

# Elasticity of thermotropic liquid crystals

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**In this article I describe the elasticity associated with liquid crystalline structures. The deviations from a spatially constant ground state of configurations of liquid crystals often arise due to imposition of boundary conditions, from external fields, or from thermal fluctuations. Since the characteristic distances involved in these phenomena are large compared to molecular dimensions, liquid crystals are assumed to be continuum with a set of elastic constants. I also discuss a microscopic theory involving the molecular parameters for the elastic constants. This theory which is based on the density-functional formalism, leads to expressions for the elastic constants of any system with continuous broken symmetry and are expressed in terms of the order parameters characterizing the degree and type of ordering and the pair correlation functions of an effective isotropic phase.**

THE liquid crystals are systems in which a liquid-like positional order or more appropriately, disorder exists at least in one direction of space and in which some degree of long range ordering in orientation of molecules or aggregates formed by association of molecules is present. The liquid crystalline phases therefore possess many of the mechanical properties of a liquid, i.e. high fluidity, inability to support shear, formation of droplets, etc. At the same time, these phases are similar to crystals in that they exhibit anisotropy in their optical, electrical, magnetic and even in some mechanical properties. The liquid crystalline phases successively break the continuous symmetries of the isotropic liquid phase and have symmetries that lie intermediate between the highest symmetry liquid phase and lowest symmetry crystal phase. For example, the nematic phase in which molecules on the average, align along a particular direction, breaks the continuous orientational symmetry of the isotropic liquid phase and a smectic phase<sup>1,2</sup> breaks the translational symmetry along one direction in addition to orientational symmetry. Spontaneous symmetry breaking is ubiquitous and is accompanied by important phenomena: acquisition of rigidity, the existence of low energy excitations, and the possibility of topological defects<sup>3,4</sup>.

There are two broad classes of liquid crystals: (i) Thermotropic and (ii) Lyotropic. Thermotropic systems are usually formed from a simple chemical compound and the mesomorphic phases appear primarily as a func-

tion of temperature. In contrast, lyotropic systems are not pure substances but solutions of unlike molecules in which one is a normal or mesogenic liquid and the other is an amphiphilic compound or surface active agent (surfactant). In the case of lyotropic liquid crystals, the concentration plays the role that temperature does in thermotropic liquid crystals; the transition from one phase to another can be accomplished by changing the concentration. In this article we concentrate only on the thermotropic liquid crystals.

In an ideal (or ground) state, a liquid crystal has a uniform structure characterized by position independent order parameters. When constraints are imposed on the sample by limiting its surfaces (e.g. walls of a container) and by external fields (magnetic, electric, etc.) acting on the molecules, the liquid crystal structure gets deformed. Since deformations cost energy, they are accompanied by restoring forces which oppose the deformations. The constant of proportionality between a deformation and the corresponding restoring force is known as elastic constant. In a crystalline solid, as is well known, the material undergoes homogeneous strain under deformation and restoring force arises to oppose the change in distance between neighbouring points. This restoring force, however, cannot exist in a positionally disordered material (e.g. liquids). But, if the material is orientationally ordered (e.g. nematic liquid crystals) restoring torques may arise to oppose the orientational deformations (curvatures). In those phases of liquid crystals which have both the (partial) positional and orientational orders, the restoring force and torque may arise simultaneously. The phenomena which liquid crystals exhibit under the influence of external fields are usually distinguished by two characteristics: (i) the energy involved per molecule in producing these effects is small compared to the strength of intermolecular interaction, and (ii) the characteristic distances involved in these phenomena are large compared to molecular dimensions. In describing these long-length phenomena, it is convenient to regard the liquid crystal as a continuum with a set of elastic constants than on a molecular basis.

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* (i.e. a unit vector along the direction of alignment of mole-

cules) is manipulated by external fields (display devices)<sup>5</sup>. Secondly, 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* fluctuations and defect stability in them<sup>4</sup>. Because of these reasons the study of the elastic constants has drawn considerable interest in recent years<sup>6</sup>.

### Liquid crystalline phases and order parameters

A liquid crystalline phase is characterized by the spatial and orientational configurations of molecules. At the phase transition point these configurations undergo a modification, i.e. 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  $\rho(\mathbf{x})$ .  $\rho(\mathbf{x})$  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 functional 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<sup>7</sup> to be discussed later.

For an ordered phase  $\rho(\mathbf{x})$  can be expressed in Fourier series and Wigner rotation matrices<sup>6</sup>.

$$\rho(\mathbf{x}) \equiv \rho(\mathbf{r}, \Omega) = \rho_0 \sum_G \sum_{lmn} Q_{lmn}(G) \exp(i\mathbf{G} \cdot \mathbf{r}) D_{mn}^l(\Omega), \quad (1)$$

where the expansion coefficients

$$Q_{lmn}(G) = \frac{2l+1}{N} \int d\mathbf{r} \int d\Omega \rho(\mathbf{r}, \Omega) \exp(-i\mathbf{G} \cdot \mathbf{r}) D_{mn}^{l*}(\Omega),$$

are the order parameters,  $G$  the reciprocal lattice vector and  $\rho_0$  the mean number density of the system. In simple cases  $Q_{lmn}(G)$  attains the following forms;

$$Q_{000}(0) = 1$$

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

$$Q_{lmn}(0) = (2l+1) \langle D_{mn}^{l*} \rangle = \frac{2l+1}{N} \int d\mathbf{r} \int d\Omega \rho(\mathbf{r}, \Omega) D_{mn}^{l*}(\Omega)$$

$$Q_{100}(G) = (2l+1) \tau_{G1} = \frac{2l+1}{N} \int d\mathbf{r} \int d\Omega \rho(\mathbf{r}, \Omega) P_l(\cos\theta) \exp(-i\mathbf{G} \cdot \mathbf{r}). \quad (2)$$

Here  $\mu_G$  for  $G \neq 0$  measure the degree of order in the distribution of centers of mass of molecules and are called positional order parameters whereas  $\langle D_{mn}^{l*} \rangle$  measure the degree of order in the orientation of molecules and are called orientational order parameters. There can be up to  $(2l+1)^2$  order parameters of rank  $l$  for a given  $G$ .  $\tau_{lG}$  for  $l \neq 0$  and  $G \neq 0$  measure the coupling between the orientational and translational order.

When the symmetries of the phase and of the constituent molecules are taken into account, the number of order parameters needed to describe the phase reduce to few. For example, for a cylindrically symmetric liquid crystal composed of cylindrically symmetric molecules,  $m = n = 0$ . Therefore the number of orientational order parameters for a given  $l$  is just one, i.e.

$$\langle D_{00}^{l*} \rangle = \langle P_l(\cos\theta) \rangle = \bar{P}_l.$$

It is often enough to use one orientational order parameter  $\bar{P}_2$  (in some cases one may need two  $\bar{P}_2$  and  $\bar{P}_4$ ) to describe a uniaxial phase made of cylindrically symmetric molecules. However, many mesogenic molecules do not possess cylindrical symmetry but may have two mirror planes that contain molecular symmetry axis and are mutually perpendicular. A prolate ellipsoid or a rectangular parallelepiped are examples of such a molecular model. For this case the orientational order parameters for  $l = 2$  are

$$\bar{P}_2 = \langle D_{00}^{2*} \rangle = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle,$$

$$\eta = \langle D_{02}^{2*} \rangle = \left( \frac{3}{8} \right)^{1/2} \langle \sin^2 \theta \cos 2\phi \rangle = \langle D_{0-2}^{l*} \rangle. \quad (3)$$

While the order parameters  $\bar{P}_l$  measure the degree of alignment of molecular axis along the director ( $z$ -direction), the other order parameter measure the difference in the degree of alignment of  $a$  and  $b$  molecular axis along  $z$ -direction.

As another example let us consider a mesophase having symmetry of three mutually orthogonal mirror planes with inversion symmetry through their intersection. This is an example of biaxial ordering. If the constituent molecules also have the same symmetry as that of the mesophase one needs four order parameters at  $l = 2$  level to describe the orientational ordering. They are

$$\bar{P}_2 = \langle D_{00}^2(\Omega)^* \rangle = \langle P_2(\cos\theta) \rangle,$$

$$\begin{aligned}\eta &= \langle D_{02}^2(\Omega)^* \rangle = \left(\frac{3}{8}\right)^{1/2} \langle \sin^2 \theta \cos 2\chi \rangle, \\ \xi &= \langle D_{20}^2(\Omega)^* \rangle = \left(\frac{3}{8}\right)^{1/2} \langle \sin^2 \theta \cos 2\phi \rangle, \\ \zeta &= \langle D_{22}^2(\Omega)^* \rangle = \frac{1}{4} \langle (1 + \cos \theta)^2 (\cos 2\phi \cos 2\chi \\ &\quad - \sin 2\phi \sin 2\chi) \rangle.\end{aligned}\quad (4)$$

While the first two order parameters, i.e.  $\bar{P}_2$  and  $\eta$  have the same physical meaning as in the case of a uniaxial phase. The other two order parameters  $\xi$  and  $\zeta$  are the measure of the biaxial ordering in the system.

For the smectic phase with positional order in one dimension only (e.g. *SmA* and *SmC*) we can restrict the series (1) to

$$\rho(\mathbf{r}, \tilde{\mathbf{Y}}) = \rho_0 \sum_{\tilde{G}} \sum_{lmn} Q_{lmn}(G_z) \exp(iG_z z) D_{mn}^l(\tilde{\mathbf{Y}}), \quad (5)$$

where  $G_z = \mathbf{G} \cdot \tilde{\mathbf{z}}$  is parallel to the layer normal. Again, eq. (5) can be simplified by using the symmetry of the constituent molecules and the mesophase. For example, for a phase having symmetry  $D_{\infty h} \times T(2) \times Z$  and composed of cylindrically symmetric molecules, the singlet orientational distribution has to depend only on the angle  $\theta$  between the director and the molecular symmetry axis. Accordingly we have

$$\rho(\mathbf{r}, \tilde{\mathbf{Y}}) = \rho_0 \sum_{q=0}^{\infty} Q_{ql} \cos(2\pi qz/d) P_l(\cos \theta), \quad (6)$$

where  $G_z = 2\pi qz/d$ ,  $d$  being the average interlayer spacing. The prime on the sum indicates the condition that  $l$  is even. Again  $Q_{q0} = \mu_q$  represents the positional,  $Q_{l00}(0) = (2l+1)\bar{P}_l$  the orientational order parameters, respectively. The  $Q_{ql} = (2l+1)\tau_{ql}$  the mixed order parameter.

In *SmA* phase the director is normal to the smectic layer and is therefore uniaxial. It is described by order parameters  $\mu_q$ ,  $\bar{P}_l$  and  $\tau_{lq}$ . The *SmC* in which the director makes a finite angle with the normal to the layer is biaxial with point group symmetry  $C_{2h}$ . To describe the ordered structure of *SmC* phase we therefore need the orientational order parameters of biaxial phase (see eq. (4)) and corresponding mixed order parameters in addition to  $\mu_q$ . The chiral *SmC* (*SmC\**) phase has structure which is modulated at scale dimension of the order of 1  $\mu\text{m}$  and larger. The modulated (helical) structure occurs as a result of a precession of the director tilt about an axis perpendicular to the layers plane. The tilt direction is rotated through an azimuthal angle  $\phi$  on

moving from one layer to the next. In this phase the mirror plane (of *SmC*) is lost but the  $C_2$  axis is present. The  $C_2$  axis is a polar axis and because of this *SmC\** admits the existence of a spontaneous polarization along it.

The hexatic smectic phases (*SmB<sub>h</sub>*, *SmI* and *SmF*) have bond-orientational (BO) order in smectic layers. One may discuss quantitatively the BO ordering by defining  $\theta(r)$  to be an angle between the bond direction at position  $r$  and some reference axis. In a plane with the 6-fold rotational symmetry BO order parameter is defined as

$$\psi_6(r_{\perp}) = \langle \exp(i6\theta(r_{\perp})) \rangle,$$

where the angular bracket indicates the coarse-grained average. The position vector  $r_{\perp}$  is confined in a 2-dimensional space.

In a columnar phase, molecules are arranged in (liquid) columns and these columns in turn form a two-dimensional lattice. A number of invariants of this structure is found<sup>1</sup>. They differ from each other in 2-dimensional lattice structure, angles between the director and the axis of columns and the arrangement of centre of mass of discotic molecules in a column.

### Elastic continuum theory

Since the free energy of a system with broken continuous symmetry is invariant with respect to spatially uniform displacements that take the system from one point in a ground state manifold to another, the free energy density is expanded in terms of the spatial derivatives of the order parameter fields. The elastic continuum theory deals only with small spatial derivatives. Consequently, only the lowest order terms in the expansion are taken into account. The contribution to  $f(r)$  due to deformation is called elastic free energy density  $f_d(r)$ , which by definition, is function of the spatial derivatives of the order parameter fields.

In addition to  $f_d(r)$  we may have contributions to  $f(r)$  due to external fields (if any) on the sample. Thus, in general

$$f(r) = f_0 + f_d(r) + f_e(r), \quad (7)$$

where  $f_0$  and  $f_e(r)$ , represent, respectively, the free energy density of a spatially uniform state and contribution due to external fields. Since the liquid crystal molecules are generally diamagnetic, electrically polarizable and anisotropic in their magnetic and electric properties, the application of a field usually help to align molecules and oppose the distortion. Therefore,  $f_e(r)$  is opposite in sign to that of  $f_d(r)$ . Often due to competition between the alignment favoured by the field, deformed structures are created. Experimentally, it is possible to fix the orientation of the molecules at a

boundary by surface treatment of the container walls and therefore to generate desired deformations with outside external field. This ability of creating controlled deformations has put liquid crystals to practical use<sup>5</sup>.

### Elastic free energy density of nematics and cholesterics phases

A system of a nematic or cholesteric liquid crystal is a macroscopic medium with broken rotation symmetries. A uniaxial nematic liquid crystal is visualized as a system consisting of rotationally symmetric ellipsoids, the orientational order of which is denoted by a unit vector (director)  $\mathbf{n}$ . The biaxiality of the nematic system can be thought of as a breaking of rotational symmetry of the ellipsoids around  $\mathbf{n}$ . Thus the biaxial nematic phase can be visualized as a system that breaks all the three rotational symmetries but none of the translational ones and consists of oriented ellipsoids with different axes, or equivalently of oriented bricks. Depending on the discrete symmetries these systems can vary widely. In principle, all familiar symmetry groups, orthorhombic, triclinic, hexagonal, cubic, etc. are admissible. We, therefore, need to derive a general expression for the free energy without any *a priori* symmetry consideration. Such an expression has been derived by Stalings and Vertogen<sup>8</sup>.

A general expression for the elastic free energy density of a medium with broken orientational symmetries is derived assuming that the magnitude of the order parameter field remains constant independent of position, only the orientation of the local coordinate frame chosen to define the orientation of the director field rotates slightly (weak deformation) in going from one point to the other and the spatial derivatives of these orthonormal vectors are small. The resulting expression is

$$f_d(r) = k_{ij} D_{ij} + \frac{1}{2} K_{ijkl} D_{ij} D_{kl} + L_{ijk} S_{ijk}, \quad (8)$$

where  $S_{ijk} = S_{jik} = \partial_\alpha (R_{i\alpha} D_{jk} + R_{j\alpha} D_{ik})$  and  $k_{ij}$ ,  $K_{ijkl}$  and  $L_{ijk}$  are elastic constants.  $R_{i\alpha}$  is the transformation matrix which makes the local body-fixed frame to coincide with the space-fixed frame and is described in terms of Euler angles.  $D_{ij}$  are rotational invariants formed by transformation matrix. Thus

$$D_{ij} = \frac{1}{2} \epsilon_{jkl} R_{i\alpha} R_{k\beta} \partial_\alpha R_{l\beta},$$

where  $\epsilon_{ijk}$  is the Levi-Civita symbol. The elastic constants satisfy the relations:  $K_{ijkl} = K_{klij}$  and  $L_{ijk} = L_{jkl}$ .

The first term of eq. (8) represents the contribution to the elastic free energy density due to the linear first-order terms in the expansion of free energy density in

terms of the spatial derivatives of the order parameter fields and contains three surface terms. The second arises due to contributions from the quadratic first-order terms and the linear second-order terms and contains six surface terms which are due to quadratic first-order terms. The last term of eq. (8) has 18 surface terms that are due to linear second-order terms.

The number of independent elastic constants reduce, often drastically when symmetry requirements of a given system are imposed. Under the symmetry operations elastic constants do not change. This means that, in mathematical terms, number of systems of local basis vectors connected by symmetry operations lead to the same elastic constants, i.e.

$$k'_{ij} = k_{ij}, \quad K'_{ijkl} = K_{ijkl} \quad \text{and} \quad L'_{ijk} = L_{ijk},$$

where constants with prime are for new rotated frame connected with the previous one by symmetry operations.

For example, for a uniaxial system with basis vector  $\mathbf{n}$  along the axis of continuous rotation symmetry, the following constraints should be satisfied for a system of  $D_\infty$  symmetry: (i)  $f_d(r)$  must be invariant in the continuous group of rotation about the local  $\mathbf{n}(\mathbf{r})$ , and (ii)  $f_d(r)$  must be even in  $\mathbf{n}(\mathbf{r})$  as the state  $\mathbf{n}(\mathbf{r})$  and  $-\mathbf{n}(\mathbf{r})$  are indistinguishable.

These requirements lead to the following well known Frank expression for the chiral uniaxial nematics

$$\begin{aligned} f_d(r) = & k(\mathbf{n} \cdot \nabla \times \mathbf{n}) + \frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 \\ & + \frac{1}{2} K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2} K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2 \\ & + \frac{1}{2} K_4 \nabla \cdot [(\mathbf{n} \cdot \nabla) \mathbf{n} - \mathbf{n}(\nabla \cdot \mathbf{n})] \\ & + \frac{1}{2} K_5 \nabla \cdot [(\mathbf{n} \cdot \nabla) \mathbf{n} + \mathbf{n}(\nabla \cdot \mathbf{n})]. \end{aligned} \quad (9)$$

This equation has four bulk and two surface elastic constants. Since surface terms do not, in general, contribute to bulk properties, they are dropped. They, however, play important role in surface properties of liquid crystals and are attracting lot of attention in recent years<sup>9</sup>. Information about anchoring energy can be derived from their measurements. The cholesteric liquid crystals have continuous symmetry group of  $D_\infty$  and exhibit helical ordering on a macroscopic scale. Taking  $q_0 = k/K_2$  the (bulk) free energy density for a cholesteric phase can be written as

$$f_0^{(b)}(r) = f_0(r) + f_d^{(b)}(r),$$

where

$$f_0 = f_u(r) - \frac{1}{2} K_2 q_0^2$$

and

$$f_d^{(b)}(r) = \frac{1}{2} [K_1 (\nabla \cdot \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n} - q_0)^2 + K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2]. \quad (10)$$

Thus the state of lowest free energy density has a finite twist

$$\mathbf{n} \cdot \nabla \times \mathbf{n} = q_0,$$

while other deformations are zero. This twist has full pitch of  $2\pi/q_0$ , but since  $\mathbf{n}(\mathbf{r})$  and  $-\mathbf{n}(\mathbf{r})$  are physically indistinguishable, the physical period of repetition is  $\pi/q_0$ . The twist term in  $f_d^{(b)}(r)$  can be considered to be a contribution due to deformation from this uniform helical structure.

For a uniaxial nematic phase of  $D_{\infty h}$  symmetry  $k = 0$  and

$$f_d^{(b)}(r) = \frac{1}{2} K_1 (\nabla \cdot \mathbf{n})^2 + \frac{1}{2} K_2 (\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + \frac{1}{2} K_3 (\mathbf{n} \times \nabla \times \mathbf{n})^2. \quad (11)$$

This is standard expression for the elastic free energy density associated with distortion of the director field  $\mathbf{n}(\mathbf{r})$  for a nematic liquid crystal in the absence of chiral or polar effects. The term  $(\nabla \cdot \mathbf{n})^2$  called **splay**,  $(\mathbf{n} \cdot \nabla \times \mathbf{n})^2$  **twist** and  $\mathbf{n} \times \nabla \times \mathbf{n}$  **bend**.

A biaxial nematic phase has two-fold (rotation or inversion) in three mutually perpendicular direction. The point groups of an orthorhombic system corresponds to  $D_2$  or  $(222)$ ,  $C_{2v}$  or  $(mm2)$  and  $D_{2h}$  or  $(mmm)$ . When eq. (8) is simplified with this requirement, one gets expression for the elastic free energy density which has three chiral elastic constants, twelve quadratic first-order bulk elastic constants, three quadratic first-order surface elastic constants and three linear second-order surface elastic constants. The three chiral terms vanish for point group symmetry  $D_{2h}$ . We, therefore, need 12 bulk elastic constants to describe biaxial nematics of  $D_{2h}$  point group symmetry within the framework of the elastic continuum theory.

Since  $f_d$  must be positive in order to give stability for the uniformly aligned state, all the  $K$ 's must be positive. Their values can be obtained from a theory which links the continuum theory with a microscopic theory including the molecular parameters. From the experimental data<sup>10</sup> of the Frank elastic constants one finds that for rod-shaped molecules  $K_2$  is always the smallest of the three;

$$0.5 < \frac{K_3}{K_1} < 3.0, \quad 0.5 < \frac{K_2}{K_1} < 0.8.$$

But for the discotic nematic,  $K_2$  is the largest and  $K_3$  smallest, i.e.  $K_2 > K_1 > K_3$ . The value of these constants is found to depend on the molecular length-to-width ratio but not on dipole moment, if any, of constituent molecules. For nematics that show a smectic phase at lower temperature a presmectic stiffening of  $K_2$  and  $K_3$  is observed.

### Smectics

Smectics have liquid-like structure along the plane of the layers and respond like solids to a force perpendicular to the layers. These features of smectics impose certain restrictions on the types of deformations that can be created in them. As a result, the continuum theory of smectics becomes more complicated compared to that of nematics discussed above. One may, however, take a simpler view and distinguish between two essentially different situations: one is when the thickness of the layers is strictly invariable, but they may have any curvature. The other is when their curvature is small and relaxed by the variation in thickness of layers.

An undeformed smectics has parallel and equidistant layers. 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 layers normal to their planes. A layer at  $z_0$  before displacement is now at

$$z(x, y) = z_0 + u(x, y, z).$$

One can easily see that a uniform displacement provides a uniform  $u$  and this does not change the energy. Furthermore, any spatial distortion of  $u$  that corresponds to a rigid rotation of the layers must have zero energy. It is easy to realize that the first-order derivatives parallel to the smectic layers, i.e.  $\partial u / \partial x$  and  $\partial u / \partial y$  correspond to the rigid rotation of the layers. The second-order derivatives of  $u$  which correspond to a curvature of the planes contribute to distortion free energy.

While the elasticity of smectic ( $Sm$ )  $A$  in the limit of weak deformations is adequately described in terms of displacement field  $u(x, y, z)$ , the other smectic phase may need additional variables.

### $Sm A$

In  $Sm A$  the director  $\mathbf{n}$  is normal to the layers. Since, as stated above  $\partial u / \partial x$  and  $\partial u / \partial y$  correspond to a simple rotation of the smectic layers, it follows to second-order

$$n_x = -\frac{\partial u}{\partial x} \left( 1 + \frac{\partial u}{\partial z} \right),$$

$$n_y = -\frac{\partial u}{\partial y} \left( 1 + \frac{\partial u}{\partial z} \right),$$

$$n_z = 1 - \frac{1}{2}(\nabla_{\perp} u)^2,$$

where

$$\nabla_{\perp} u = \begin{pmatrix} \frac{\partial u}{\partial x} \\ \frac{\partial u}{\partial y} \end{pmatrix}.$$

This equation simply states that at each point in the sample  $\mathbf{n}$  is normal to the layers which leads to the interesting consequence that  $\mathbf{n} \cdot \nabla \times \mathbf{n} = 0$ . Thus, the twist deformation that was allowed in nematics becomes forbidden in *Sm A*. Though bend deformation in *Sm A* is not strictly prohibited, its role is negligible. For most practical purposes, the elastic properties of *Sm A* is described by two constants  $K$  and  $B$ ,

$$f_d(r) = \frac{1}{2}K(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}B\left(\frac{\partial u}{\partial z}\right)^2. \quad (12)$$

The first term of this equation represents the splay deformation as in a nematic phase and the second compression (dilation) of the layers. Since  $B$  has the dimension of (energy)/(length)<sup>3</sup> and  $K$  has dimension of energy/length, it, therefore, useful to associate a length parameter  $\lambda$  defined as  $\lambda = (K/B)^{1/2}$ .  $\lambda$  is comparable to the layer thickness. In the vicinity of *Sm A* to nematic transition,  $B$  tends to zero and therefore  $\lambda$  infinity. Eq. (12) can be generalized to  $d$  dimensions by allowing  $\nabla_{\perp}$  be derivative in the  $(d-1)$  dimensional space perpendicular to  $\mathbf{n}$ .

### *Sm C*

The director  $\mathbf{n}$  in *Sm C* is tilted with respect to the layer normal. Its projection on the smectic plane, director  $\hat{\mathbf{c}}$  may rotate independent of displacement  $u$ , without changing the free energy. The knowledge of the rotation of the director  $\hat{\mathbf{c}}$  is needed to specify the state of *Sm C*. We therefore have two variables: (i) the displacement of layers normal to their planes  $u(x, y, z)$  (as used in *Sm A*) and (ii) a rotation  $\Omega_z$  about the normal to layers which specify the location of director  $\hat{\mathbf{c}}$  in the smectic plane.

We choose a space-fixed coordinate frame such that  $z$ -axis is along the normal to the unperturbed smectic layers. The system is described by (i) The angle  $\Omega_z$  of director  $\hat{\mathbf{c}}$  with respect to  $ox$ -axis, and (ii) the vertical displacement  $u$  of the layers whose derivatives

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

represent small angles of rotation about  $x$ - and  $y$ -axis, respectively.

The elastic free energy density must be function of the derivatives of  $\Omega$ , since as argued in the case of *Sm A*, a rotation of a whole must not cost energy. On the other hand, because of 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 centre of symmetry) and by the transformation  $y \rightarrow -y$ , the vertical  $xoz$  being a plane of symmetry. This leads to<sup>2</sup>

$$f(r) = f_{dc}(r) + f_{dk}(r) + f_{dck}(r) + f_{dl}(r),$$

where

$$f_{dc}(r) = \frac{1}{2}B_1(\Omega_{z,x})^2 + \frac{1}{2}B_2(\Omega_{z,y})^2 + \frac{1}{2}B_3(\Omega_{z,z})^2 + B_{13}\Omega_{z,x}\Omega_{z,z},$$

$$f_{dk}(r) = \frac{1}{2}A(\Omega_{x,x})^2 + \frac{1}{2}A_{12}(\Omega_{y,x})^2 + \frac{1}{2}A_{21}(\Omega_{x,y})^2,$$

$$f_{dck}(r) = C_1\Omega_{x,x}\Omega_{z,x} + C_2\Omega_{x,y}\Omega_{z,y},$$

$$f_{dl}(r) = \frac{1}{2}\bar{B}\gamma^2. \quad (13)$$

Here  $\gamma = \partial u / \partial z$  describes the variations in the thickness of layers and  $\Omega_{i,j} = \partial \Omega_i / \partial x_j$ .  $f_{dc}$  represents the contribution arising due to distortion of director  $\hat{\mathbf{c}}$  while  $f_{dk}$  is associated with curvatures of layers.  $f_{dck}$  represents the contribution arising due to coupling of different deformation modes and  $f_{dl}$  represents the contribution due to variation in layer thickness as in *Sm A*. The expressions for  $f_{dc}$ ,  $f_{dk}$  and  $f_{dck}$  given above can be derived using the formalism of orientational elasticity discussed above.

### *Sm C\**

Since *Sm C\** has no inversion symmetry, its elastic free energy density has linear terms. In terms of the  $\Omega$  vector field

$$f_d^{(1)}(r) = D_1\Omega_{z,x} + D_2\Omega_{x,x} + D_3\Omega_{z,z}.$$

Out of the three terms, 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 the  $D_2$  tends to transform a flat layer into a twisted ribbon. The terms  $D_1$  and  $D_2$  are expected to be insignificant compared to  $D_3$  term.

If  $q_0 = -(D_3/B_3)$  where  $B_3$  is defined in eq. (13) the contribution to  $f_{dc}(r)$  for *Sm C\** is modified to

$$f_{dc}(r) = \frac{1}{2}B_1(\Omega_{z,x})^2 + \frac{1}{2}B_2(\Omega_{z,y})^2 + \frac{1}{2}B_3(\Omega_{z,z} + q_0)^2 + B_{13}\Omega_{z,x}\Omega_{z,z} \quad (14)$$

while other terms of eq. (13) remain same. Thus the ground state of a *Sm C\** has a helical structure.

### *Sm B*

*Sm B<sub>h</sub>* are characterized by six-fold modulation of the density–density correlation function in the layer direction. One can rotate the six-fold modulation pattern (i.e. bond-order) independent of a layer displacement  $u$  around normal to the layer. Therefore we need two variables  $u$  and  $\Omega_z$  to describe the elastic theory of *Sm B<sub>h</sub>*. Thus

$$f_d(r) = \frac{1}{2}K_{\perp} \left[ \left( \frac{\partial \Omega_z}{\partial x} \right)^2 + \left( \frac{\partial \Omega_z}{\partial y} \right)^2 \right] + \frac{1}{2}K_{\parallel} \left( \frac{\partial \Omega_z}{\partial z} \right)^2 + \frac{1}{2}B \left( \frac{\partial u}{\partial z} \right)^2 + \frac{1}{2}K_{\perp} \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2. \quad (15)$$

The expression for the elastic free energy density for *Sm F*, *Sm I* and *Sm K* are similar to that of *Sm C* as the symmetry of these phases are exactly that of *Sm C*. Difference can only be quantitative.

### Columnar phase

In a columnar phase, molecules are arranged in columns and these columns in turn form a two-dimensional lattice. The two basic deformations which contribute to elastic free energy of this phase are (i) the curvature deformation (or bending) of the columns without distortion of lattice, and (ii) lattice dilation (compression) and shear without column curvature.

Deformations (ii) are the usual modes of deformation of a two-dimensional lattice. The coupling between (i) and (ii) can be adsorbed into the bend term by rescaling the bend elastic constant and therefore, the elastic free energy density for a columnar phase can be written as

$$f_d(r) = \frac{1}{2}K_3 \left[ \left( \frac{\partial^2 u_x}{\partial z} \right)^2 + \left( \frac{\partial^2 u_y}{\partial z} \right)^2 \right] + \frac{1}{2}B \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right)^2 + \frac{1}{2}D \left[ \left( \frac{\partial u_x}{\partial x} - \frac{\partial u_y}{\partial y} \right)^2 + \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right)^2 \right], \quad (16)$$

where  $\bar{B}$  and  $D$  are the elastic constants for the deformations of a two-dimensional lattice (In the notation of the standard crystal elastic theory,  $\bar{B} = \frac{1}{2}(C_{11} + C_{12})$  and  $D = \frac{1}{2}(C_{11} - C_{12})$ ).  $K_3$  is the Frank constant for the curvature deformation (bending) of the columns.

The experimental procedures used to measure the elastic constants of liquid crystals are rather delicate and involved. As a result, most of the efforts made so far are confined to simple phases, namely, uniaxial nematic and *Sm A* phases. Even for these systems the results reported by different workers do not agree with each other.

The experimental methods used to measure the Frank elastic constants are based on (i) Freedericksz transition, (ii) light scattering, (iii) alignment–inversion walls and (iv) cholesteric–nematic transition<sup>11</sup>. Any of the anisotropic properties, such as the birefringence, dielectric permittivity or the electrical or thermal conductivity can be used to measure the average state of the director in the sample. The simplest but perhaps most basic experiment for *Sm A* consists in imposing a stress on one of the boundaries of a *Sm A* homeotropic sample and measuring how it is transmitted to the other boundary. It is, however, more convenient to impose a displacement<sup>12</sup>  $\delta d$ . The strain  $\partial u / \partial z$  is simply given by  $\delta d / d$  and the transmitted stress by  $\bar{B} (\delta d / d)$ . This experiment thus provides a direct measure of elastic constant  $\bar{B}$ . As has been emphasized above, in *Sm C* we have extra variable  $\Omega_z$  in expansion of elastic free energy. The free-standing film geometry is particularly well suited for singling out this variable<sup>13</sup> and measuring corresponding elastic constants.

The value of the elastic constants can be obtained from a theory which links the continuum theory with a microscopic theory involving the molecular parameters. Such a theory has been developed using the formalism of density functional theory<sup>6,14</sup> which I now describe.

### Density-functional theory for elastic constants

The elastic free energy density is derived from the excess Helmholtz free energy arising due to intermolecular interactions<sup>14</sup>. In the density functional formulation the free energy of a system is expressed in terms of the direct correlation function of the medium<sup>6</sup>. Taking a reference system characterized by the singlet distribution  $\rho_r(\mathbf{x})$  the excess free energy of a system of singlet distribution  $\rho(\mathbf{x})$  is expressed as<sup>15</sup>

$$\beta \Delta A[\rho] = \beta A[\rho] - \beta A[\rho_r] = \beta \Delta A[\rho_r] - \int d\mathbf{x}_1 \Delta \rho(\mathbf{x}_1)$$

$$\int_0^1 ds c^{(1)}(\mathbf{x}_1; [s\rho_r]) - \int d\mathbf{x}_1 \int d\mathbf{x}_2 \rho(\mathbf{x}_1) \Delta \rho(\mathbf{x}_2)$$

$$\int_0^1 ds \int_0^1 ds' c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; [s\rho(\mathbf{x}_1, s'), s'\rho(\mathbf{x}_2, s')]), \quad (17)$$

where

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

and

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

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

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

where  $\Delta \rho(\mathbf{x}) = \rho(\mathbf{x}) - \rho_r(\mathbf{x})$ .

The function  $c^{(1)}$  and  $c^{(2)}$  appearing in eq. (17) 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 path of integration.

If the reference density  $\rho(\mathbf{x})$  is taken zero everywhere, we find from eq. (17)

$$\beta \Delta A[\rho] = -\frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 \rho(\mathbf{x}_1) \rho(\mathbf{x}_2) \bar{c}(\mathbf{x}_1, \mathbf{x}_2), \quad (18)$$

where

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

Note that eqs (17) and (18) are exact but need the values of  $c^{(1)}$  and  $c^{(2)}$ . Assuming that one can calculate the values of  $c^{(2)}$  for any density along the path of integration, any one of the above equations provides a useful way for calculating  $\beta \Delta A$ . 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. It is therefore, necessary that these equations be written 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 of  $c^{(1)}$  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. Using the symmetry of the system and neglecting the terms which involve  $c^{(n)}(\rho_f)$  with  $n \geq 3$ , the following expression for the deformation free energy is obtained

$$\begin{aligned} \beta \Delta A_d[\rho] &= \beta (\Delta A[\rho] - \Delta A[\rho_0]) \\ &= -\frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 [\rho_d(\mathbf{x}_1) \rho_d(\mathbf{x}_2) \\ &\quad - \rho_0(\mathbf{x}_1) \rho_0(\mathbf{x}_2)] c_{(2)}(\mathbf{x}_1, \mathbf{x}_2; \rho_f), \end{aligned} \quad (19)$$

where  $\Delta A[\rho_0]$  and  $\rho_0(\mathbf{x})$  are, respectively, the excess free energy and singlet distribution of the undistorted ordered phase.

In an alternative approach one uses eq. (18) to calculate the excess free energy of a nonuniform system and replaces the unknown function  $c^{(2)}$  by the direct pair correlation function of an effective isotropic reference fluid. In a scheme which is an extension of the scheme of Denton and Ashcroft<sup>16</sup> proposed for atomic system to the molecular system, one gets<sup>17</sup>

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

where  $\rho_0$  is the averaged density of the ordered phase and  $\omega$  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  $\omega$  must satisfy the normalization condition

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

Requiring that  $\omega$  satisfy

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

exactly, one finds

$$\begin{aligned} -\omega(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}) &= -\frac{1}{2\Delta a'(\bar{\rho})} \\ &\times \left[ \beta^{-1} c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}) + \frac{1}{V} \bar{\rho} \Delta a''(\bar{\rho}) \right], \end{aligned} \quad (20)$$

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



$$\beta \Delta A_d[\rho] = -\frac{1}{2} \int d\mathbf{x}_1 \int d\mathbf{x}_2 [\rho_d(\mathbf{x}_1) \rho_d(\mathbf{x}_2) - \rho_0(\mathbf{x}_1) \rho_0(\mathbf{x}_2)] c^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \bar{\rho}). \quad (21)$$

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

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

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

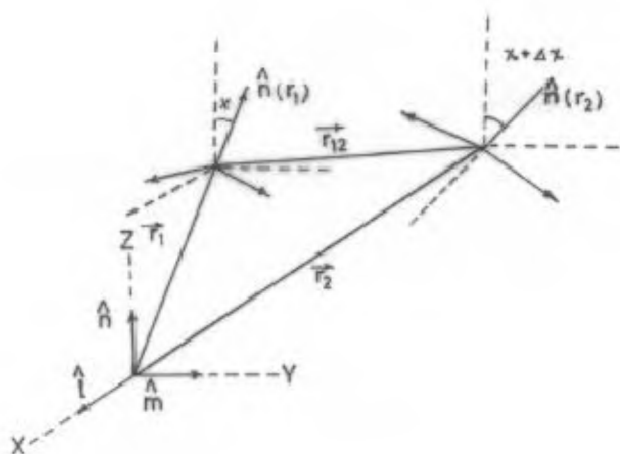
In the limit of long-wavelength distortion the magnitudes of the order parameters are assumed to remain unchanged. The changes occur in the direction of the directors making them position dependent and on the reciprocal lattice vector  $G$ . The reciprocal lattice vector  $G_d$  of the strained structure is related to  $G$  of the unstrained structure as

$$\mathbf{G}_d = (\mathbf{I} + \boldsymbol{\varepsilon})^{-1} \mathbf{G},$$

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

$$\rho_d(\mathbf{x}) = \rho_0 \sum_G \sum_{lmn} Q_{lmn}(G) \exp(i\mathbf{G}_d \cdot \mathbf{r}) D_{mn}^l(\Omega_d).$$

All angles without subscript  $d$  refer to a space fixed (SF) frame (see Figure 1). Let the molecule 1 be at  $\mathbf{r}_1$  from the origin where the principal director  $\mathbf{n}(\mathbf{r}_1)$  makes



**Figure 1.** Deviation angle for director triad at  $\mathbf{r}_2$  with respect to director triad at  $\mathbf{r}_1$ .

an angle  $\chi$  with the SF Z-axis and molecule 2 at distance  $\mathbf{r}_2$  from the origin, where  $\mathbf{n}(\mathbf{r}_2)$  represents the direction of the local principal director. The rotational property of generalized spherical harmonics may be used to express  $D_{mn}^l(\Omega_d)$  in terms of the angle  $\Omega$  with respect to the SF frame and  $\Delta\chi$  which is the angle between the principal directors at  $\mathbf{r}_1$  and  $\mathbf{r}_2$ .

As shown in ref. 18, the harmonics  $D_{mn}^l(\Delta\chi)$  can be expressed in terms of elastic variables which also appear in expressions of continuum theory discussed above. By comparing the resulting expressions with the corresponding expression of the continuum theory, expressions for elastic constants of different ordered phases can be obtained<sup>18,19</sup>. These expressions for the elastic constants contain order parameters which specify the nature and amount of ordering in the given phase and the structural parameters which involve the direct pair correlation functions of an effective isotropic liquid.

## Discussions

We now have a microscopic theory involving the molecular parameters for elastic constants of any ordered phase including plastic crystals, liquid crystals and crystalline solids. However, to obtain the numerical values of the elastic constants, we should know the relevant order parameters of the phase and direct pair correlation functions of an effective liquid consisting the molecules of the system. These quantities appear in the theory as input information.

The values of the direct pair correlation functions as a function of intermolecular separations and orientations at a given temperature and pressure are found either by computer simulations or by semi-analytic approximate methods<sup>20</sup>. In the latter approach one solves the Ornstein-Zernike (OZ) equation

$$h(1,2) - c(1,2) = \gamma(1,2) = \rho_f \int c(1,3) [\gamma(2,3) + c(2,3)] d\mathbf{x}_3,$$

where  $\mathbf{i} = \mathbf{x}_i$  with suitable closure relations such as the Percus-Yevick (PY) equation, hyper-netted chain (HNC) equation, mean spherical approximation, etc. Approximations are introduced in the theory through these closure relations. Note that these equations are highly nonlinear and solutions are often difficult. The method commonly adopted involves expansion of the pair correlation functions in a series of suitably chosen angle dependent basis functions. When such expansions are substituted in the OZ equation, it reduces to a set of algebraically coupled equations relating the harmonic coefficients of the direct and total correlation functions. These equations include one variable ( $r$  or  $k$ ) instead of the five or more variables appearing in the original OZ equation.

It may, however, be noted that in any numerical calculation one can handle only a finite number of the expansion (harmonic) coefficients, for each orientation dependent function. The accuracy of the result depends on this number. As the anisotropy in the shape of molecules (or in interactions) and value of the fluid density increase, more harmonics are needed to get proper convergence. Unfortunately the error arising due to truncation affect the values of correlations near the contact point which contribute significantly to the elastic properties.

The other difficulty which 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 polyatomic molecules is to sum the interatomic or site-site potentials 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 interactions on molecular orientations in this expression is implicit so that it is difficult to use it in calculation of angular correlations which give rise to liquid crystals.

In another and more convenient approach, one uses rigid molecule approximation in which it is assumed that the intermolecular potential energy depends only on the position of the centre of mass and on their orientations. This means that the vibrational coordinates of the molecules are dynamically and statistically independent of the centre of mass and orientation coordinates and that internal rotations are either absent or independent of the position and orientation coordinates of molecules. Therefore, this kind of approach ignores the flexibility of molecular structure which plays an important role in the stability of many liquid crystalline phases.

In view of various complexities in intermolecular interactions, 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 means of adjustable parameters fitted to experimental data for interaction between two molecules. Most commonly used models are hard-ellipsoids of revolution, hard-spherocylinders, cut-sphere, Kihara

core model, Berne-Pechukas and Gay-Berne models. The future direction of works in this area are likely to focus on using more realistic potential models.

Before I end I would like to mention that the theory discussed above is for systems consisting of short length ( $\sim 30\text{--}100\text{ \AA}$ ) mesogenic molecules. The wavelengths associated with the distortions are assumed to be much larger than the molecular lengths. As a result the elastic constants became wave-vector independent. However, in polymeric liquid crystals the molecular length ( $\sim 1000\text{ \AA}$ ) is of the order of the size of the wavelength of distortions. One therefore needs for this case a nonlocal theory of elasticity<sup>21</sup> which is yet to be fully developed.

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