in the layer in a three-dimensional stacked hexatic system. The director $\hat{\mathbf{n}}$, as in Sm-C, makes a finite angle with the layer normal. These phases, in spite of having quite different local order, have the same symmetry as a Sm-C phase. The phase transition between Sm-C and

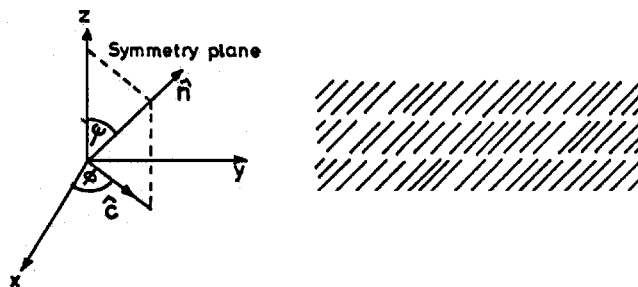


FIG. 1. Molecular arrangements in Sm-C, the directors $\hat{\mathbf{n}}$, $\hat{\mathbf{c}}$, and the space-fixed coordinate frame.

one of the tilted hexatic phases is found to be first order. This transition is analogous to the three-dimensional liquid to vapor transition, which is first order up to a critical point, and beyond the critical point there is no real phase transition. One can go continuously from one to the other phase without a phase transition at all. The expressions for the elastic free energy density of these phases are, therefore, similar to that of Sm-C; the difference can be only quantitative. In view of this we discuss the elasticity of Sm-C phase only.

The chiral smectic-C (Sm-C*) has a modulated structure at a scale dimension of the order of 1 μm and larger. The modulated (helical) structure occurs as a result of a precession of the molecular tilt about an axis perpendicular to the layer planes. The tilt direction is rotated through an azimuthal angle ϕ on moving from one layer to the next. As the rotation is in a constant direction, a helix is formed, which is either left or right handed. In Sm-C* the mirror plane is lost but the C_2 axis is present locally in each smectic layer (it is perpendicular to the plane containing the molecular axes). The C_2 axis in the case of Sm-C* phase is a polar axis, which admits the existence of a spontaneous polarization along it. The Sm-C* phase therefore exhibits ferroelectricity.

Many compounds exhibit phases such as antiferroelectric (Sm-C_A*), ferroelectric (Sm-C_r*), etc. in addition to Sm-C*, as the temperature is varied. The director $\hat{\mathbf{n}}$ in the Sm-C_A* phase, like in Sm-C* phase, is uniformly tilted with respect to the layer normal. However, unlike in Sm-C* phase, the difference in azimuthal angle of \mathbf{n} in successive layers is $\pi + \alpha$. The small angle α gives rise to a helical structure of \mathbf{n} along the layer normal and arises from the chirality of the constituent molecules. In Sm-C_r* the layers are stacked in such a way that there is a net overall (in contrast to Sm-C_A* phase) spontaneous polarization. This means the number of layers of opposite polarization is not equal. The elasticity associated with the structure of all chiral smectic phases is same as that of Sm-C* phase.

The paper is organized as follows. In Sec. II we describe the elastic continuum theory for Sm-C and Sm-C* phases and derive expressions for the elastic free energy density. This expression is then written in terms of deformation variables so that it becomes appropriate for comparison with an expression found from microscopic theory. The density-functional approach has been used in Sec. III to describe the deformed state of smectics with tilted orientational order. The expression for the deformation free energy density derived here is more general than that given in I in the sense that all the cases discussed in I correspond to tilt angle equal to zero. The expressions for the elastic constants are derived by comparing the elastic free energy found from the density-functional theory with that given in Sec. II. These expressions of the elastic constants involve the order parameters that measure the nature and amount of ordering in the system and the direct pair correlation function (DPCF) of an effective isotropic liquid. In Sec. IV we discuss the relative magnitude of these constants using reasonable guesses for the order parameters and the spherical harmonic coefficients of the DPCF.

II. CONTINUUM THEORY FOR ELASTIC FREE ENERGY DENSITY

An undeformed smectic has parallel and equidistant layers and a position independent director. When some small amplitude long wavelength distortions are imposed on this ideal state, layers may get displaced and curved. Let $u(x, y, z)$ represent displacements of the layer normal to their planes. A layer at z_0 before displacement is now at

$$\mathbf{z}(x, y) = \mathbf{z}_0 + u(x, y, z). \quad (2.1)$$

We choose a space-fixed (SF) frame S^0 such that its z axis is along the normal to the unperturbed smectic layers (see Fig. 1). The system is described by (i) the angle Ω_z of director $\hat{\mathbf{c}}$ with respect to the x axis and (ii) the vertical displacement u of the layers whose derivatives

$$\Omega_x = \frac{\partial u}{\partial y} \quad \text{and} \quad \Omega_y = -\frac{\partial u}{\partial x} \quad (2.2)$$

represent small angles of rotation about x and y axes, respectively.

Since the free energy of a system with broken continuous symmetry is invariant with respect to spatially uniform displacements and rotations that take the system from one point in the ground state manifold to another, the elastic free energy must be a function of derivatives of Ω or second order derivatives of u , which correspond to the curvature of the planes. The contribution to free energy density due to deformation is called elastic free energy density $f_e(r)$. To find $f_e(r)$ one expands $f(r)$, which belongs to the deformed state around the ideal state having the free energy density f_u . The expansion is expressed in terms of the spatial derivative of the order parameter fields. The elastic continuum theory deals only with small spatial derivatives. Consequently, only the lowest order terms in the expansions are taken into account.

Because of the symmetry of Sm-C the free energy density must be invariant of the simultaneous transformations $x \rightarrow -x$, $y \rightarrow -y$, and $z \rightarrow -z$ (due to center of symmetry) and of the transformation $y \rightarrow -y$ as the vertical xz plane is the plane of symmetry. Thus for the elastic free energy density one has [4]

$$f_e(r) = f_{dc}(r) + f_{dk}(r) + f_{dck}(r) + f_{dl}(r), \quad (2.3)$$

where f_{dc} represents contribution arising due to distortion of director $\hat{\mathbf{c}}$ while f_{dk} is associated with curvature of layers. f_{dck} represents the contribution arising due to coupling of different deformation modes whereas f_{dl} represents the contribution due to variation in layer thickness as in Sm-A. Thus [1]

$$f_{dl} = \frac{1}{2} \bar{B} \gamma^2, \quad (2.4)$$

where $\gamma = \partial u / \partial z$ describes the variation in the thickness of layers.

To derive expressions for f_{dc} , f_{dk} , f_{dck} we consider a director triad formed by three orthonormal unit vectors $\hat{\mathbf{c}}$, $\hat{\mathbf{k}}$, $\hat{\mathbf{p}}$ and let, at the origin, the director $\hat{\mathbf{c}}$ be along the x axis of the SF frame, $\hat{\mathbf{k}}$ along z axis, i.e., along the normal to the layers, and $\hat{\mathbf{p}}$ along y axis, i.e.,

$$\hat{\mathbf{c}}_0 = (1, 0, 0), \quad \hat{\mathbf{p}}_0 = (0, 1, 0), \quad \hat{\mathbf{k}}_0 = (0, 0, 1). \quad (2.5)$$

The orientation of the director triad at a neighboring point is rotated with respect to the space-fixed coordinate frame due to deformation and is given as

$$\hat{\mathbf{c}} = (1, c_y, c_z), \quad \hat{\mathbf{p}} = (p_x, 1, p_z), \quad \hat{\mathbf{k}} = (k_x, k_y, 1). \quad (2.6)$$

Because of orthonormality condition of the director triad

$$p_x = -c_y, \quad p_z = -k_y, \quad c_z = -k_x. \quad (2.7)$$

For small deviations we have

$$k_x = -\frac{\partial u}{\partial y} = \Omega_y, \quad k_y = -\frac{\partial u}{\partial x} = -\Omega_x, \quad (2.8)$$

and

$$c_y = \Omega_z.$$

Combining the three orthonormal vectors $\hat{\mathbf{c}}$, $\hat{\mathbf{k}}$, $\hat{\mathbf{p}}$ we can form nine invariants. The elastic free energy density can be expressed in terms of these invariants [5]

$$\begin{aligned} D_{11} &= c_\alpha p_\beta \partial_\alpha k_\beta = \hat{\mathbf{c}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{p}} = -\frac{\partial \Omega_x}{\partial x}, \\ D_{21} &= p_\alpha p_\beta \partial_\alpha k_\beta = \hat{\mathbf{p}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{p}} = -\frac{\partial \Omega_x}{\partial y}, \\ D_{31} &= k_\alpha p_\beta \partial_\alpha k_\beta = \hat{\mathbf{k}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{p}} = -\frac{\partial \Omega_x}{\partial z} = -\frac{\partial^2 u}{\partial x \partial z}, \\ D_{12} &= c_\alpha k_\beta \partial_\alpha c_\beta = -\hat{\mathbf{c}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{c}} = -\frac{\partial \Omega_y}{\partial x}, \\ D_{22} &= p_\alpha k_\beta \partial_\alpha c_\beta = -\hat{\mathbf{p}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{c}} = -\frac{\partial \Omega_y}{\partial y} = D_{11}, \\ D_{32} &= k_\alpha k_\beta \partial_\alpha c_\beta = -\hat{\mathbf{k}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{c}} = -\frac{\partial \Omega_y}{\partial z} = -\frac{\partial^2 u}{\partial y \partial z}, \\ D_{13} &= c_\alpha c_\beta \partial_\alpha p_\beta = -\hat{\mathbf{c}} \cdot \nabla \hat{\mathbf{c}} \cdot \hat{\mathbf{p}} = -\frac{\partial \Omega_z}{\partial x}, \\ D_{23} &= p_\alpha c_\beta \partial_\alpha p_\beta = -\hat{\mathbf{p}} \cdot \nabla \hat{\mathbf{c}} \cdot \hat{\mathbf{p}} = -\frac{\partial \Omega_z}{\partial y}, \\ D_{33} &= k_\alpha c_\beta \partial_\alpha p_\beta = -\hat{\mathbf{k}} \cdot \nabla \hat{\mathbf{c}} \cdot \hat{\mathbf{p}} = -\frac{\partial \Omega_z}{\partial z}. \end{aligned} \quad (2.9)$$

Note that the invariants D_{31} and D_{32} correspond to variation of layer compression (or dilation) along y and x axes, respectively,

$$\begin{aligned} D_{31} &= -\frac{\partial \Omega_x}{\partial z} = -\frac{\partial^2 u}{\partial y \partial z} = -\frac{\partial \gamma}{\partial y} = -\hat{\mathbf{p}} \cdot \nabla \gamma, \\ D_{32} &= -\frac{\partial \Omega_y}{\partial z} = -\frac{\partial^2 u}{\partial x \partial z} = -\frac{\partial \gamma}{\partial x} = -\hat{\mathbf{c}} \cdot \nabla \gamma. \end{aligned} \quad (2.10)$$

These terms are omitted as their contributions are small compared to linear term f_{dl} [see Eq. (2.4)]. We are therefore left with six independent invariants.

The elastic free energy density due to orientational deformation of Sm-C can be written in terms of these six independent invariants. Each term should, however, satisfy the symmetry elements of Sm-C. Note that $(\hat{\mathbf{k}}, \hat{\mathbf{c}})$ plane is a symmetry plane, $\hat{\mathbf{p}}$ is C_2 axis, and there is also inversion symmetry. We can therefore write elastic free energy density as a sum of the square of each invariant and their products taken in such a way that $\hat{\mathbf{k}}$ and $\hat{\mathbf{c}}$ enter the expansion an even number of times (i.e., $\hat{\mathbf{k}}$ and $\hat{\mathbf{c}}$ are considered without discrimination), and $\hat{\mathbf{p}}$ also appears even number of times but on its own. Thus

$$f_{dc} = \frac{1}{2} B_1 D_{13}^2 + \frac{1}{2} B_2 D_{23}^2 + \frac{1}{2} B_3 D_{33}^2 + B_{13} D_{13} D_{33}, \quad (2.11a)$$

$$f_{dk} = \frac{1}{2} A (D_{11} + D_{22})^2 + \frac{1}{2} A_{12} D_{12}^2 + \frac{1}{2} A_{21} D_{21}^2, \quad (2.11b)$$

$$f_{dck} = C_1 D_{11} D_{13} + C_2 D_{21} D_{23} + C_3 D_{12} D_{23} + C_4 D_{12} D_{21}. \quad (2.11c)$$

Since

$$\begin{aligned} D_{12} D_{23} &= \left(\frac{\partial \Omega_y}{\partial x} \right) \left(\frac{\partial \Omega_z}{\partial y} \right) = \frac{\partial}{\partial y} \left(\Omega_z \frac{\partial \Omega_y}{\partial x} \right) - \frac{\partial}{\partial x} \left(\Omega_z \frac{\partial \Omega_y}{\partial y} \right) \\ &\quad + \frac{\partial \Omega_z}{\partial x} \frac{\partial \Omega_y}{\partial y}, \end{aligned} \quad (2.12)$$

it is the sum of two gradient terms (surface terms) and a term analogous to $D_{11} D_{13}$. Similar decomposition can also be made for $D_{12} D_{21}$. We therefore have only two independent terms in the expression of f_{dck} due to coupling between the deformation of director \mathbf{c} and the curvature of smectic layers, as given in Ref. [4].

Since f_{dc} involves director $\hat{\mathbf{c}}$, it can be written in terms of $(\nabla \cdot \hat{\mathbf{c}})^2$, $(\hat{\mathbf{c}} \cdot \nabla \times \hat{\mathbf{c}})^2$, and $(\hat{\mathbf{c}} \times \nabla \times \hat{\mathbf{c}})^2$ as

$$(\nabla \cdot \hat{\mathbf{c}})^2 = \left(\frac{\partial \Omega_z}{\partial y} \right)^2 = D_{23}^2, \quad (2.13)$$

$$(\hat{\mathbf{c}} \cdot \nabla \times \hat{\mathbf{c}})^2 = \left(\frac{\partial \Omega_z}{\partial z} \right)^2 = D_{33}^2,$$

$$(\hat{\mathbf{c}} \times \nabla \times \hat{\mathbf{c}})^2 = \left(\frac{\partial \Omega_z}{\partial x} \right)^2 = D_{13}^2,$$

and

$$(\hat{\mathbf{k}} \cdot \nabla \times \hat{\mathbf{c}})(\hat{\mathbf{c}} \cdot \nabla \times \hat{\mathbf{c}}) = \left(\frac{\partial \Omega_z}{\partial x} \right) \left(\frac{\partial \Omega_z}{\partial z} \right) = D_{13} D_{33}.$$

Therefore the constants B_1 , B_2 , B_3 , B_{13} can be identified as elastic constants associated with bend, splay, twist, and coupled twist-bend modes of deformations of director $\hat{\mathbf{c}}$ and have the dimension of energy per unit length (dynes). The last term in Eq. (2.11a) is allowed because Sm C is invariant under the simultaneous transformation $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$ and $\hat{\mathbf{c}} \rightarrow -\hat{\mathbf{c}}$. These constants are expected to be comparable in magnitude to the Frank elastic constants of a homologous nematic phase.

The contribution f_{dk} is analogous to Sm-A and is due to layer deformation (curvature). The terms A , A_{12} , and A_{21} represent splay contribution of system of monoclinic symmetry as Sm-C has C_{2h} symmetry in contrast to $D_{\infty h}$ of Sm-A. The value of these constants are therefore expected to be of the same order of magnitude as in Sm-A phase. \bar{B} [see Eq. (2.4)], which has dimensions of energy per unit volume, is associated with possible change of interlayer distance.

Since Sm-C* has no inversion symmetry, its elastic free energy density may have terms linear in invariants of Eq. (2.9). However, due to symmetry requirements only those invariants that involve $\hat{\mathbf{k}}$ and $\hat{\mathbf{c}}$ in pairs without discrimination, and $\hat{\mathbf{p}}$ alone contribute to linear terms. Thus

$$f_d^{(1)} = -D_1(\hat{\mathbf{c}} \cdot \nabla \hat{\mathbf{c}} \cdot \hat{\mathbf{p}}) + D_2(\hat{\mathbf{p}} \cdot \nabla \hat{\mathbf{k}} \cdot \hat{\mathbf{c}}) - D_3(\hat{\mathbf{k}} \cdot \nabla \hat{\mathbf{c}} \cdot \hat{\mathbf{p}}), \quad (2.14)$$

where superscript 1 stands for linear terms. In terms of Ω vector field

$$f_d^{(1)} = D_1 \left(\frac{\partial \Omega_z}{\partial x} \right) + D_2 \left(\frac{\partial \Omega_x}{\partial x} \right) + D_3 \left(\frac{\partial \Omega_z}{\partial z} \right). \quad (2.15)$$

Out of the three terms in Eq. (2.15) the term D_3 is most important as it corresponds to simple twist of director $\hat{\mathbf{c}}$. The term D_1 corresponds to bend of director $\hat{\mathbf{c}}$ while D_2 tends to transform a flat layer into a twisted ribbon. The terms D_1 and D_2 are expected to be negligible in comparison to the D_3 term.

If $q_0 = -(D_3/B_3)$ where B_3 is defined in Eq. (2.11a), the contribution $f_{dc}(r)$ for Sm-C* is modified to

$$f_{dc}(r) = \frac{1}{2} B_1 \left(\frac{\partial \Omega_z}{\partial x} \right)^2 + \frac{1}{2} B_2 \left(\frac{\partial \Omega_z}{\partial y} \right)^2 + \frac{1}{2} B_3 \left(\frac{\partial \Omega_z}{\partial z} + q_0 \right)^2 + B_{13} \left(\frac{\partial \Omega_z}{\partial x} \right) \left(\frac{\partial \Omega_z}{\partial z} \right), \quad (2.16)$$

while other terms of Eq. (2.11) remain same. The ground state of Sm-C* has a helical structure. The B_3 term can

therefore be considered to be a contribution due to deformation from this uniform helical structure.

The expressions for the elastic constants are obtained by comparing the expression of elastic free energy density obtained from the continuum theory and from a microscopic theory involving molecular parameters. In order to make this comparison possible we have to rewrite Eq. (2.16) in terms of distortion vectors defined below.

Since in the ground state, the directors are position independent, we take S^0 to be the unperturbed director frame at a point R . Let S^0 be described by the unit vectors $\mathbf{N}_0^{(j)}$ such that [see Eq. (2.5)]

$$\mathbf{N}_0^{(1)} = \hat{\mathbf{c}}_0, \quad \mathbf{N}_0^{(2)} = \hat{\mathbf{p}}_0, \quad \mathbf{N}_0^{(3)} = \hat{\mathbf{k}}_0. \quad (2.17)$$

Let S be the perturbed director frame described by the unit vector $\mathbf{N}^{(j)}$ such that [see Eq. (2.6)]

$$\begin{aligned} \mathbf{N}^{(1)} &= \hat{\mathbf{c}} = \hat{\mathbf{c}}_0 + \boldsymbol{\sigma}^{(1)}, & \mathbf{N}^{(2)} &= \hat{\mathbf{p}} = \hat{\mathbf{p}}_0 + \boldsymbol{\sigma}^{(2)}, \\ \mathbf{N}^{(3)} &= \hat{\mathbf{k}} = \hat{\mathbf{k}}_0 + \boldsymbol{\sigma}^{(3)}, \end{aligned} \quad (2.18)$$

where $\boldsymbol{\sigma}^{(j)}$ may be regarded as the distortion vectors, and let

$$\mathbf{N}_k^{(j)} = \mathbf{N}^{(j)} \cdot \mathbf{N}_0^{(k)} = \delta_{jk} + \sigma_k^{(j)} \quad (2.19)$$

be the components of the perturbed directors with respect to S^0 frame.

The transformation from S^0 to S is effected by a 3×3 orthogonal matrix T with element

$$T_{jk} = \mathbf{N}_k^{(j)} = \delta_{jk} + \sigma_k^{(j)}$$

such that

$$\mathbf{N}^{(j)} = T_{jk} \mathbf{N}_0^{(k)} = \mathbf{N}_0^{(j)} + \boldsymbol{\sigma}_k^{(j)} \mathbf{N}_0^{(k)}.$$

The orthogonality condition $T_{ij} T_{ik} = \delta_{jk}$ leads to

$$\begin{aligned} \sigma_j^{(k)} &= -\sigma_k^{(j)} - \sigma_j^{(i)} \sigma_k^{(i)} \quad \text{for } j \neq k, \\ \sigma_j^{(j)} &= -\frac{1}{2} \sum_i' \sigma_j^{(i)2} \quad \text{for } j = k, \end{aligned} \quad (2.20)$$

where the prime on summation indicates no summation over j . Thus for small deformations

$$\sigma_j^{(k)} \sim O \quad \text{and} \quad \sigma_j^{(j)} \sim O^2,$$

where O means first order small quantity.

From above relations it follows that $\sigma_2^{(1)}$, $\sigma_1^{(3)}$, and $\sigma_3^{(2)}$ can be regarded as basic independent distortion variables; all as a function of R . Every other component can be constructed with the help of Eq. (2.20).

From above discussions we find

$$\begin{aligned} c_y &= \Omega_z = \sigma_2^{(1)}, \\ k_x &= \Omega_y = \sigma_1^{(3)}, \\ k_y &= -\Omega_x = -\sigma_3^{(2)}. \end{aligned} \quad (2.21)$$

Using these relations we rewrite Eq. (2.11) as

$$F_{dc} = \int d\mathbf{R} \left[\frac{1}{2} B_1 \left(\frac{\partial \sigma_2^{(1)}}{\partial x} \right)^2 + \frac{1}{2} B_2 \left(\frac{\partial \sigma_2^{(1)}}{\partial y} \right)^2 + \frac{1}{2} B_3 \left(\frac{\partial \sigma_2^{(1)}}{\partial z} \right)^2 + B_{13} \left(\frac{\partial \sigma_2^{(1)}}{\partial x} \right) \left(\frac{\partial \sigma_2^{(1)}}{\partial z} \right) \right], \quad (2.22a)$$

$$F_{dk} = \int d\mathbf{R} \left[\frac{1}{2} A \left(\frac{\partial \sigma_3^{(2)}}{\partial x} \right)^2 + \frac{1}{2} A_{12} \left(\frac{\partial \sigma_1^{(3)}}{\partial x} \right)^2 + \frac{1}{2} A_{21} \left(\frac{\partial \sigma_3^{(2)}}{\partial y} \right)^2 \right], \quad (2.22b)$$

$$F_{dck} = \int d\mathbf{R} \left[C_1 \left(\frac{\partial \sigma_3^{(2)}}{\partial x} \right) \left(\frac{\partial \sigma_2^{(1)}}{\partial x} \right) + C_2 \left(\frac{\partial \sigma_3^{(2)}}{\partial y} \right) \left(\frac{\partial \sigma_2^{(1)}}{\partial y} \right) \right]. \quad (2.22c)$$

It is often convenient to assume long wavelength deformations in the space-fixed frame having the form

$$\sigma_k^{(j)} = B_k^{(j)} \sin(\mathbf{q} \cdot \mathbf{R}), \quad (2.23)$$

where $B_k^{(j)}$ are small amplitudes and q is the wave vector. Substituting this into Eq. (2.22) leads to

$$\frac{F_{dc}}{V} = \frac{1}{4} [B_1 (B_2^{(1)})^2 q_x^2 + B_2 (B_2^{(1)})^2 q_y^2 + B_3 (B_2^{(1)})^2 q_z^2 + B_{13} (B_2^{(1)})^2 q_x q_z], \quad (2.24a)$$

$$\frac{F_{dk}}{V} = \frac{1}{4} [A (B_3^{(2)})^2 q_x^2 + A_{12} (B_1^{(3)})^2 q_x^2 + A_{21} (B_3^{(2)})^2 q_y^2], \quad (2.24b)$$

$$\frac{F_{dck}}{V} = \frac{1}{2} C_1 (B_3^{(2)} B_2^{(1)}) q_x^2 + \frac{1}{2} C_2 (B_3^{(2)} B_2^{(1)}) q_y^2. \quad (2.24c)$$

In writing the above equations we have used the relations

$$\int d\mathbf{R} \sin^2(\mathbf{q} \cdot \mathbf{R}) = \int d\mathbf{R} \cos^2(\mathbf{q} \cdot \mathbf{R}) = \frac{V}{2}$$

and

$$\int d\mathbf{R} \sin(\mathbf{q} \cdot \mathbf{R}) \cos(\mathbf{q} \cdot \mathbf{R}) = 0.$$

III. DENSITY-FUNCTIONAL APPROACH

A. Expression for the distortion free energy

A liquid crystalline phase is characterized by the spatial and orientational configuration of molecules. At the phase transition point these configurations undergo a modification,

i.e., an abrupt change may take place in the symmetries of the system. The molecular configurations of most ordered phases are adequately described by the single particle density distribution $\rho(\mathbf{x})$. The vector \mathbf{x} is taken here to indicate both the location \mathbf{r} of the center of a molecule and its relative orientation $\mathbf{\Omega}$ described by Euler angles ϕ, θ, ψ . For an isotropic uniform system, $\rho(\mathbf{x})$ is independent of positions and orientations.

The single-particle density distribution $\rho(\mathbf{x})$ provides us with a convenient variational quantity to specify an arbitrary state of a system. One may consider a variational thermodynamic potential $W(T, P, [\rho(\mathbf{x})])$ as a function of $\rho(\mathbf{x})$. The equilibrium state of the system at a given T and P is described by the density $\rho(T, P, \mathbf{x})$ corresponding to the minimum of W with respect to $\rho(\mathbf{x})$. This forms the basis of the density-functional theory [2].

The basic thermodynamic potential used to determine the isothermal elastic properties of a system, consisting of N particles in volume V at temperature T , is the Helmholtz free energy $A[\rho]$. Elasticity is associated with the behavior of $A[\rho]$ with respect to a small deformation of the system away from its equilibrium (ground) state [1].

In the density-functional formalism the free energy of a system is expressed in terms of the direct correlation function of the medium [2]

$$\beta A[\rho] = \beta A_{id}[\rho] + \beta \Delta A[\rho], \quad (3.1)$$

where the ideal gas part

$$\beta A_{id}[\rho] = \int d\mathbf{x} \rho(\mathbf{x}) \{ \ln[\rho(\mathbf{x}) \Lambda] - 1 \} \quad (3.2)$$

and $\beta \Delta A[\rho]$ is the excess reduced free energy arising due to intermolecular interactions. Here $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant and T is the temperature. In the weighted density-functional approach

$$\beta \Delta A[\rho] = - \frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \rho(\mathbf{x}_1) c(\mathbf{x}_1, \mathbf{x}_2, \bar{\rho}) \rho(\mathbf{x}_2). \quad (3.3)$$

Here the function c represents the DPCF of an effective isotropic fluid. The effective density $\bar{\rho}$ is found using the relation [6]

$$\bar{\rho}[\rho] = \frac{1}{\rho_0 V} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \omega(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}), \quad (3.4)$$

where ρ_0 is the averaged 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 must satisfy

$$-c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_0) = \lim_{\rho \rightarrow \rho_0} \frac{\delta^2(\beta\Delta A)}{\delta\rho(\mathbf{x}_1)\delta\rho(\mathbf{x}_2)} \quad (3.5)$$

exactly, one finds

$$\omega(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}) = -\frac{1}{2\Delta a'(\bar{\rho})} \left[\beta^{-1} c(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}) + \frac{1}{V\bar{\rho}} \Delta a''(\bar{\rho}) \right], \quad (3.6)$$

where $\Delta a(\bar{\rho})$ is the excess free energy per particle and primes on it denote derivatives with respect to density.

The contribution to the free energy due to deformation is given as [1]

$$\begin{aligned} \beta\Delta A_d[\rho] &= \beta(\Delta A_d[\rho] - \Delta A_u[\rho]) \\ &= -\frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 [\rho_d(\mathbf{x}_1)\rho_d(\mathbf{x}_2) \\ &\quad - \rho(\mathbf{x}_1)\rho(\mathbf{x}_2)] c(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}), \end{aligned} \quad (3.7)$$

where $\beta\Delta A_u[\rho]$ and $\rho(\mathbf{x})$ are, respectively, the excess free energy and single particle density distribution of the ground state of the ordered phase. The subscript d refers to the corresponding quantities of the deformed state. In writing Eq. (3.7) it is assumed that the direct pair correlation functions do not change due to deformation.

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

$$\begin{aligned} c(\mathbf{r}, \Omega_1, \Omega_2) &= \sum_{l_1 l_2 l} \sum_{m_1 m_2 m} \sum_{n_1 n_2} \\ &\quad \times c(l_1, l_2, l; n_1, n_2; r) C_g(l_1, l_2, l; m_1, m_2, m) \\ &\quad \times D_{m_1, n_1}^{l_1*}(\Omega_1) D_{m_2, n_2}^{l_2*}(\Omega_2) Y_{lm}^*(\hat{r}), \end{aligned} \quad (3.8)$$

where $C_g(l_1, l_2, l; m_1, m_2, m)$ are the Clebsch-Gordon coefficients, $c(l_1, l_2, l; n_1, n_2; r)$ is the harmonic expansion coefficient of the DPCF, and $\hat{r} = \mathbf{r}/|\mathbf{r}|$ is a unit vector along the intermolecular axis.

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 (ground) 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 ground state. One defines the elastic free energy per unit volume as

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

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

For an ordered (liquid crystalline) phase, $\rho(\mathbf{x})$ is expressed in terms of the Fourier series and the Wigner rotation matrices [2] as

$$\rho(\mathbf{x}) = \rho(\mathbf{r}, \Omega') = \rho_0 \sum_{\mathbf{G}} \sum_{lmn} Q_{lmn}(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] D_{mn}^l(\Omega'), \quad (3.9a)$$

where the expansion coefficients

$$\begin{aligned} Q_{lmn}(\mathbf{G}) &= \frac{2l+1}{N} \int d\mathbf{r} \int d\Omega' \rho(\mathbf{r}, \Omega') \\ &\quad \times \exp(-i\mathbf{G} \cdot \mathbf{r}) D_{mn}^{l*}(\Omega'). \end{aligned} \quad (3.9b)$$

Here $\{\mathbf{G}\}$ are the reciprocal lattice vectors (RLV's) of the positionally ordered structure that might be present in the system and ρ_0 is the mean number density of the system. All the angles that appear in Eq. (3.9) refer to a coordinate frame, the z axis of which is along the director $\hat{\mathbf{n}}$. Using the rotational property of the D matrices [7], we rewrite Eq. (3.9a) so that all the angles appearing in it refer to the space-fixed coordinate frame shown in Fig. 1. Thus

$$\rho(\mathbf{r}, \Omega) = \rho_0 \sum_{\mathbf{G}} \sum_{lmn} \sum_q Q_{lmn}(\mathbf{G}) \exp[i\mathbf{G} \cdot \mathbf{r}] D_{qm}^{l*}(\hat{\mathbf{n}}) D_{qn}^l(\Omega). \quad (3.10)$$

In the limit of long wavelength distortion, the magnitude of the order parameters is 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}_d of the strained structure are related to \mathbf{G} of the unstrained structure as

$$\mathbf{G}_d = (\mathbf{I} + \boldsymbol{\epsilon})^{-1} \mathbf{G}. \quad (3.11)$$

Here $\boldsymbol{\epsilon}$ is a strain matrix that governs the change in position. Thus for a deformed state,

$$\begin{aligned} \rho_d(\mathbf{r}, \Omega) &= \rho_0 \sum_{\mathbf{G}} \sum_{lmn} \sum_q Q_{lmn}(\mathbf{G}) \\ &\quad \times \exp(i\mathbf{G}_d \cdot \mathbf{r}) D_{qm}^{l*}(\hat{\mathbf{n}}_d) D_{qn}^l(\Omega), \end{aligned} \quad (3.12)$$

where $\hat{\mathbf{n}}_d(r)$ indicates the direction of director at r of the deformed state. In the deformed state, the director orientations become position dependent. One uses the rotational properties of D matrices to rewrite Eq. (3.11) in terms of the director of a chosen point. Substituting Eqs. (3.8)–(3.12) into Eq. (3.7) and after some simplifications we get

$$\begin{aligned} \frac{\beta \Delta A_d}{V} = & -\frac{1}{2} \rho_0^2 \sum_{l_1 l_2 l} \sum_{m_1' m_2' m'} \sum_{m \lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} \frac{Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G})}{(2l_1+1)(2l_2+1)} \times C_g(l_1 l_2 l; m_1' m' \lambda) D_{m \lambda}^{l*}(\hat{\mathbf{n}}) \int d\mathbf{r} [\exp(i\mathbf{G}_d \cdot \mathbf{r}) D_{m' m_2'}^{l_2}(\Delta\chi) \\ & - \delta_{m' m_2'} \exp(i\mathbf{G} \cdot \mathbf{r})] c(l_1 l_2 l; n_1 n_2; r) Y_{lm}^*(\hat{\mathbf{r}}), \end{aligned} \quad (3.13)$$

where $\hat{\mathbf{n}}$ indicates the orientation of the director at the reference point \mathbf{R} and $\Delta\chi$ indicates the angle between the directors at \mathbf{R} and $\mathbf{R} + \mathbf{r}$. Equation (3.13) presents a general expression for the distortion free energy density for the continuous symmetry broken phases with tilted orientational order in the limit of long wavelength distortion. Since for uniaxial phases the director is along the z axis of the SF coordinate frame, $D_{m \lambda}^{l*}(n=0) = \delta_{m \lambda}$. When this is substituted in Eq. (3.13) it reduces to Eq. (3.9) of I.

Equation (3.13) can be used to derive expressions for the contributions arising due to curvature in the director orientation and dilation in layer thickness. The term that represents the coupling of these two terms of distortions is neglected. Thus

$$\frac{\beta \Delta A_d}{V} = f_1 + f_2, \quad (3.14)$$

where

$$\begin{aligned} f_1 = & -\frac{1}{2} \rho_0^2 \sum_{l_1 l_2 l} \sum_{m_1' m_2' m'} \sum_{m \lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} \frac{Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G})}{(2l_1+1)(2l_2+1)} C_g(l_1 l_2 l; m_1' m' \lambda) \\ & \times D_{m \lambda}^{l*}(\hat{\mathbf{n}}) \int d\mathbf{r} \exp(i\mathbf{G} \cdot \mathbf{r}) [D_{m' m_2'}^{l_2}(\Delta\chi) - \delta_{m' m_2'}] Y_{lm}^*(\hat{\mathbf{r}}) c(l_1 l_2 l; n_1 n_2; r), \end{aligned} \quad (3.15)$$

$$\begin{aligned} f_2 = & -\frac{1}{2} \rho_0^2 \sum_{l_1 l_2 l} \sum_{m_1' m_2' m'} \sum_{m \lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} \frac{Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G})}{(2l_1+1)(2l_2+1)} C_g(l_1 l_2 l; m_1' m' \lambda) \\ & \times D_{m \lambda}^{l*}(\hat{\mathbf{n}}) \int d\mathbf{r} [\exp(i\mathbf{G}_d \cdot \mathbf{r}) - \exp(i\mathbf{G} \cdot \mathbf{r})] \delta_{m' m_2'} Y_{lm}^*(\hat{\mathbf{r}}) c(l_1 l_2 l; n_1 n_2; r). \end{aligned} \quad (3.16)$$

While f_1 includes all contributions arising due to curvature in directors orientations, f_2 is the contribution due to dilation (compression) in layer thickness.

B. Expressions for the elastic constants associated with directors orientations

All the elastic constants associated with curvature in director orientations can be derived from the expression of f_1 given in Eq. (3.15). Using the procedure outlined in II we rewrite Eq. (3.15) in terms of the director components. Thus

$$\begin{aligned} f_1 = & -\frac{1}{2} \rho_0^2 \sum_{l_1 l_2 l} \sum_{m_1' m_2' m'} \sum_{m \lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} \frac{Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G})}{(2l_1+1)(2l_2+1)} D_{m \lambda}^{l*}(\hat{\mathbf{n}}) \int dr r^4 \int d\hat{\mathbf{r}} \\ & \times \left[\frac{1}{2} |B_1^{(3)}|^2 \{ (a_{11} + a_{12})(q_z^2 - q_x^2)(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})(\hat{\mathbf{r}} \cdot \hat{\mathbf{z}}) + (a_{23} + a_{21} + a_{22}) [q_x^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})^2 + \dots] \} \right. \\ & + \frac{1}{2} |B_2^{(3)}|^2 \{ i(a_{12} - a_{11}) q_y^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{y}})(\hat{\mathbf{r}} \cdot \hat{\mathbf{z}}) + (a_{23} - a_{21} - a_{22}) [q_x^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})^2 + q_y^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{y}})^2 + \dots] \} \\ & \left. + \frac{1}{2} |B_2^{(1)}|^2 \left\{ i b_2 (q_x^2 - q_y^2)(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})(\hat{\mathbf{r}} \cdot \hat{\mathbf{y}}) - \frac{1}{2} b_2^2 [q_x^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})^2 + q_y^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{y}})^2 + q_z^2(\hat{\mathbf{r}} \cdot \hat{\mathbf{z}})^2] - b_2^2 q_z q_x (\hat{\mathbf{r}} \cdot \hat{\mathbf{z}})(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) + \dots \right\} \right] \end{aligned}$$

$$\begin{aligned}
& + B_2^{(1)} B_2^{(3)} \left\{ -\frac{1}{4} (a_{11} + a_{12}) [q_x^2 (\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})^2 + q_y^2 (\hat{\mathbf{r}} \cdot \hat{\mathbf{y}})^2 + \dots] + \frac{i}{2} (a_{11} - a_{12}) [(q_x^2 - q_y^2) (\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) (\hat{\mathbf{r}} \cdot \hat{\mathbf{y}}) + \dots] \right. \\
& \left. + \frac{i b_2}{2} [(q_z^2 - q_y^2) (\hat{\mathbf{r}} \cdot \hat{\mathbf{y}}) (\hat{\mathbf{r}} \cdot \hat{\mathbf{z}}) + \dots] - \frac{1}{2} m_2' (a_{11} - a_{12}) [q_x^2 (\hat{\mathbf{r}} \cdot \hat{\mathbf{x}})^2 + q_y^2 (\hat{\mathbf{r}} \cdot \hat{\mathbf{y}})^2 + \dots] \right\} + \dots \Big] \\
& \times \exp(i \mathbf{G} \cdot \mathbf{r}) Y_{lm}^* (\hat{\mathbf{r}}) c(l_1 l_2 l; n_1 n_2; r), \tag{3.17}
\end{aligned}$$

where

$$a_{11} = -\frac{1}{2} \{(l_2 + m_2' + 1)(l_2 - m_2')\}^{1/2} C_g(l_1 l_2 l; m_1', m_2' + 1, \lambda),$$

$$a_{12} = \frac{1}{2} \{(l_2 - m_2' + 1)(l_2 + m_2')\}^{1/2} C_g(l_1 l_2 l; m_1', m_2' - 1, \lambda),$$

$$a_{21} = \frac{1}{8} \{(l_2 + m_2' + 2)(l_2 - m_2' - 1)(l_2 + m_2' + 1)(l_2 - m_2')\}^{1/2} \\ \times C_g(l_1 l_2 l; m_1', m_2' + 2, \lambda),$$

$$a_{22} = \frac{1}{8} \{(l_2 - m_2' + 2)(l_2 + m_2' - 1)(l_2 - m_2' + 1)(l_2 + m_2')\}^{1/2} \\ \times C_g(l_1 l_2 l; m_1', m_2' - 2, \lambda),$$

$$a_{23} = -\frac{1}{8} \{(l_2 + m_2')(l_2 - m_2' + 1) + (l_2 - m_2')(l_2 + m_2' + 1)\} \\ \times C_g(l_1 l_2 l; m_1', m_2', \lambda),$$

$$b_{21} = m_2' C_g(l_1 l_2 l; m_1', m_2', \lambda),$$

$$b_{22} = m_2'^2 C_g(l_1 l_2 l; m_1', m_2', \lambda).$$

Since the plane wave $\exp(i \mathbf{G} \cdot \mathbf{r})$ travelling in the z direction (because of the layered structure of smectic phases) is symmetrical about the z axis and can be expanded as a series of Legendre polynomials referring to this axis,

$$e^{i \mathbf{G} z_{12}} = \sum_{l'} (i)^{l'} (2l' + 1) j_{l'}(Gr) P_{l'}(\cos \theta), \tag{3.18}$$

where $j_{l'}(Gr)$ are the spherical Bessel functions and θ is the angle between the z axis and intermolecular axis r .

After performing the angular integration over $\hat{\mathbf{r}}$ we compare the resulting expression with Eq. (2.24) and obtain the following expressions for the elastic constants.

$$\begin{aligned}
\beta B_1 = & -\rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m \lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m \lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} \left[\frac{b_{21}}{\sqrt{6}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000) \{ C_g(2l'l; 202) \delta_{m_2} - C_g(2l'l; \underline{202}) \delta_{m_2} \} \right. \\
& - \frac{b_{22}}{6} \left\{ \delta_{l l'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000)^2 \delta_{m_0} + \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000) \right. \\
& \left. \left. \times [C_g(2l'l; 202) \delta_{m_2} + C_g(2l'l; \underline{202}) \delta_{m_2}] \right\} \right], \tag{3.19}
\end{aligned}$$

$$\begin{aligned}
\beta B_2 = & \rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m \lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m \lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} \left[\frac{b_{21}}{\sqrt{6}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000) \{ C_g(2l'l; 202) \delta_{m_2} - C_g(2l'l; \underline{202}) \delta_{m_2} \} \right]
\end{aligned}$$

$$\begin{aligned}
& + \frac{b_{22}}{6} \left\{ \delta_{ll'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000) \delta_{m_0} - \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000) \right. \\
& \left. \times [C_g(2l'l;202) \delta_{m_2} + C_g(2l'l;\underline{202}) \delta_{m_2}] \right\}, \tag{3.20}
\end{aligned}$$

$$\begin{aligned}
\beta B_3 = & \rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} \frac{(i)^{l'}}{6} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} b_{22} \left[\delta_{ll'} \delta_{m_0} + 2 \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000)^2 \delta_{m_0} \right], \tag{3.21}
\end{aligned}$$

$$\begin{aligned}
\beta B_{13} = & -\rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} \frac{1}{2\sqrt{6}} \frac{1}{\sqrt{(2l+1)}} Q_{l_1 m_1' n_1}(\mathbf{G}) \\
& \times Q_{l_2 m_2' n_2}(-\mathbf{G}) D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} b_{22} C_g(2l'l;000) [C_g(2l'l;101) \delta_{m_1} + C_g(2l'l;\underline{101}) \delta_{m_1}], \tag{3.22}
\end{aligned}$$

$$\begin{aligned}
\beta A = & -\rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} \frac{1}{3} (a_{23} - a_{21} - a_{22}) Q_{l_1 m_1' n_1}(\mathbf{G}) \\
& \times Q_{l_2 m_2' n_2}(-\mathbf{G}) D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} \left[\delta_{ll'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000)^2 \delta_{m_0} + \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} \right. \\
& \left. \times C_g(2l'l;000) \{C_g(2l'l;202) \delta_{m_2} + C_g(2l'l;\underline{202}) \delta_{m_2}\} \right], \tag{3.23}
\end{aligned}$$

$$\begin{aligned}
\beta A_{12} = & -\rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} \left[\frac{1}{\sqrt{6}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} (a_{11} + a_{12}) C_g(2l'l;000) \{C_g(2l'l;101) \delta_{m_1} + C_g(2l'l;\underline{101}) \delta_{m_1}\} \right. \\
& + \frac{1}{3} (a_{23} + a_{21} + a_{22}) \left\{ \delta_{ll'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000)^2 \delta_{m_0} + \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000) \right. \\
& \left. \left. \times [C_g(2l'l;202) \delta_{m_2} + C_g(2l'l;\underline{202}) \delta_{m_2}] \right\} \right], \tag{3.24}
\end{aligned}$$

$$\begin{aligned}
\beta A_{21} = & -\rho_0^2 \sqrt{4\pi} \sum_{l_1 l_2 l l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l l'}^{n_1 n_2} \left[-\frac{1}{\sqrt{6}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} (a_{12} - a_{11}) C_g(2l'l;000) \{C_g(2l'l;101) \delta_{m_1} - C_g(2l'l;\underline{101}) \delta_{m_1}\} \right. \\
& + \frac{1}{3} (a_{23} - a_{21} - a_{22}) \left\{ \delta_{ll'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000)^2 \delta_{m_0} - \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l;000) \right. \\
& \left. \left. \times [C_g(2l'l;202) \delta_{m_2} + C_g(2l'l;\underline{202}) \delta_{m_2}] \right\} \right], \tag{3.25}
\end{aligned}$$

$$\begin{aligned}
\beta C_1 = & \frac{\rho_0^2 \sqrt{4\pi}}{2} \sum_{l_1 l_2 l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l'}^{n_1 n_2} \left[\frac{1}{\sqrt{6}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} (a_{11} - a_{12}) C_g(2l'l; 000) \{ C_g(2l'l; 202) \delta_{m_2} - C_g(2l'l; \underline{202}) \delta_{m_2} \} \right. \\
& - \frac{1}{3} \left\{ \frac{1}{2} (a_{11} + a_{12}) + m_2' (a_{11} - a_{12}) \right\} \left\{ \delta_{l'l'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000)^2 \delta_{m_0} + \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000) \right. \\
& \left. \left. \times [C_g(2l'l; 202) \delta_{m_2} + C_g(2l'l; \underline{202}) \delta_{m_2}] \right\} \right], \tag{3.26}
\end{aligned}$$

$$\begin{aligned}
\beta C_2 = & -\frac{\rho_0^2 \sqrt{4\pi}}{2} \sum_{l_1 l_2 l'} \sum_{m_1' m_2'} \sum_{m\lambda} \sum_{n_1 n_2} \sum_{\mathbf{G}} (i)^{l'} \frac{\sqrt{(2l'+1)}}{(2l_1+1)(2l_2+1)} Q_{l_1 m_1' n_1}(\mathbf{G}) Q_{l_2 m_2' n_2}(-\mathbf{G}) \\
& \times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) J_{l_1 l_2 l'}^{n_1 n_2} \left[\frac{1}{\sqrt{6}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} (a_{11} - a_{12}) C_g(2l'l; 000) \{ C_g(2l'l; 202) \delta_{m_2} - C_g(2l'l; \underline{202}) \delta_{m_2} \} \right. \\
& + \frac{1}{3} \left\{ \frac{1}{2} (a_{11} + a_{12}) + m_2' (a_{11} - a_{12}) \right\} \left\{ \delta_{l'l'} \delta_{m_0} - \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000)^2 \delta_{m_0} - \sqrt{\frac{3}{2}} \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000) \right. \\
& \left. \times [C_g(2l'l; 202) \delta_{m_2} + C_g(2l'l; \underline{202}) \delta_{m_2}] \right\} - \frac{1}{\sqrt{6}} m_2' C_g(2l'l; m_1' m_2' \lambda) \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l'l; 000) \{ C_g(2l'l; 101) \delta_{m_1} \\
& - C_g(2l'l; \underline{101}) \delta_{m_1} \} \left. \right], \tag{3.27}
\end{aligned}$$

where

$$J_{l_1 l_2 l'}^{n_1 n_2} = \int dr r^4 j_L(Gr) c(l_1 l_2 l'; n_1 n_2; r)$$

are the structural parameters. A line under a number denotes a negative quantity. Equations (3.18)–(3.26) give general expressions for the curvature elastic constants of the Sm-C and other phases of this class in the long wavelength limit. From these results one can obtain expressions for the elastic constants of a given phase by using the appropriate order parameters corresponding to the phase.

The structures of smectic phases are characterized by three different class of order parameters: (i) orientational, (ii) positional, and (iii) mixed [2]. In general there can be upto $(2l+1)^2$ orientational and so many mixed order parameters of rank l for a given value of the reciprocal lattice vector \mathbf{G} . One uses the symmetries of the phase and of the constituent molecule to reduce this number. Since Sm-C phase is biaxial with point symmetry C_{2h} , we choose the following orientational order parameters at $l=2$ level (molecules are assumed to be cylindrically symmetric):

$$\bar{P}_2 = \frac{1}{5} Q_{20} = \langle P_2(\cos \theta) \rangle, \tag{3.28a}$$

$$\omega_1 = \frac{1}{5} Q_{21} = -\frac{1}{5} Q_{21} = \left(\frac{3}{2} \right)^{1/2} \langle \sin \theta \cos \theta \cos \phi \rangle, \tag{3.28b}$$

$$\omega_2 = \frac{1}{5} Q_{22} = \frac{1}{5} Q_{22} = \left(\frac{3}{8} \right)^{1/2} \langle \sin^2 \theta \cos 2\phi \rangle. \tag{3.28c}$$

While \bar{P}_2 measures the degree of alignment of molecular axis along the director \mathbf{n} , which makes a nonzero angle with the smectic plane normal, ω_1 and ω_2 measure the degree of alignment along the director \mathbf{c} and the biaxial ordering. The angular bracket indicates the average over the orientational distribution.

For positional ordering one may choose as in the case of Sm-A phase, one order parameter corresponding to $G = G_z = 2\pi/d$ where d is the layer spacing in equilibrium. Thus

$$\mu = Q_{00}(G) = \left\langle \cos 2\pi \frac{z}{d} \right\rangle. \tag{3.29}$$

The coupling between the positional and orientational ordering may be described by the order parameters τ_1 , τ_2 , and τ_3 , where

$$\tau_1 = \frac{1}{5} Q_{20}(G) = \left\langle \cos \frac{2\pi z}{d} P_2(\cos \theta) \right\rangle, \quad (3.30a)$$

$$\begin{aligned} \tau_2 &= \frac{1}{5} Q_{21}(G) = -\frac{1}{5} Q_{21}(G) \\ &= \left(\frac{3}{2} \right)^{1/2} \left\langle \cos \frac{2\pi z}{d} \sin \theta \cos \theta \cos \phi \right\rangle, \end{aligned} \quad (3.30b)$$

$$\begin{aligned} \tau_3 &= \frac{1}{5} Q_{22}(G) = \frac{1}{5} Q_{22}(G) \\ &= \left(\frac{3}{8} \right)^{1/2} \left\langle \cos \frac{2\pi z}{d} \sin^2 \theta \cos 2\phi \right\rangle. \end{aligned} \quad (3.30c)$$

Using these order parameters we give below explicit expressions for the curvature elastic constants for Sm-C phase consisting of cylindrically symmetric molecules;

$$B_1 = M_1 \sin^2 \psi + M_2 \cos \psi + M_3, \quad (3.31a)$$

$$B_2 = M_4 \sin^2 \psi - M_2 \cos \psi + M_5, \quad (3.31b)$$

$$B_3 = M_6 \sin^2 \psi + M_7, \quad (3.31c)$$

$$B_{13} = 0, \quad (3.31d)$$

$$A = M_8 \sin^2 \psi + M_9, \quad (3.31e)$$

$$A_{12} = M_{10} \sin^2 \psi + M_{11}, \quad (3.31f)$$

$$A_{21} = M_{12} \sin^2 \psi + M_{13}, \quad (3.31g)$$

$$\begin{aligned} C_1 &= M_{14} \sin^2 \psi + M_{15} (1 + \cos \psi)^2 + M_{16} (1 - \cos \psi)^2 \\ &+ M_{17} \sin \psi + M_{18} \sin \psi \cos \psi + M_{19}, \end{aligned} \quad (3.31h)$$

$$\begin{aligned} C_2 &= M_{20} \sin^2 \psi + M_{21} (1 + \cos \psi)^2 + M_{22} (1 - \cos \psi)^2 \\ &- M_{17} \sin \psi + M_{23} \sin \psi \cos \psi + M_{24}. \end{aligned} \quad (3.31i)$$

Here ψ is the tilt angle. The directors $\hat{\mathbf{n}}$ and $\hat{\mathbf{c}}$ of a uniform phase are assumed to be in the xz plane. The expressions for the constants M_1 to M_{24} , which involve the order and structural parameters and are, therefore, temperature and density dependent, are given in Appendix A. In writing these expressions we have taken into account the fact that, for a system of rigid axially symmetric molecules, $n_1 = n_2 = 0$ and

$$c(l_1 l_2 l; 00; r) = \frac{1}{4\pi} \sqrt{(2l_1 + 1)(2l_2 + 1)} c_{l_1 l_2 l}(r). \quad (3.32)$$

The structural parameters are connected with harmonic coefficients $c_{l_1 l_2 l}$ as

$$J_{l_1 l_2 l}(0) = \frac{\rho_0^2}{\sqrt{4\pi}} \int_0^\infty dr r^4 c_{l_1 l_2 l}(r) \quad (3.33)$$

and

$$J_{l_1 l_2 l l'} = \frac{\rho_0^2}{\sqrt{4\pi}} \int_0^\infty dr r^4 j_{l'}(Gr) c_{l_1 l_2 l}(r). \quad (3.34)$$

Our results, given in Eqs. (3.31), show that for cylindrically symmetric molecules $B_{13} = 0$. This is, however, not true in general. For molecules with broken cylindrical symmetry, B_{13} will be nonzero. Its magnitude, however, appears to be small compared to B_1 , B_2 , and B_3 . Madhusudana and co-workers [8] have found $B_{13}/B_1 \approx 0.3$

C. Expression for the elastic constant \bar{B}

As mentioned above the expression for the elastic constant \bar{B} is derived from the expression of f_2 given by Eq. (3.16). Since Sm-C as well as Sm-C* have one-dimensional positional ordering in addition to orientational ordering we have

$$\begin{aligned} f_2 &= -\frac{1}{2} \rho_0^2 \sum_G \sum_{l_1 l_2 l} \sum_{m'_1 m'_2 m'} \sum_{m\lambda} \sum_{n_1 n_2} \frac{Q_{l_1 m'_1 n_1}(G) Q_{l_2 m'_2 n_2}(-G)}{(2l_1 + 1)(2l_2 + 1)} C_g(l_1 l_2 l; m'_1 m' \lambda) \\ &\times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) \int d\mathbf{r} [\exp(iG_d z_{12}) - \exp(iG z_{12})] \delta_{m'_1 m'_2} c(l_1 l_2 l; n_1 n_2; r) Y_{lm}^*(\hat{\mathbf{r}}), \end{aligned} \quad (3.35)$$

where $G = 2\pi k/d$ and $G_d = 2\pi k/d_e$; d_e and d are the interlayer spacing of the distorted and undistorted Sm-C (and Sm-C*) phase. Using Eq. (3.11) we expand the above equation in ascending powers of the dilation parameter $\epsilon = d_e/d - 1$. The term associated with $(1/2)\epsilon^2$ defines the bulk elastic constant \bar{B} . Comparing Eq. (3.35) and with Eq. (2.4) we get

$$\begin{aligned} \bar{B} &= \frac{kT}{2} \rho_0^2 \sum_G \sum_{l_1 l_2 l} \sum_{m'_1 m'_2 m'} \sum_{m\lambda} \sum_{n_1 n_2} \frac{Q_{l_1 m'_1 n_1}(G) Q_{l_2 m'_2 n_2}(-G)}{(2l_1 + 1)(2l_2 + 1)} C_g(l_1 l_2 l; m'_1 m' \lambda) \\ &\times D_{m\lambda}^{l*}(\hat{\mathbf{n}}) G^2 \int d\mathbf{r} z_{12}^2 \exp(iG z) c(l_1 l_2 l; n_1 n_2; r) Y_{lm}^*(\hat{\mathbf{r}}). \end{aligned} \quad (3.36)$$

Using Eq. (3.18) we have

$$\begin{aligned} \bar{B} = & \frac{kT\rho_0^2}{6} \sqrt{4\pi} \sum_G \sum_{l_1 l_2 l'} \sum_{m_1' m_2' m'} \sum_{\lambda} \sum_{n_1 n_2} (i)^{l'} \frac{Q_{l_1 m_1' n_1}(\mathcal{G}) Q_{l_2 m_2' n_2}(-\mathcal{G})}{(2l_1+1)(2l_2+1)} \\ & \times \mathcal{G}^2 (2l'+1)^{1/2} D_{0\lambda}^{l'*}(\hat{\mathbf{n}}) C_g(l_1 l_2 l; m_1' m' \lambda) J_{l_1 l_2 l'}^{n_1 n_2} \left[\delta_{ll'} + 2 \left(\frac{2l'+1}{2l+1} \right)^{1/2} C_g(2l' l; 000)^2 \right]. \end{aligned} \quad (3.37)$$

As shown in I, the term proportional to ϵ in the free energy expansion gives the condition for the interlayer spacing. In terms of the order parameters given by Eqs. (3.29)–(3.30), Eq. (3.37) can be written as

$$\beta \bar{B} = L_1 \sin^2 \psi + L_2 \sin \psi \cos \psi + L_3. \quad (3.38)$$

The expressions for L_1 , L_2 , and L_3 for a system consisting of cylindrically symmetric molecules are given in Appendix B.

IV. DISCUSSIONS

In order to estimate the values of elastic constants given above we need the values of the order parameters, generalized spherical harmonic coefficients of the direct pair correlation functions of an effective fluid as a function of temperature and density, and the information about the constituent molecules, viz., electric multipole moments, geometry of the repulsive core, length-to-width ratio, etc. as input parameters.

Since in the limit of long-wavelength distortions the magnitude of the order parameters are assumed to remain unchanged, the value of the order parameters at a given temperature and the density may be either determined experimentally or calculated from a theory. The c harmonics for a given system can, in principle, be found either by solving the Ornstein-Zernike equation with suitable closure relations [6] or by adopting a perturbative scheme, which is based on the fact that the fluid structure at high densities is primarily controlled by the repulsive part of the interactions. However, such calculations for nonaxial molecules are very complicated and may need enormous computational efforts to generate reliable data for c harmonics [9].

The difficulty that arises in applying the theory to real systems is related to the potential energy of interaction between mesogenic molecules. The mesogenic molecules are large and have groups of atoms with their own local features. One way to construct the potential energy of interaction between two such molecules is to sum the interatomic or site-site potential between atoms or between interaction sites. However, for mesogenic molecules there are too many terms in this sum to be practical. Moreover, the dependence of interaction on molecular orientations in this expression is implicit so that it is difficult to use it in the calculation of angular orientation, which gives rise to liquid crystals.

In another and more convenient approach one uses rigid molecular approximation in which it is assumed that the in-

termolecular potential energy depends upon only the position of the center of mass and on their orientations. This kind of approach neglects the flexibility of molecular structure, which plays an important role in the stability of many liquid crystalline phases. In view of various complexities in the intermolecular interaction one is often forced to use a phenomenological description, either as a straightforward model unrelated to any particular physical system, or as a basis for describing by adjustable parameters fitted to experimental data for interaction between two molecules. Most commonly used models are hard ellipsoids of revolution, hard spherocylinders, cut sphere [10], and Gay-Berne (GB) [11]. However, none of these are known to show the existence of Sm-C phase.

The computer simulation study [12] shows that the GB model exhibits Sm-A and Sm-B phases. The GB potential contains four independent parameters that control the anisotropy in the attractive and repulsive interactions and can be written as

$$\begin{aligned} u(1,2) = & 4\epsilon(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) \left[\left\{ \frac{\sigma_0}{r - \sigma(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) + \sigma_0} \right\}^{12} \right. \\ & \left. - \left\{ \frac{\sigma_0}{r - \sigma(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) + \sigma_0} \right\}^6 \right]. \end{aligned} \quad (4.1)$$

Here $\epsilon(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$ and $\sigma(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)$ are angle dependent strength and range parameters, respectively, and are defined as

$$\begin{aligned} \epsilon(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) &= \epsilon_0 [1 - \chi^2 (\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)^2]^{-1/2} \left[1 - \chi' \right. \\ & \left. \times \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_1)^2 + (\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_2)^2 - 2\chi' (\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_1)(\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_2)(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)}{1 - \chi'^2 (\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)^2} \right]^2, \\ \sigma(\hat{\mathbf{r}}, \mathbf{\Omega}_1, \mathbf{\Omega}_2) &= \sigma_0 \left[1 - \chi \right. \\ & \left. \times \frac{(\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_1)^2 + (\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_2)^2 - 2\chi (\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_1)(\hat{\mathbf{r}} \cdot \hat{\mathbf{e}}_2)(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)}{1 - \chi^2 (\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2)^2} \right]^{-1/2}, \end{aligned} \quad (4.2)$$

where $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are the unit vectors along the symmetry axes of two interacting molecules. ϵ_0 and σ_0 are parameters that provide a measure of the attractive interactions and the width of the molecule. The anisotropy parameter χ and χ' are defined as

$$\chi = \frac{x_0^2 - 1}{x_0^2 + 1} \quad \text{and} \quad \chi' = \frac{k'^{1/2} - 1}{k'^{1/2} + 1},$$

where $x_0 = 2a/2b$ is the length (major axis) to breadth (minor axis) ratio and k' is the ratio of the potential well depth for the side by side and end to end configurations. We have taken here $x_0 = 3.0$ and $k' = 5$. The harmonics were generated by solving the Ornstein-Zernike equation using the Percus-Yevick closure relation [13]. Using these c harmonics we have calculated the values of the structural parameters at $k_B T / \epsilon_0 = 0.8$ and the packing fraction $\eta = (\pi/6)x_0\rho_0\sigma_0^3 = 0.49$. The values of few structural parameters for $G = 0$ and $G = 2\pi/x_0 = 2.0944$ so obtained are as follows:

$$\begin{aligned} J_{220}(0) &= 2.231\,74, & J_{0000} &= -2.789\,02, \\ J_{222}(0) &= 0.333\,24, & J_{0002} &= -4.611\,92, \\ J_{224}(0) &= -4.022\,96, & J_{2020} &= 0.075\,39, \\ J_{242}(0) &= 0.309\,51, & J_{2022} &= -2.058\,25, \\ J_{244}(0) &= -1.062\,09, & J_{2024} &= -0.565\,03, \\ J_{440}(0) &= 0.498\,93, & J_{2200} &= 0.133\,22, \\ J_{442}(0) &= -0.091\,14, & J_{2202} &= 0.6818, \\ J_{444}(0) &= 0.130\,77, & J_{2220} &= -0.493\,32, \\ & & J_{2222} &= -0.006\,27, \\ & & J_{2224} &= 0.177\,76, \\ & & J_{2240} &= 0.540\,22, \\ & & J_{2420} &= -0.258\,49. \end{aligned}$$

Since the values of the order parameters are not known, we assume them to be equal to 0.5 to estimate the relative contributions made by different terms in Eqs. (3.31) and (3.38). It is found that (i) dominant contributions for all elastic constants come from the angle independent term, (ii) coefficients of linear terms, i.e., terms involving $\sin \psi$ or $\cos \psi$ are small compared to terms involving $\sin^2 \psi$, and (iii) the relative contributions to A , A_{12} , A_{21} made by angle dependent terms are small compared to their relative contributions to B_1 , B_2 , and B_3 . The values of all these constants except B_{13} are found to be of the order of 10^{-6} dynes. As has already been pointed out, for a linear rigid molecule B_{13} is zero. For molecules with broken axial symmetry, B_{13} is non-zero but its value is less compared to other elastic constants. The elastic constant \bar{B} is found to be of the same order as in Sm-A. However, as tilt angle increases the value of \bar{B} decreases. The two angle dependent terms in Eqs. (3.38) are found to cancel each other, and therefore, the major contribution is due to the angle independent term.

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APPENDIX A

In this appendix we give explicit expressions for the coefficients M_1 to M_{24} in units of $k_B T / \sigma_0$ [see Eqs. (3.31)]. As is obvious from Eqs. (3.19)–(3.27), they involve order and structural parameters of all orders. We list only first few nonvanishing terms,

$$\begin{aligned} M_1 &= -\omega_1^2 \left[\frac{1}{2} \sqrt{\frac{5}{14}} J_{222}(0) \right] + \omega_2^2 \left[6 \sqrt{\frac{10}{7}} J_{222}(0) \right] \\ &\quad + \bar{P}_2 \omega_2 \left[-\frac{4}{3} \sqrt{\frac{15}{7}} J_{222}(0) \right] + \dots, \end{aligned}$$

$$M_2 = \omega_1^2 \left[2 \sqrt{\frac{5}{14}} J_{222}(0) \right] - \bar{P}_2 \omega_2 \left[4 \sqrt{\frac{5}{21}} J_{222}(0) \right] + \dots,$$

$$M_3 = \omega_1^2 \left[\frac{1}{3} \sqrt{\frac{5}{14}} \{-2J_{222}(0) + \sqrt{14}J_{220}(0)\} \right]$$

$$+ \omega_2^2 \left[4 \frac{\sqrt{5}}{3} \left\{ J_{220}(0) - \sqrt{\frac{2}{7}} J_{222}(0) \right\} \right]$$

$$+ \bar{P}_2 \omega_2 \left[4 \sqrt{\frac{5}{21}} J_{222}(0) \right] + \dots,$$

$$M_4 = -\tau_1 \tau_3 \left[\frac{30}{7} \sqrt{\frac{10}{7}} J_{2222} \right] + \dots,$$

$$M_5 = \omega_1^2 \left[\frac{1}{3} \sqrt{\frac{5}{14}} (4J_{222}(0) + \sqrt{14}J_{220}(0)) \right]$$

$$+ \omega_2^2 \left[4 \frac{\sqrt{5}}{3} (J_{220}(0) - \sqrt{\frac{2}{7}} J_{222}(0)) \right]$$

$$- \bar{P}_2 \omega_2 \left[4 \sqrt{\frac{5}{21}} J_{222}(0) \right] + \dots,$$

$$M_6 = -\omega_2^2 \left[4 \sqrt{\frac{10}{7}} J_{222}(0) \right] + \bar{P}_2 \omega_2 \left[\frac{4}{3} \sqrt{\frac{15}{7}} J_{222}(0) \right] + \dots,$$

$$M_7 = -\omega_1^2 \left[\frac{1}{3} \sqrt{\frac{10}{7}} (J_{222}(0) - \sqrt{\frac{7}{2}} J_{220}(0)) \right]$$

$$+ \omega_2^2 \left[4 \frac{\sqrt{5}}{3} (J_{220}(0) + 2 \sqrt{\frac{2}{7}} J_{222}(0)) \right] + \dots,$$

$$M_8 = -\bar{P}_2^2 \left[2 \sqrt{\frac{10}{7}} J_{222}(0) \right] + \dots,$$

$$M_9 = \omega_1^2 \left[-\frac{2}{3} \sqrt{\frac{5}{14}} J_{222}(0) + \frac{\sqrt{5}}{3} J_{220}(0) \right] \\ - \bar{P}_2^2 \left[\frac{3\sqrt{5}}{2} \left\{ J_{220}(0) - \frac{2}{3} \sqrt{\frac{2}{7}} J_{222}(0) \right\} \right] + \dots,$$

$$M_{10} = -\bar{P}_2^2 \left[\sqrt{\frac{10}{7}} J_{222}(0) \right] + \dots,$$

$$M_{11} = \omega_1^2 \left[\frac{4}{21} \sqrt{\frac{5}{14}} \left\{ -14 J_{222}(0) + \frac{35\sqrt{14}}{8} J_{220}(0) \right\} \right] \\ + \bar{P}_2^2 \left[\frac{\sqrt{5}}{2} J_{220}(0) \right] + \dots,$$

$$M_{12} = -\tau_1^2 \left[\frac{15}{7} \sqrt{\frac{10}{7}} J_{222} \right] + \dots,$$

$$M_{13} = \omega_1^2 \left[\frac{1}{21} \sqrt{\frac{5}{14}} \left\{ 28 J_{222}(0) + 7\sqrt{14} J_{220}(0) \right\} \right] \\ + \bar{P}_2^2 \left[\frac{\sqrt{5}}{2} J_{220}(0) \right] + \dots,$$

$$M_{14} = -\bar{P}_2 \omega_1 \left[\frac{35}{8} \sqrt{\frac{3}{35}} J_{222}(0) \right] + \dots,$$

$$M_{15} = \bar{P}_2 \omega_1 \left[\frac{25}{16\sqrt{105}} J_{222}(0) \right] + \dots,$$

$$M_{16} = \bar{P}_2 \omega_1 \left[\frac{5}{16\sqrt{105}} J_{222}(0) \right] + \dots,$$

$$M_{17} = -\bar{P}_2^2 \left[\frac{1}{2} \sqrt{\frac{5}{14}} J_{222}(0) \right] + \dots,$$

$$M_{18} = \bar{P}_2^2 \left[\frac{1}{2} \sqrt{\frac{5}{14}} J_{222}(0) \right] + \dots,$$

$$M_{19} = \bar{P}_2 \omega_1 \left[\frac{5}{28} \sqrt{\frac{3}{35}} \left\{ 7 J_{222}(0) + \frac{28}{3} \sqrt{\frac{7}{2}} J_{220}(0) \right\} \right] + \dots,$$

$$M_{20} = -\bar{P}_2 \omega_1 \left[\frac{5}{8} \sqrt{\frac{3}{35}} J_{222}(0) \right] + \dots,$$

$$M_{21} = -\bar{P}_2 \omega_1 \left[\frac{25}{48} \sqrt{\frac{3}{35}} J_{222}(0) \right] + \dots,$$

$$M_{22} = -\bar{P}_2 \omega_1 \left[\frac{5}{48} \sqrt{\frac{3}{35}} J_{222}(0) \right] + \dots,$$

$$M_{23} = \tau_1^2 \left[\frac{15}{28} \sqrt{\frac{5}{14}} J_{222} \right] + \dots,$$

$$M_{24} = \bar{P}_2 \omega_1 \left[\frac{5}{28} \sqrt{\frac{3}{35}} \left\{ 7 J_{222}(0) + \frac{14\sqrt{14}}{3} J_{220}(0) \right\} \right] + \dots.$$

APPENDIX B

We give explicit expressions for the coefficients L_1 , L_2 , L_3 involving the first few terms of order and structural parameters,

$$L_1 = \frac{1}{6} \sum_G \left[\left(\frac{\sqrt{6}}{2} - 3 \right) G^2 \mu \tau_1 I_{022} \right. \\ \left. + \sqrt{\frac{5}{7}} \left(\frac{3}{\sqrt{2}} + \sqrt{3} \right) G^2 \tau_1^2 I_{222} + \dots \right],$$

$$L_2 = \frac{1}{6} \sum_G \left[\sqrt{6} G^2 \mu \tau_2 I_{022} + \sqrt{\frac{5}{7}} (3\sqrt{2} - \sqrt{3}) G^2 \tau_1 \tau_2 I_{222} \right. \\ \left. + \dots \right],$$

$$L_3 = \frac{1}{6} \sum_G \left[\mu^2 G^2 I_{000} + 2G^2 \mu \tau_1 I_{022} + \sqrt{5} G^2 \tau_1^2 I_{220} \right. \\ \left. - \sqrt{\frac{10}{7}} G^2 \tau_1^2 I_{222} + \dots \right],$$

where

$$I_{000} = J_{0000} - 2J_{0002},$$

$$I_{022} = 2J_{0220} - \frac{55}{7} J_{0222} + \frac{36}{7} J_{0224},$$

$$I_{220} = J_{2200} - 2J_{2202},$$

$$I_{222} = 2J_{2220} - \frac{55}{7} J_{2222} + \frac{36}{7} J_{2224}.$$

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