Physics of liquid crystals

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This review discusses the physical properties of nematic, cholesteric, and smectic liquid crystals. Molecular theories of the liquid crystal phases are discussed and the molecular field theories of the phase transitions between the various liquid crystal phases are presented. The elastic theory and hydrodynamics of liquid crystals is developed. A wide variety of phenomena in liquid crystals, including elastic distortions, disclinations, flow properties, fluctuations, light scattering, wave propagation, nuclear magnetic resonance, effects of magnetic and electric fields, electrohydrodynamics, and optical properties, is discussed.

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I. LIQUID CRYSTALS IN GENERAL

Liquid crystals are a state of matter intermediate between that of a crystalline solid and an isotropic liquid. They possess many of the mechanical properties of a liquid, e.g., high fluidity, inability to support shear, formation, and coalescence of droplets. At the same time they are similar to crystals in that they exhibit anisotropy in their optical, electrical, and magnetic properties. The name liquid crystal was first suggested by Lehmann (1889) to characterize this state of matter. Such terms as mesomorphs or mesoforms, mesomorphic states, paracrystals, and anisotropic or ordered liquids or fluids have also been proposed and used in the literature. Liquid crystals which are obtained by melting a crystalline solid are called thermotropic. Liquid crystalline behavior is also found in certain colloidal solutions, such as aqueous solutions of tobacco mosaic virus (Bawden and Pirie, 1937; Oster, 1950) and certain polymers (Robinson, Ward, and Beevers, 1958). This type of liquid crystal is called lyotropic. For this class, concentration (and secondarily temperature) is the important controllable parameter, rather than temperature (and secondarily pressure) as in the thermotropic case. Most of the present discussion is equally valid for either class, although we will generally have a thermotropic liquid crystal in mind.

The quintessential property of a liquid crystal is its anisotropy. In this section we will list some of its manifestations and introduce an order parameter which characterizes and quantifies it. The bulk of this review will then develop the physical implications of this anisotropy. Essentially no other assumptions about the nature of a liquid crystals are necessary.

Liquid crystals are found among organic compounds; the organic molecules may be of a variety of chemical types, such as acids, azo- or azoxy-compounds, and cholesteric esters. An extensive listing is given by Kast (1969). The role of molecular geometry in liquid crystals has been discussed by Gray (1962). Certain structural features are often found in the molecules forming liquid crystal phases, and they may be summarized as follows:

(a) The molecules are elongated. Liquid crystallinity is more likely to occur if the molecules have flat segments, e.g., benzene rings.

(b) A fairly rigid backbone containing double bonds defines the long axis of the molecule.

(c) The existence of strong dipoles and easily polarizable groups in the molecule seems important.

(d) The groups attached to the extremities of the molecules are generally of lesser importance.

Two liquid crystals, para-azoxyanisole (PAA) and *p,p* methoxybenzylidene *n*-butylaniline (MBBA), which have been extensively studied are shown in Fig. 1. Some important physical properties of these two liquid crystals are given in Sec. XIX.

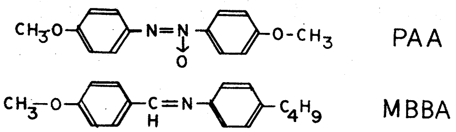

FIG. 1. Molecular structure of para-azoxyanisole (PAA) and *p*-methoxy benzilidene *p-n*-butylaniline (MBBA).

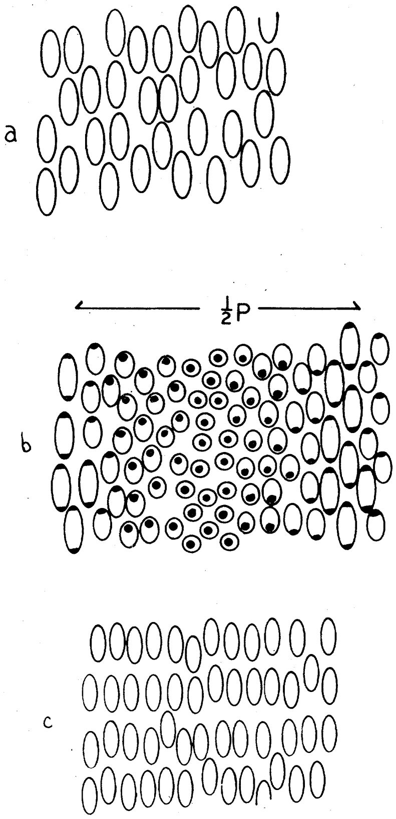

FIG. 2. The arrangement of molecules in liquid crystal phases. (a) The nematic phase. The molecules tend to have the same alignment but their positions are not correlated. (b) The cholesteric phase. The molecules tend to have the same alignment which varies regularly through the medium with a periodicity distance $p/2$. The positions of the molecules are not correlated. (c) The smectic A phase. The molecules tend to lie in planes with no configurational order within the planes and to be oriented perpendicular to the planes.

A classification of liquid crystals based on their structural properties was first proposed by G. Friedel (1922), and they are generally divided into three main classes:

1. *Nematic.* A simplified picture of the relative arrangement of the molecules in the nematic phase is shown in Fig. 2a. The long planar molecules which are usually involved are symbolized by ellipses. The nematic phase is characterized by long-range orientational order, i.e., the long axes of the molecules tend to align along a preferred direction. The locally preferred direction may vary throughout the medium, although in the unstrained (equilibrium) nematic it does not. Much of the interesting phenomenology of liquid crystals involves the geometry and dynamics of the preferred axis, and so it is useful to define a vector field $\mathbf{n}(\mathbf{r})$ giving its local orientation. This vector is called the director. Since its magnitude has no significance, it is

taken to be unity. The director field is easily distorted and can be aligned by magnetic and electric fields, and by surfaces which have been properly prepared. On optical examination of a nematic, one rarely sees the idealized equilibrium configuration. Some very prominent structural perturbations appear as threads from which nematics take their name. These threads are analogous to dislocations in solids and have been termed disclinations by Frank (1958). They are discussed in Sec. V.

There is no long-range order in the positions of the centers of mass of the molecules of a nematic, but a certain amount of short-range order may exist as in ordinary liquids. The molecules appear to be able to rotate about their long axes and also there seems to be no preferential arrangement of the two ends of the molecules if they differ (hence the sign of the director is of no physical significance). Thus optically, a nematic behaves as a uniaxial material with a center of symmetry. The existence of a center of symmetry in a nematic is indicated by the absence of ferroelectric phenomena, and also by the absence of second harmonic generation in light scattering (Durand and Lee, 1968).

This structure for a nematic is supported by the x-ray data [a review of x-ray work on liquid crystals has been given by Chistyakov (1966) and Delord (1969)]. Recently de Vries (1970) has suggested on the basis of x-ray and optical data that another type of nematic phase (cybotactic) exists. In this phase the molecules are arranged in groups in such a way that the centers of mass of the molecules in each group lie in a plane, i.e., there is short-range order of the smectic type.

2. *Cholesteric.* The cholesteric phase is like the nematic phase in having long-range orientational order and no long-range order in the positions of the centers of mass of molecules. It differs from the nematic phase in that the director varies in direction throughout the medium in a regular way. The configuration is precisely what one would obtain by twisting about the x axis a nematic initially aligned along the y axis. The director and the Fresnel ellipsoid are seen to rotate as one progresses along the twist axis. In any plane perpendicular to the twist axis the long axes of the molecules tend to align along a single preferred direction in this plane, but in a series of equidistant parallel planes, the preferred direction rotates through a fixed angle, as illustrated in Fig. 2b.

This secondary structure of the cholesteric is characterized by the distance measured along the twist axis over which the director rotates through a full circle. This distance is called the pitch of the cholesteric. The periodicity length of the cholesteric is actually only half this distance since $\mathbf{n}$ and $-\mathbf{n}$ are indistinguishable. For some reason, the structure of cholesterics is frequently referred to as a helix (with the appropriate pitch and axis); this usage has metaphoric value but little physical content.

A nematic liquid crystal is just a cholesteric of infinite pitch, and is not really an independent case. In particular, there is no phase transition between nematic and cholesteric phases in a given material, and nematic liquid crystals doped with enantiomorphic (not mirror symmetric) materials become cholesterics of long (but finite) pitch. The molecules forming this phase are always optically active, i.e., they have distinct right- and left-handed forms. The spiral arrangement has the opposite sense for the two types of molecules. A racemic mixture of right- and left-handed forms has a nematic structure (Robinson, 1966).

The pitch of the common cholesterics is of the order of several thousand angstroms, and thus comparable with the wavelength of visible light. The spiral arrangement is responsible for the characteristic colors of cholesterics in reflection (through Bragg reflection by the periodic structure) and their very large optical rotatory power (see Sec. XVIII). The pitch can be quite sensitive to temperature, flow, chemical composition, and applied magnetic or electric fields.

Again one rarely sees, on optical examination of a cholesteric, the idealized equilibrium configuration described above. An important type of disclination often observed in cholesterics was first described by Grandjean (1921). If the cholesteric is confined in a wedge-shaped space between tilted glass plates, optical patterns consisting of alternate light and dark stripes are observed. The stripes are parallel to lines of equal thickness along the glass surface and have been commonly referred to as Grandjean planes. The Grandjean planes are actually singular lines: an undistorted spiral structure can only be realized in regions where the gap width is an integral multiple of the half-pitch and in between the spiral is deformed (see Sec. V).

3. *Smectics.* The important feature of the smectic phase, which distinguishes it from the nematic, is its stratification. The molecules are arranged in layers and exhibit some correlations in their positions in addition to the orientational ordering. A number of different classes of smectics have been recognized [a review has been given by Sackmann and Demus (1969)]. In the smectic A phase the molecules are aligned perpendicular to the layers, with no long-range crystalline order within a layer (see Fig. 2c). The layers can slide freely over one another. In the smectic C phase the preferred axis is not perpendicular to the layers, so that this phase has biaxial symmetry. This phase was first identified by de Vries (1970) and by Chistyakov *et al.* (1969) by x-ray diffraction. The smectic B phase has been studied by Levelut and Lambert (1971) by x-ray diffraction. The observations suggest that there is hexagonal crystalline order within the layers. A model of the smectic B phase has been proposed by de Gennes and Sarma (1972) in which the layers can slip on each other but cannot rotate on each other. The smectic D and E modifications have been reported by Sackmann and co-workers [see Sackmann and Demus (1969)]. Optically the D modification appears to have a cubic structure, and the x-ray patterns are consistent with a cubic packing. The x-ray patterns obtained from the smectic E phase prove the presence of a layered structure, and also indicate that there is a high degree of order of the molecular arrangement within the planes (Diele, Brand, and Sackmann, 1972b). Further work is required to elucidate the nature of these phases.

In general a smectic, when placed between glass slides, does not assume the simple form of Fig. 2c. The layers, preserving their thickness, become distorted and can slide over one another in order to adjust to the surface conditions. The optical properties (focal conic texture) of the smectic state arise from these distortions of the layers. From observation it is inferred that the layers form a series of Dupin cycides [a simple discussion has been given by Bragg (1934) and in Sec. XV].

A number of substances exhibit nematic (or cholesteric) and smectic phases. An extensive study of the phase diagrams of a large number of compounds has been made by Sackmann and co-workers (Sackmann and Demus, 1969). The general rule appears to be that the lower temperature phases have a greater degree of crystalline order. Examples are: (i) the nematic phase always occurs at a higher temperature than the smectic phase; (ii) the smectic phases occur in the order A → C → B as the temperature decreases.

Further background material is available in the following list of review articles, books, and conference proceedings:

Brown and Shaw (1957); Gray (1962); Fergason (1964); Brown, Dienes and Labes (1965); Chistyakov (1966); De Gennes (1974); Durand and Litsler (1973); Saupe (1973); Porter and Johnson (1967); Saupe (1968); Brown (1969); Sackmann and Demus (1969); Pincus (1970); Heilmeier (1970); Brown, Doane, and Neff (1970); Brown and Labes (1972).

A. The order parameter

Suppose, for simplicity, that the molecules composing a nematic or cholesteric liquid crystal are rigid and rodlike in shape. Then we can introduce a unit vector $\boldsymbol{\nu}^{(i)}$ along the axis of the ith molecule which describes its orientation. This vector should not be confused with the direcior $\mathbf{n}$ which gives the average preferred direction of the molecules. Since liquid crystals possess a center of symmetry, the average of $\boldsymbol{\nu}^{(i)}$ vanishes. It is thus not possible to introduce a vector order parameter for a liquid crystal analogous to the magnetization in a ferromagnet, and it is necessary to consider higher harmonics or tensors. A natural order parameter to describe the ordering in a nematic or cholesteric is the second rank tensor

$$S_{\alpha\beta}(\mathbf{r}) = \frac{1}{N}\sum_i \left(\nu_\alpha^{(i)}\nu_\beta^{(i)} - \tfrac{1}{3}\delta_{\alpha\beta}\right) \tag{1.1}$$

when the sum is over all the N molecules in a small but macroscopic volume located at the point $\mathbf{r}$. The ν_α are the components of $\boldsymbol{\nu}$ referred to by a set of laboratory fixed axes. This order parameter is a symmetric traceless tensor of rank two and in general has five independent components. In the isotropic state, where the molecules have random orientations, $S_{\alpha\beta}$ vanishes.[1]

In order to define an order parameter for nonlinear rigid molecules, we introduce a Cartesian coordinate system $x'y'z'$ fixed in the molecules. In the case of a uniaxial liquid crystal the order parameter tensor is defined by (Saupe, 1965)

$$S_{\alpha'\beta'}(\mathbf{r}) = \langle \cos\theta_{\alpha'}\cos\theta_{\beta'} - \tfrac{1}{3}\delta_{\alpha'\beta'}\rangle, \tag{1.2}$$

where $\cos\theta_{\alpha'}$ is the angle between the α' molecular axis, and the preferred direction or optic axis and the angular brackets indicate an average over the molecules in a small but macroscopic volume as in Eq. (1.1). In the case of linear molecules, or molecules with a well defined long axis about which they rotate rapidly, the two definitions (1.1) and (1.2) are equivalent. The order parameter (1.2) is necessary in the interpretation of the NMR spectra of nematics (see Sec. XIV).

In real liquid crystals the molecules may be flexible in contrast to the rigid models considered above. Different parts of the molecules would then have to be described by different $S_{\alpha\beta}$ tensors. It is then preferable, as suggested by de Gennes (1971a), to define the amount of order in terms of a macroscopic property which is independent of any assumptions about the rigidity of the molecules. Such a definition of the order parameter is also preferable from a thermodynamic point of view. The macroscopic property chosen by de Gennes to represent the amount of order is the anisotropy in the diamagnetic susceptibility. We define[2]

$$Q_{\alpha\beta} = \chi_{\alpha\beta} - \tfrac{1}{3}\delta_{\alpha\beta}\chi_{\gamma\gamma}, \tag{1.3}$$

where $\chi_{\alpha\beta}$ is the magnetic susceptibility tensor per unit volume. $Q_{\alpha\beta}$ is again a symmetric traceless tensor of rank two and has five independent components.

Since magnetic interactions between molecules are small, the susceptibility is approximately the sum of the susceptibilities of the individual molecules; then $Q_{\alpha\beta}$ is simply related to $S_{\alpha'\beta'}$ for rigid molecules. Let the principal susceptibilities of a molecule be $\chi_1^{(0)}$, $\chi_2^{(0)}$, and $\chi_3^{(0)}$, and choose the molecular fixed axes x', y', and z' to coincide with the principal axes of the susceptibility. Then it is not difficult to show for a uniaxial liquid crystal

$$\begin{aligned} Q_{xx} = Q_{yy} = 2N[(S_{y'y'} + S_{z'z'})\chi_1^{(0)} + (S_{z'z'} + S_{x'x'})\chi_2^{(0)} \\ + (S_{x'x'} + S_{y'y'})\chi_3^{(0)}] \\ Q_{zz} = N(S_{x'x'}\chi_1^{(0)} + S_{y'y'}\chi_2^{(0)} + S_{z'z'}\chi_3^{(0)}), \end{aligned} \tag{1.4}$$

where N is the number of molecules per unit volume. Owing to the identity $S_{x'x'} + S_{y'y'} + S_{z'z'} = 0$, there are two independent parameters on the right-hand side. For molecules with axial symmetry we have

$$Q_{\alpha\beta} = N\chi_a^{(0)}S_{\alpha\beta}, \tag{1.5}$$

where $\chi_a^{(0)} = \chi_{\parallel}^{(0)} - \chi_{\perp}^{(0)}$ is the anisotropy in the susceptibility [$\chi_{\parallel}^{(0)}$ and $\chi_{\perp}^{(0)}$ are the susceptibilities along and perpendicular to the axis, respectively].

Any other second-rank tensor property of a liquid crystal could be used in place of Eq. (1.3). We could, for example, have chosen to define $Q_{\alpha\beta}$ in terms of the electric susceptibility. However, then the simple relation (1.4) could not be expected to hold. The electric susceptibility cannot be taken as the sum of the susceptibilities of the individual molecules, as local field corrections are much more important in the electric case.

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[1] Strictly speaking $S_{\alpha\beta}$ only vanishes in the isotropic state when the thermodynamic limit of Eq. (1.1) is taken. A certain amount of short-range orientational order is present in the isotropic state.

[2] By convention repeated indices are to be summed over.

It is possible to describe both uniaxial or biaxial ordering in liquid crystals by means of the order parameters (1.1)–(1.3).

1. Uniaxial symmetry

The single preferred direction of the molecules in this case is along the director **n**. For uniaxial symmetry the order parameter (1.1) can be written in the form

$$S_{\alpha\beta} = S(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), \tag{1.6}$$

where n_α are the components of **n** in a laboratory fixed coordinate system. In particular, if we choose **n** along the z axis of this coordinate system, the three nonzero components of S are

$$S_{zz} = \tfrac{2}{3}S, \qquad S_{xx} = S_{yy} = -\tfrac{1}{3}S. \tag{1.7}$$

The scalar quantity S is a measure of the alignment of the molecules. Quantitatively, if $f(\theta)\sin\theta\, d\theta$ is the fraction of molecules whose axes make angles between θ and $\theta + d\theta$ with the preferred direction,

$$S = \int_0^\pi (1 - \tfrac{3}{2}\sin^2\theta) f(\theta) \sin\theta\, d\theta. \tag{1.8}$$

In the isotropic phase $S = 0$, and in the nematic or cholesteric phases $0 < S < 1$. The limit $S = 1$ corresponds to perfect alignment of all the molecules and, of course, can never be realized in practice.

In the uniaxial case the order parameter (1.3) can be written in the form

$$Q_{\alpha\beta} = Q(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}). \tag{1.9}$$

The quantity $Q = \chi_{\|} - \chi_{\perp}$ is the anisotropy in the magnetic susceptibility.

The most important classes of liquid crystals belong to the uniaxial case (the smectic C phase being the principal counterexample). According to Eq. (1.6), the order parameter for all such systems can be characterized by a magnitude Q and a direction **n**, where the latter is the principal axis of the order parameter tensor. The theoretical development below depends merely upon the existence of **n** and is by no means restricted to the case of rigid symmetric molecules.

2. Biaxial symmetry

Biaxial phases of nematic and cholesteric liquid crystals have not been observed. The smectic C phase is an example of a liquid crystal with biaxial symmetry. The order parameter can be put in the general diagonal form

$$\begin{aligned} Q_{zz} &= \chi_{zz} - \tfrac{1}{3}\chi_{\gamma\gamma} = P, \\ Q_{xx} &= \chi_{xx} - \tfrac{1}{3}\chi_{\gamma\gamma} = -\tfrac{1}{2}(P - R), \\ Q_{yy} &= \chi_{yy} - \tfrac{1}{3}\chi_{\gamma\gamma} = -\tfrac{1}{2}(P + R). \end{aligned} \tag{1.10}$$

It now depends on two scalar quantities, P and R, which are given by

$$\begin{aligned} P &= \tfrac{1}{3}(2\chi_{zz} - \chi_{xx} - \chi_{yy}) \\ R &= \chi_{xx} - \chi_{yy}. \end{aligned} \tag{1.11}$$

Once two axes are fixed, the third is also determined so that this is the most general type of symmetry that can occur for a second-rank symmetric traceless tensor. Possible biaxial forms of nematic liquid crystals have been discussed by Freiser (1970), Fan and Stephen (1970), and Alben (1973).

II. MOLECULAR FIELD THEORIES OF LIQUID CRYSTALS

A. Landau theory

Let us assume, following Landau (1937); Landau and Lifshitz (1958), that the Gibbs free energy density $g(P, T, S_{\alpha\beta})$ is an analytic function of the order parameter tensor $S_{\alpha\beta}$. In particular this quality is supposed to obtain near the transition temperature. To the extent that $S_{\alpha\beta}$ is a small parameter, we may expand g in a power series. Since the free energy must be invariant under rigid rotations, all terms of the expansion must be scalar functions of the tensor $S_{\alpha\beta}$. The most general such expansion has the form

$$\begin{aligned} g = g_i &+ \tfrac{1}{2}A S_{\alpha\beta}S_{\alpha\beta} - \tfrac{1}{3}B S_{\alpha\beta}S_{\beta\gamma}S_{\gamma\alpha} \\ &+ \tfrac{1}{4}C S_{\alpha\beta}S_{\alpha\beta}S_{\gamma\delta}S_{\gamma\delta} - \tfrac{1}{2}\chi_a H_\alpha S_{\alpha\beta} H_\beta \end{aligned} \tag{2.1}$$

correct to fourth order in $S_{\alpha\beta}$ (de Gennes, 1969a). Here g_i is the free energy density of the isotropic phase. There is just one distinct invariant of order 2, 3, and 4, as shown: other forms (such as $S_{\alpha\beta}S_{\beta\gamma}S_{\gamma\delta}S_{\delta\alpha}$) can be reduced for uniaxial liquid crystals to one of the forms given ($\tfrac{1}{2}S_{\alpha\beta}S_{\alpha\beta}S_{\gamma\delta}S_{\gamma\delta}$, in the example) when consideration is taken of the fact that the trace $S_{\alpha\alpha}$ vanishes. The last term of (2.1) is the magnetic anisotropy energy due to the presence of the applied field H.

The coefficients A, B, and C are in general functions of P and T. We shall see below that this model equation of state predicts a phase transition near the temperature where A vanishes. We will assume A has the form

$$A = A'(T - T^*). \tag{2.2}$$

The transition temperature itself will prove to be somewhat above T^*. The coefficients B and C need have no particular properties near T^*; we will regard them as constants.

The assumption that g is analytic in $S_{\alpha\beta}$ cannot be justified, although in succeeding sections we will give some examples of models for which it seems to hold. The validity of the expansion restricts us to small values of S. Experimentally $S \sim 0.5$ just below the transition, for which the expansion (2.1) can only be qualitatively correct.

In a uniaxial liquid crystal $S_{\alpha\beta}$ takes the form

$$S_{\alpha\beta} = S(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}). \tag{2.3}$$

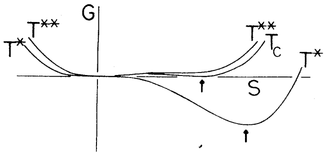

FIG. 3. Landau theory: dependence of the Gibbs free energy on the order parameter. The cases of the three special temperatures, T^{**}, T_c, and T^* are shown. The equilibrium value of the order parameter (which minimizes G) is indicated in the latter two cases.

Substituting this into Eq. (2.1), it becomes

$$g = g_i + \tfrac{1}{3}AS^2 - \tfrac{2}{27}BS^3 + \tfrac{1}{9}CS^4 \tag{2.4}$$

in the absence of a magnetic field. The equilibrium value of S is that which gives the minimum value for the free energy. The dependence of g_i on S for several choices of T is shown in Fig. 3, and for each case the equilibrium value of S is indicated. We see that there is a discontinuous phase transition at a temperature T_c slightly above T^*. The source of this first-order phase transition lies in the presence of the odd-order powers of S in the expansion (2.4); the existence of these terms is in turn due to the fact that the sign of S has physical meaning. A general discussion of the relationship between symmetry and the order of a phase transition has been given by Landau and Lifshitz (1958).

The value of S which minimizes Eq. (2.4) can be found algebraically. It will be a root of the derivative of (2.4), which is

$$AS - \tfrac{1}{3}BS^2 + \tfrac{2}{3}CS^3 = 0. \tag{2.5}$$

The solutions of this equation are

$$\begin{aligned} &S = 0 && \text{isotropic phase} \\ &S = (B/4C)[1 + (1 - 24\beta)^{1/2}] && \text{nematic phase,} \end{aligned} \tag{2.6}$$

where $\beta = AC/B^2$. A third solution, corresponding to a maximum of the free energy, has been suppressed. Of the two solutions to Eq. (2.6), the one with the lower free energy will obtain; the transition temperature T_c will be such that the free energies of isotropic and nematic phases are equal, as shown in Fig. 3. From Eqs. (2.6) and (2.4) this point can be determined to be

$$\beta = \tfrac{1}{27}; \qquad T_c = T^* + \tfrac{1}{27}(B^2/A'C). \tag{2.7}$$

Above T_c the isotropic phase is stable; below T_c the nematic is stable.

The value of the order parameter at the phase transition is

$$S_c = B/3C. \tag{2.8}$$

The difference in entropy between the two phases is found by differentiating Eq. (2.4) with respect to temperature. The resultant latent heat per unit volume is

$$L = (A'B^2/27C^2)T_c. \tag{2.9}$$

The temperature T^* corresponds to the limit of metastability of the isotropic phase. It should be possible, in principle, to supercool the isotropic liquid to this temperature. At T^*, where the coefficient A in the free energy changes sign, the isotropic phase becomes unstable (because $S = 0$ is not a local minimum of the free energy, as shown in Fig. 3). Likewise, the nematic phase becomes unstable when $\beta > \frac{1}{24}$. This determines a temperature $T^{**} = T^* + B^2/24A'C$ which is the limit of metastability of the nematic phase on heating. The temperatures T^* and T^{**} also have the significance that they are the apparent "critical points" for the isotropic and ordered phases, respectively. Thus susceptibilities and correlation lengths, which increase as the transition point is approached, will appear to be headed for a divergence at a temperature slightly beyond the transition temperature T_c.

Further applications of Landau's theory to the properties of nematogens in the isotropic phase will be discussed in Sec. XIII.

B. Theory of Maier and Saupe

Maier and Saupe in a series of papers (1958, 1959, 1960) have given a microscopic model for the phase transition in a nematic liquid crystal. They consider the orientation-dependent part of the van der Waals interaction between pairs of rodlike, nonpolar molecules, which they reduce to an internal field seen by one molecule by averaging over the positions and orientations of all the other molecules. In performing this averaging, it is assumed that there is no anisotropy in the positional correlations (that is, the neighbors of a given molecule are arranged in a spherically symmetric way), and that the distribution of orientations of each molecule is sufficiently and accurately described by the average order parameter tensor $S_{\alpha\beta}$. The result is that a given molecule feels an effective potential

$$V(\mathbf{v}, S) = -\tfrac{3}{2}A_0 S_{\alpha\beta}(\nu_\alpha \nu_\beta - \tfrac{1}{3}\delta_{\alpha\beta}), \tag{2.10}$$

where $\mathbf{v}$ is a unit vector along the axis of the molecule, and A_0 is a quantity independent of orientations and dependent on interparticle spacing according to

$$A_0 = a\langle \sum_j R_{1j}^{-6} \rangle, \tag{2.11}$$

where the sum runs over all particles except particle 1, the average is an ensemble average, and a is a constant.

The probability distribution for the orientation of a molecule in the presence of this internal field is

$$f(\mathbf{v}) = C\exp[-V(\mathbf{v}, S)/kT] \tag{2.12}$$

where

$$C^{-1} = \int d\mathbf{v} \exp[-V(\mathbf{v}, S)/kT]. \tag{2.13}$$

Here $d\mathbf{v}$ indicates an integration over all orientations of $\mathbf{v}$. The theory is made self-consistent by requiring that the average value of $\nu_\alpha\nu_\beta - \frac{1}{3}\delta_{\alpha\beta}$ be equal to $S_{\alpha\beta}$ [see Eq. (1.1)]:

$$S_{\alpha\beta} = \int d\mathbf{v}(\nu_\alpha\nu_\beta - \tfrac{1}{3}\delta_{\alpha\beta})f(\mathbf{v}). \tag{2.14}$$

In the case of a uniaxial liquid crystal this equation can be simplified. Taking the preferred direction to be the z axis, and defining θ to be the angle between $\mathbf{v}$ and z, the zz component of Eq. (2.14) can be written

$$S = 2\pi C \int_0^\pi (\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}) \exp[-V(\theta, S)/kT] \sin\theta \, d\theta, \tag{2.15}$$

where, according to Eq. (2.10)

$$V(\theta, S) = -A_0 S(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}) \tag{2.16}$$

and C may now be written

$$C^{-1} = 2\pi \int_0^\pi \exp[-V(\theta, S)/kT] \sin\theta \, d\theta. \tag{2.17}$$

The other components of Eq. (2.14) vanish or give no new information.

It is readily seen that one solution of Eqs. (2.15) and (2.17) is $S = 0$, which corresponds to the isotropic phase. Nontrivial solutions can also be found. After an integration by parts, and with Eq. (2.17) substituted, Eq. (2.15) can be written

$$S = \tfrac{3}{4}[\exp(x^2)/xD(x) - 1/x^2] - \tfrac{1}{2}, \tag{2.18}$$

where $x = (\tfrac{3}{2}A_0 S/kT)^{1/2}$ and D is Dawson's integral (Abramowitz and Stegun, 1964, p. 319)

$$D(x) = \int_0^x \exp(y^2) \, dy. \tag{2.19}$$

For each value of x Eq. (2.18) determines a corresponding value of S and T. The resulting relationship between S and T is shown in Fig. 4.

We see from this figure that for a range of temperature there are three possible solutions to Eq. (2.15). The solution which will actually obtain is that which gives the lowest free energy per particle, which may be calculated as

$$F(T, S) = -\tfrac{1}{2}A_0 S^2 + kT \ln C/4\pi. \tag{2.20}$$

It should be noted that Eq. (2.15) is the derivative with respect to S at fixed T of the free energy, so that the solutions to Eq. (2.15) are automatically extrema of F. The free energy as a function of temperature is also shown in Fig. 4. The Maier–Saupe theory predicts a first-order phase transition at a temperature T_c defined by

$$k_B T_c = 0.220 A_0; \tag{2.21}$$

the value of the order parameter at the transition is

$$S_c = 0.43, \tag{2.22}$$

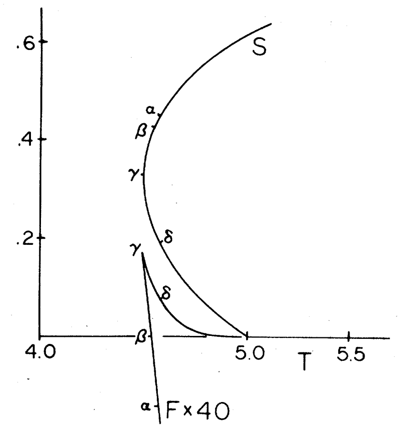

FIG. 4. Maier–Saupe theory: dependence of free energy F and order parameter S on temperature. Along the horizontal axis the parameter A_0/kT is plotted. Corresponding points are indicated by Greek letters; the phase transition occurs at β where $A_0/kT_c = 4.55$; the phases γ and δ are unstable.

independent of A_0.

In reality the nematic–isotropic phase transition occurs at constant pressure, and there is a small discontinuous change in density at T_c. The location of the phase transition is then determined by the equality of the Gibbs free energy per particle of the nematic and isotropic phases. When this density change is taken into account S_c and A_0/kT_c are no longer constants at T_c but vary weakly in the pressure (or density).

To summarize, the Maier–Saupe theory is based on three assumptions:

(a) an attractive, orientation-dependent van der Waals interaction between molecules,

(b) the configuration of the centers of mass is not affected by the orientational-dependent interaction,

(c) the mean field approximation.

The interaction in the Maier–Saupe model has been criticized by Kaplan and Drauglis (1971). They pointed out that the van der Waals interaction leads to a value of the constant A_0 which is too small to explain the observed values of T_c. The experimental measurements of the order parameter in PAA by McColl and Shih (1972a, b) also indicate that short-range repulsive forces are important. A number of authors have considered the effects of attractive and repulsive forces on the ordering in liquid crystals (Alben, 1971; Wulf, 1971; Deloche, Cabane, and Jerome, 1971). The Maier–Saupe theory is thus best viewed as a semiphenomenological model based on the mean field Hamiltonian (2.10). The parameter A_0 is to be regarded as containing the contributions from both attractive and repulsive intermolecular forces with quadrupole symmetry. A generalization of the Maier–Saupe model to include forces of other symmetry has been given by Freiser (1971) and Chandrasekhar and Madhusudana (1970).

The free energy [Eq. (2.20)] can be expanded in powers of S and put into Landau form with the identifications

$$A = \frac{3}{2}\frac{A_0}{T}\left(T - \frac{A_0}{5k_B}\right)$$

$$B = \frac{9}{70}\frac{A_0{}^3}{(k_BT)^2}$$

$$C = \frac{9}{700}\frac{A_0{}^4}{(k_BT)^3}. \tag{2.23}$$

In the isotropic phase, where S is small (even in the presence of perturbations), the expansion is accurate: Landau theory and Maier–Saupe theory give identical predictions for the isotropic phase.

C. Onsager theory

We consider a collection of orientable particles interacting pairwise through some potential $V(\mathbf{r}, \mathbf{m}; \mathbf{s}, \mathbf{n})$ which depends on both position $(\mathbf{r}, \mathbf{s})$ and orientation $(\mathbf{m}, \mathbf{n})$. Onsager (1949) has shown how the Mayer cluster theory (1958) may be used to give an expansion for the equation of state of this system. The terms of this series also depend on the orientation distribution function f, which gives the fraction of molecules per unit solid angle having various orientations. Onsager's expression for the Helmholtz free energy per particle is (for number density ρ)

$$\begin{aligned} F/kT = {} & \int f(\mathbf{n}) \ln f(\mathbf{n})\, d\mathbf{n} + \ln\rho \\ & + \tfrac{1}{2}\rho \int f(\mathbf{m}) f(\mathbf{n}) B(\mathbf{m},\mathbf{n})\, d\mathbf{m}\, d\mathbf{n} \\ & + \tfrac{1}{3}\rho^2 \int f(\mathbf{l}) f(\mathbf{m}) f(\mathbf{n}) C(\mathbf{l},\mathbf{m},\mathbf{n})\, d\mathbf{l}\, d\mathbf{m}\, d\mathbf{n} - \cdots . \end{aligned} \tag{2.24}$$

The coefficients $B(\mathbf{m}, \mathbf{n})$ and $C(\mathbf{l}, \mathbf{m}, \mathbf{n})$ are called second and third virial coefficients, respectively. They may be calculated from $V(\mathbf{r}, \mathbf{m}; \mathbf{s}, \mathbf{n})$ as

$$B(\mathbf{m},\mathbf{n}) = -\int \Phi(\mathbf{r},\mathbf{m};\mathbf{s},\mathbf{n})\, d\mathbf{r} \tag{2.25}$$

$$\begin{aligned} C(\mathbf{l},\mathbf{m},\mathbf{n}) = {} & -\int \Phi(\mathbf{r},\mathbf{l};\mathbf{s},\mathbf{m})\Phi(\mathbf{r},\mathbf{l};\mathbf{t},\mathbf{n}) \\ & \times \Phi(\mathbf{s},\mathbf{m};\mathbf{t},\mathbf{n})\, d\mathbf{r}\, d\mathbf{s}, \end{aligned} \tag{2.26}$$

where $\Phi = \exp(-V/kT) - 1$. For the particular case of hard-wall interactions, $B(\mathbf{m}, \mathbf{n})$ is just the volume which a particle of orientation $\mathbf{m}$ may not enter due to the presence of another particle of orientation $\mathbf{n}$. In the particular case of cylindrical rods with spherical caps,

$$B(\gamma) = 2\pi LD^2 + \tfrac{4}{3}\pi D^3 + 2L^2D\,|\sin\gamma|, \tag{2.27}$$

where γ is the angle between $\mathbf{m}$ and $\mathbf{n}$, and L and D are the length and diameter of the rods (Onsager, 1949).

Onsager neglected the third and higher virial terms on the basis of estimates of their magnitude near the transition density. Numerical calculations for a model indicate that the ratio of the contribution of the third virial term to that of the second is approximately $10D/L$ near the phase transition (Straley, 1973c). Thus the expansion (2.24) is rapidly convergent for very long rods, so that the Onsager theory may lay claim to a sort of exactitude; however, there are few liquid crystals for which the condition $L/D > 10$ can be said to hold,[3] and thus few systems to which the Onsager theory can be literally applied.

The equilibrium form of f can now be determined as that form which minimizes the free energy subject to the normalization condition

$$\int f(\mathbf{n})\, d\mathbf{n} = 1 \tag{2.28}$$

implicit in the definition of f. A variational derivative of Eq. (2.24) (with the third virial term discarded) leads to the integral equation

$$f(\mathbf{n}) = C \exp\left[-\rho \int B(\mathbf{n},\mathbf{m}) f(\mathbf{m})\, d\mathbf{m}\right], \tag{2.29}$$

where C is a constant to be determined by normalization. Comparison of this equation with Eq. (2.12) shows that we are dealing with a form of molecular field theory, with the difference that the configurational average energy of orientation in Eq. (2.12) has been replaced by an orientation-dependent configurational entropy. The second virial coefficient will be temperature-dependent for a general interaction [through Eq. (2.25)]; however, for a hard-wall interaction B is independent of temperature, and the phase transition will be brought about by changing the density ρ.

The integral (2.29) can be solved numerically for any form of the second virial coefficient which can be expanded in Legendre polynomials (Lasher, 1970). The procedure is to expand f (or its logarithm) in a series by some iteration technique. The solutions are qualitatively similar to those of the Maier–Saupe equation. The principal remaining difference is that the Maier–Saupe theory is commonly applied to liquids, which are only slightly compressible, whereas the Onsager expansion is most appropriately applied to dilute suspensions of particles for which the change in free energy with density is relatively small. Therefore the Onsager theory predicts large changes in density at the transition, as is appropriate to such systems.

Other approaches to the orientable rod gas have been given by di Marzio (1961), Isihara (1951), Cotter and Martire (1971), Lasher (1970), and Alben (1971). Straley (1973b) has compared these theories and showed how they apply to poly(γ-benzyl-L-glutamate), with the conclusion that for sufficiently long rods most theories are equivalent to that of Onsager and in rough agreement with experiment, and that for shorter rods no theory seems to have a very good claim to accuracy. A molecular description of nematics has also been discussed by Lubensky (1970).

III. CURVATURE ELASTICITY THEORY

A. Curvature strains

In a given microscopic region of a liquid crystal there is a definite preferred axis along which the molecules orient themselves. Even in equilibrium the direction of this axis can vary from place to place, and it can be forced to vary by the action of external forces and boundary conditions. We will refer to the deformation of relative orientations

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[3] For PAA or MBBA, $L/D \sim 4$. Only suspensions of polymers (such as poly-γ-benzyl-L-glutamate) meet the condition.

away from the equilibrium position as curvature strains; and the restoring forces which arise to oppose these deformations we will call curvature stresses or torques. If these changes in molecular orientation vary slowly in space relative to the molecular distance scale, we will be able to describe the response of the liquid crystal with a version of continuum elastic theory. This theory of curvature in liquid crystals was originated by Zocher (1933), Oseen (1933), and Frank (1958).

We will assume a variant of Hooke's law, in which the curvature stresses are proportional to the curvature strains when these are sufficiently small; or, equivalently, that the free energy density is a quadratic function of the curvature strains in which the analog of elastic moduli appear as coefficients.

Oseen (1933) based his arguments on the assumption that the energy of the liquid crystal can be written as the sum of pairwise interactions of molecules. This pair interaction depends on the relative orientations of the two molecules. This is similar to the way in which Cauchy first considered the elastic theory of solids. It is well known that the Cauchy theory contains fewer independent elastic constants than the most general form for the elastic energy of a solid. Therefore we will follow Frank (1958) in basing the theory of the curvature elastic energy on the symmetry properties of the liquid crystal alone.

We consider a uniaxial liquid crystal and let $\mathbf{n}(\mathbf{r})$ be a unit vector giving the direction of the preferred orientation at the point $\mathbf{r}$. In most liquid crystals the sign of this vector has no physical significance, as the two ends of the molecules do not differ in an important way. For molecules with permanent dipole moments this may not be the case, and the sign of $\mathbf{n}$ becomes important. However, once $\mathbf{n}$ is defined at some point we assume it varies slowly from point to point, and thus it is defined by continuity at other points in the region. In multiply connected regions it may be necessary to introduce mathematical surfaces of discontinuity where $\mathbf{n}$ changes in sign, but there is no physical discontinuity, at least for nonpolar molecules. At $\mathbf{r}$ we introduce a local right-handed Cartesian coordinate system x, y, z with z parallel to $\mathbf{n}$. The x and y axes may be chosen arbitrarily because the liquid crystal is uniaxial. Referred to this coordinate system, the six components of curvature at this point are defined by (see Fig. 5)

$$\begin{aligned} &\text{splay} \quad & s_1 &= \partial n_x/\partial x, \quad & s_2 &= \partial n_y/\partial y, \\ &\text{twist} \quad & t_1 &= -\partial n_y/\partial x, \quad & t_2 &= \partial n_x/\partial y, \\ &\text{bend} \quad & b_1 &= \partial n_x/\partial z, \quad & b_2 &= \partial n_y/\partial z. \end{aligned} \tag{3.1}$$

These curvature strains can also be defined by expanding $\mathbf{n}(\mathbf{r})$ in a Taylor series in powers of x, y, z measured from the origin:

$$\begin{aligned} n_x(\mathbf{r}) &= s_1 x + t_2 y + b_1 z + O(r^2), \\ n_y(\mathbf{r}) &= -t_1 x + s_2 y + b_2 z + O(r^2), \\ n_z(\mathbf{r}) &= 1 + O(r^2). \end{aligned} \tag{3.2}$$

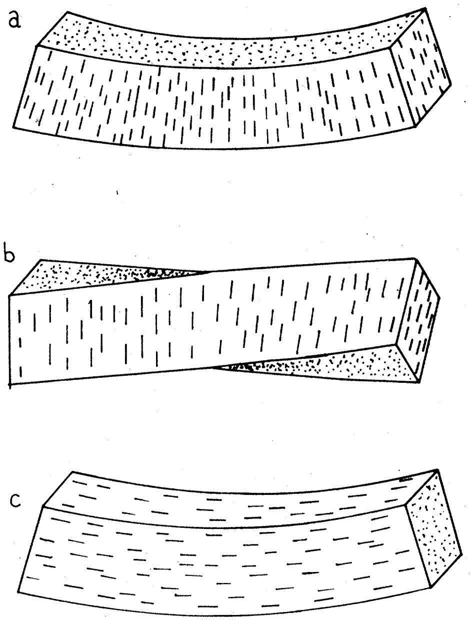

FIG. 5. The three distinct curvature strains of a liquid crystal: (a) splay, (b) twist, and (c) bend.

B. Free energy

We now postulate that the Gibbs free energy density g' of a liquid crystal, relative to its free energy density in the state of uniform orientation (which is not necessarily the equilibrium conformation), can be expanded in terms of the six curvature strains (3.1):

$$g' = \sum_{i=1}^{6} k_i a_i + \tfrac{1}{2} \sum_{i,j=1}^{6} k_{ij} a_i a_j \tag{3.3}$$

when the k_i and $k_{ij}(=k_{ji})$ are the curvature elastic constants and for convenience in notation we have put

$$a_1 = s_1, \quad a_2 = t_2, \quad a_3 = b_1, \quad a_4 = -t_1, \quad a_5 = s_2, \quad a_6 = b_2. \tag{3.4}$$

Because the crystal is uniaxial, a rotation about z will make no change in the physical description of the substance, and consequently the free energy density g' should be invariant under such rotations. By consideration of a few special cases (such as rotations of $\frac{1}{2}\pi$ and $\frac{1}{4}\pi$ about z), it is readily shown that there are only two independent moduli k_i, and that of the thirty-six k_{ij}, only five are independent. The general expression for the free energy density, written in terms of a set of eight independent moduli, becomes (Frank, 1958)

$$\begin{aligned} g' = {} & k_1(s_1+s_2) + k_2(t_1+t_2) + \tfrac{1}{2}k_{11}(s_1+s_2)^2 \\ & + \tfrac{1}{2}k_{22}(t_1+t_2)^2 + \tfrac{1}{2}k_{33}(b_1^2+b_2^2) \\ & + k_{12}(s_1+s_2)(t_1+t_2) - (k_{22}+k_{24})(s_1 s_2 + t_1 t_2). \end{aligned} \tag{3.5}$$

The last term can be written

$$s_1s_2 + t_1t_2 = \frac{\partial n_x}{\partial x}\frac{\partial n_y}{\partial y} - \frac{\partial n_y}{\partial x}\frac{\partial n_x}{\partial y}$$

$$= \frac{\partial}{\partial x}\left(n_x\frac{\partial n_y}{\partial y}\right) - \frac{\partial}{\partial y}\left(n_x\frac{\partial n_y}{\partial x}\right) \tag{3.6}$$

and consequently it will contribute only to surface energies (Ericksen, 1962a). Thus we can omit the last term in considerations involving the properties of the bulk liquid crystal. This term can only affect the boundary conditions and will be dropped henceforth.

In the presence of further symmetries g' can have still simpler forms.

(a) If the molecules are nonpolar or, if polar, are distributed with equal probability in the two directions, then the choice of the sign of $\mathbf{n}$ is arbitrary. We have chosen a right-handed coordinate system in which z is positive in the direction of $\mathbf{n}$. A reversal of $\mathbf{n}$ which retains the chirality of the coordinate system generates the transformation

$$\mathbf{n}\rightarrow -\mathbf{n}, \quad x\rightarrow x, \quad y\rightarrow -y, \quad z\rightarrow -z. \tag{3.7}$$

Invariance of the free energy under this transformation requires

$$k_1 = k_{12} = 0 \qquad \text{(nonpolar)}. \tag{3.8}$$

If $k_1 \neq 0$, the equilibrium state has finite splay. Since the ends of the molecules are distinguishable, they will in general carry a dipole moment. In an insulator the condition $\nabla\cdot\mathbf{n} \neq 0$ then implies $\nabla\cdot\mathbf{P} \neq 0$ (where $\mathbf{P}$ is the electric polarization), and a space charge will exist. Simple geometrical considerations show that it is not possible to have uniform splay in an extended three-dimensional volume. Simple examples of uniform radial splay are a thin spherical shell of radius $2/s_0$ or a thin cylindrical shell of radius $1/s_0$. Since such structures have large surface-to-volume ratio, it is not valid to neglect the effects of surface tension.

All known liquid crystals appear to have symmetry between $\mathbf{n}$ and $-\mathbf{n}$, even in the cases where the molecules themselves are not symmetric.

(b) The choice of a right-handed coordinate system is arbitrary unless the molecules are enantiomorphic[4] or enantiomorphically arranged. Practically, it appears that enantiomorphy does not occur unless the molecules are optically active and thus can be distinguished from their mirror images. Enantiomorphy also vanishes in racemic mixtures containing an equal number of left- and right-handed molecules. In the absence of enantiomorphism g' should be invariant under reflections in a plane containing the z axis, such as the transformation

$$x\rightarrow x, \quad y\rightarrow -y, \quad z\rightarrow z. \tag{3.9}$$

This introduces the constraints

$$k_2 = k_{12} = 0 \qquad \text{(mirror symmetry)}. \tag{3.10}$$

In summary, Eq. (3.5) gives the most general dependence of the free energy on the curvature strains in a uniaxial liquid crystal. Further, k_1 vanishes in the absence of polarity, k_2 in the absence of enantiomorphy, and k_{12} vanishes unless both polarity and enantiomorphy occur together.

It is conventional to define

$$s_0 = -k_1/k_{11} \qquad t_0 = -k_2/k_{22} \tag{3.11}$$

and to add constants to g'

$$\begin{aligned} g &= g' + \tfrac{1}{2}k_{11}s_0^2 + \tfrac{1}{2}k_{22}t_0^2 \\ &= \tfrac{1}{2}k_{11}(s_1+s_2-s_0)^2 + \tfrac{1}{2}k_{22}(t_1+t_2-t_0)^2 \\ &\quad + \tfrac{1}{2}k_{12}(b_1^2+b_2^2) + k_{12}(s_1+s_2)(t_1+t_2) \end{aligned} \tag{3.12}$$

so that it is now evident that s_0 and t_0 are the splay and twist of the state which minimizes the free energy—the equilibrium state. Thus the cholesteric phase is characterized by $t_0 \neq 0$.

The free energy density can be written in a vector notation. We note that

$$\begin{aligned} s_1+s_2 &= \partial n_x/\partial x + \partial n_y/\partial y = \nabla\cdot\mathbf{n}, \\ -(t_1+t_2) &= \partial n_y/\partial x - \partial n_x/\partial y = \mathbf{n}\cdot(\nabla\times\mathbf{n}), \\ b_1^2+b_2^2 &= (\partial n_x/\partial z)^2 + (\partial n_y/\partial z)^2 = (\mathbf{n}\cdot\nabla\mathbf{n})^2, \\ s_1^2+s_2^2-2t_1t_2 &= \sum_{i,j}(\nabla_i n_j)(\nabla_j n_i) \end{aligned} \tag{3.13}$$

which may be substituted into Eq. (3.5) to give

$$\begin{aligned} g &= \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n}-s_0)^2 + \tfrac{1}{2}k_{22}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n}+t_0)^2 \\ &\quad + \tfrac{1}{2}k_{33}(\mathbf{n}\cdot\nabla\mathbf{n})^2 - k_{12}(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n}). \end{aligned} \tag{3.14}$$

For the purposes of qualitative calculations it is sometimes useful to consider a nonpolar, nonenantiomorphic liquid crystal whose bend, splay, and twist constants are equal. The free energy density for this theoretician's substance is just

$$g = \tfrac{1}{2}k(\nabla\cdot\mathbf{n})^2 + \tfrac{1}{2}k(\nabla\times\mathbf{n})^2 \tag{3.15}$$

which is equivalent to

$$g = \tfrac{1}{2}k\sum_{i,j}(\nabla_i n_j)(\nabla_i n_j) \tag{3.16}$$

apart from a surface term.

Curvature elastic moduli and curvature stresses also arise in solids and in principle should also be included in the elastic theory of solids. However, the elastic moduli k associated with curvatures are generally of order of magnitude 10^{-6} dyn and the energy associated with the curvature is very small compared with the energy required to elastically deform a solid.

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[4] Materials which cannot be brought into coincidence with a reflected image are enantiomorphic. They can be distinguished as right- and left-handed, and commonly exhibit optical activity.

C. Effects of magnetic and electric fields

The diamagnetic susceptibility of a liquid crystal, owing to the anisotropic form of the molecules composing it, is also anisotropic. In the uniaxial state it is a second-rank tensor with two components $\chi_{\parallel}$ and $\chi_{\perp}$, which are the susceptibilities per unit volume along and perpendicular to the axis. The susceptibility tensor thus takes the form

$$\chi_{ij} = \chi\delta_{ij} + \chi_a n_i n_j, \tag{3.17}$$

where $\chi_a = \chi_{\parallel} - \chi_{\perp}$ is the anisotropy and is generally positive. It is thus possible to exert torques on the liquid crystal by applying a field. The presence of a magnetic field H leads to an extra term in the free energy of

$$g_m = -\tfrac{1}{2}\chi H^2 - \tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2. \tag{3.18}$$

The first term usually will be omitted as it is independent of the orientation of the director. The last term gives rise to a torque on the liquid crystal—if χ_a is positive the molecules will align parallel to the field.

The dielectric susceptibility of a liquid crystal is also anisotropic and has the same form as the magnetic susceptibility. Thus, in principle, we can achieve the same effect with an electric field as with a magnetic field. In an electric field E there will be an additional free energy

$$g_e = -(1/8\pi)\epsilon E^2 - (1/8\pi)\epsilon_a(\mathbf{n}\cdot\mathbf{E})^2, \tag{3.19}$$

where ϵ_a and ϵ are the dielectric susceptibilities defined similarly to the magnetic susceptibilities. In practice the alignment of a liquid crystal by an electric field is complicated by the presence of conducting impurities which make it necessary to use alternating electric fields (see Sec. XVII).

D. The curvature stress tensor

The curvature elastic free energy density in the presence of a magnetic field can be written

$$\begin{aligned} g(n_i, n_{i,j}) = {} & \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n} - s_0)^2 + \tfrac{1}{2}k_{22}(\mathbf{n}\cdot\operatorname{curl}\mathbf{n} + t_0)^2 \\ & + \tfrac{1}{2}k_{33}(\mathbf{n}\cdot\nabla\mathbf{n})^2 - k_{12}(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\operatorname{curl}\mathbf{n}) \\ & - \tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2. \end{aligned} \tag{3.20}$$

It depends on the components of the director n_i and on the curvature strains, $n_{i,j} = \partial n_i/\partial x_j$. We can define a curvature stress tensor by[5]

$$\begin{aligned} \Pi_{ij} &= -\partial g/\partial n_{i,j} \\ &= A e_{ijk} n_k - k_{33}(\mathbf{n}\cdot\nabla_i)n_j - B\delta_{ij}, \end{aligned} \tag{3.21}$$

where e_{ijk} is the completely antisymmetric tensor of rank 3, and

$$\begin{aligned} A &= k_{22}(\mathbf{n}\cdot\operatorname{curl}\mathbf{n} + t_0) - k_{12}(\nabla\cdot\mathbf{n}) \\ B &= k_{11}(\nabla\cdot\mathbf{n} - s_0) - k_{12}\mathbf{n}\cdot\operatorname{curl}\mathbf{n}. \end{aligned} \tag{3.22}$$

We can give physical interpretation to the curvature stress Π_{ij}. Consider the molecules lying in a plane whose normal is the unit vector $\boldsymbol{\nu}$. Then there is a torque acting on the molecules in a unit area tending to rotate them. If we regard the components of $\Pi_{im}\nu_m$ as a vector, the surface torque per unit area on a surface element in the fluid is

$$\mathbf{L}_s = -\mathbf{n} \times \boldsymbol{\Pi}\cdot\boldsymbol{\nu}. \tag{3.23}$$

The free energy [Eq. (3.20)] also depends on the components of the director n_i and we can define a body curvature force f_i by

$$\begin{aligned} f_i &= \partial g/\partial n_i \\ &= A e_{ijk} n_{k,j} + k_{33}(\mathbf{n}\cdot\nabla n_j)n_{j,i} - \chi_a H_i(\mathbf{n}\cdot\mathbf{H}). \end{aligned} \tag{3.24}$$

The body torque per unit volume is

$$\mathbf{L}_b = \mathbf{n} \times \mathbf{f}. \tag{3.25}$$

The equilibrium state of a liquid crystal is obtained by minimizing the total free energy

$$G = \int_V d\mathbf{r}\, g(n_i, n_{i,j}) \tag{3.26}$$

with appropriate boundary conditions and subject to the condition that the magnitude of $\mathbf{n}$ be unity. Allowing n_i to vary in Eq. (3.27), we obtain

$$\begin{aligned} \delta G &= \int_V d\mathbf{r}\left[\frac{\partial g}{\partial n_i}\,\delta n_i + \frac{\partial g}{\partial n_{i,j}}\,\delta n_{i,j}\right] \\ &= \int d\mathbf{r}\left[\frac{\partial g}{\partial n_i}\,\delta n_i - \delta n_i\frac{\partial}{\partial x_j}\frac{\partial g}{\partial n_{i,j}} + \frac{\partial}{\partial x_j}\left(\frac{\partial g}{\partial n_{i,j}}\,\delta n_i\right)\right]. \end{aligned} \tag{3.27}$$

The last term in the integrand can be transformed into a surface integral and only enters the boundary conditions. We then find the Euler–Lagrange equation

$$-(\partial/\partial x_j)(\partial g/\partial n_{i,j}) + \partial g/\partial n_i = \gamma n_i$$

or

$$\partial/\partial x_j \Pi_{ij} + f_i = \gamma n_i, \tag{3.28}$$

where γ is a Lagrange multiplier and is to be determined so that $\mathbf{n}^2 = 1$. Care must be exercised in assuming constrained solutions to Eq. (3.28) [an example of a constrained solution is $n_x = \cos\psi(\mathbf{r})$, $n_y = \sin\psi(\mathbf{r})$, $n_z = 0$, which automatically satisfies $\mathbf{n}^2 = 1$]. Equation (3.28) can be written $h_i = -\gamma n_i$ where

$$h_i = -\partial/\partial x_j \Pi_{ij} - f_i$$

and has been called a molecular field by de Gennes (1971a) in analogy with magnetism. Equation (3.28) is then equivalent to $\mathbf{h} \times \mathbf{n} = 0$. Assuming a constrained form for $\mathbf{n}$ initially and minimizing the elastic energy (3.26) does not necessarily lead to stable solutions.

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[5] We use a convention where repeated indices are to be summed over.

The curvature stress Π_{ij} as given by Eq. (3.21) is not unique because it is always possible to replace Π_{ij} by

$$\Pi_{ij} \rightarrow \Pi_{ij} + (\partial/\partial x_k)\Lambda_{ijk} \tag{3.29}$$

where Λ_{ijk} is antisymmetric in the indices j, k. This replacement leaves the equilibrium condition (3.28) unchanged. The last term of (3.5), which we have omitted, is of this kind and leads to

$$\Lambda_{ijk} = 2(\delta_{ij}n_k - \delta_{ik}n_j). \tag{3.30}$$

More general variational principles for liquid crystals than Eq. (3.27) have been given by Ericksen (1962b) and Leslie (1968a, b). They considered the case where the density could vary as well as the director and in this way obtained a hydrostatic theory of liquid crystals. However, the energies associated with compression are very much larger than those associated with orientational deformations, so that we will generally be able to regard the liquid crystal as incompressible.

Conversely, the curvature elastic energies are almost negligibly small in cases where the compressional energies are of interest. It is found, however, that the sound velocity is slightly affected by orientational order (see Sec. XII).

E. Long-range order in curvature elasticity theory

The Oseen–Frank curvature elasticity theory of liquid crystals is based on the assumption that there is long-range orientational order of the molecules in the liquid crystal. This means that the orientation of molecules at a point in the liquid will affect, through the curvature elastic energy, the orientation of molecules at points far removed from it. It is instructive to consider the simple situation of Fig. 6 where a nematic liquid crystal is confined to a spherical region of radius R_2. On the boundary of the region the director is constrained to be along the z axis. A small spherical region of radius R_1 at the center is constrained to have the director make an angle θ_0 with the z axis. The elastic energy of this structure is easily evaluated. For simplicity we consider the theoretician's liquid crystal (whose elastic constants are equal) so that the free energy density is given by Eq. (3.16):

$$g = (k/2)(\nabla_i n_j)(\nabla_i n_j). \tag{3.31}$$

In the region $r > R_1$ the director has the form

$$n_x = \sin\theta, \qquad n_z = \cos\theta \tag{3.32}$$

and substituting in Eq. (3.31)

$$g = (k/2)(\nabla\theta)^2. \tag{3.33}$$

The minimum free energy is obtained when θ satisfies Laplace's equation

$$\nabla^2\theta = 0. \tag{3.34}$$

The solution satisfying the boundary conditions of the problem is

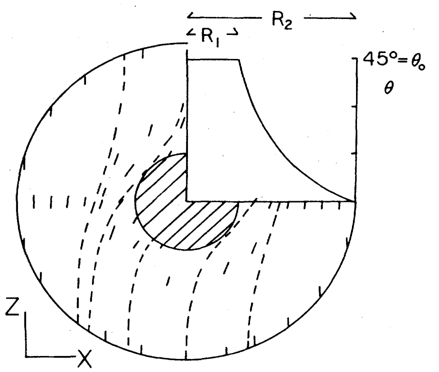

FIG. 6. A strained configuration. A liquid crystal confined between concentric spheres is constrained to have one orientation at the surface at R_2 and a different orientation at the surface at R_1. For the case $R_1 = 0.3R_2$ and $\theta_0 = 45°$, we show how the orientation varies with position, both as a graph and as a representation in cross section.

$$\theta = [R_1\theta_0/(R_2 - R_1)](R_2/r - 1). \tag{3.55}$$

The total free energy is

$$G = [2\pi k R_1 R_2/(R_2 - R_1)]\theta_0^2. \tag{3.36}$$

We see that in the limit $R_2 \rightarrow \infty$ the free energy $G = 2\pi k R_1 \theta_0^2$ is finite. Thus, however large the specimen, the boundary conditions are important and influence the orientation in the bulk of the liquid crystal: we have long-range orientational order. The older swarm theory of liquid crystals was based on the idea of strictly finite ordered regions with dimensions comparable with the wavelength of visible light. The success of the elastic theory in explaining the many phenomena discussed in the following sections leaves little doubt as to its validity.

F. Rotational symmetry

The invariance of the free energy density $g(n_i, n_{i,j})$ under rigid rotations implies an identity, originally due to Ericksen (1961), which is satisfied by the curvature stresses. This identity will be used in Sec. VI. If a liquid crystal is subject to an infinitesimal solid body rotation, the director and its derivatives transform as

$$\begin{aligned} n_i' - n_i &= \Omega_{ij}n_j \\ n_{i,j}' - n_{i,j} &= \Omega_{ik}n_{k,j} + \Omega_{jk}n_{i,k}. \end{aligned} \tag{3.37}$$

Quantities in the rotated coordinate system are denoted by a prime, and $\Omega_{xy} = -\Omega_{yx}$, etc. is the infinitesimal angle of rotation about the z axis. To first order in Ω_{ij} the variation in the free energy density is

$$g(n_i', n_{i,j}') - g(n_i, n_{i,j}) = [f_i n_j - \Pi_{ik}n_{j,k} - \Pi_{ki}n_{k,j}]\Omega_{ij}. \tag{3.38}$$

In order for this to vanish, the expression in the square bracket must be symmetric in the indices i and j (Ω_{ij} is an arbitrary antisymmetric matrix). Thus

$$f_i n_j - f_j n_i - \Pi_{ik} n_{j,k} + \Pi_{jk} n_{i,k} - \Pi_{ki} n_{k,j} + \Pi_{kj} n_{k,i} = 0 \tag{3.39}$$

which is the required identity. It may also be verified explicitly using the definitions (3.21) and (3.29).

IV. APPLICATIONS OF CURVATURE ELASTICITY THEORY

A. The nematic phase

The nematic phase lacks polarity and enantiomorphy, and thus is characterized by $s_0 = t_0 = k_{12} = 0$ in the free energy density [Eq. (3.20)]. The three nonvanishing moduli k_{11}, k_{22}, k_{33} must all be positive. The elastic free energy takes the form

$$g = \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2 + \tfrac{1}{2}k_{22}(\mathbf{n}\cdot\nabla \times \mathbf{n})^2 + \tfrac{1}{2}k_{33}(\mathbf{n}\cdot\nabla\mathbf{n})^2 - \tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2. \tag{4.1}$$

The direction of **n** in a sample is usually determined by the boundary conditions, and several techniques have been devised for the preparation of nematic monocrystals oriented by the effects of boundaries. The directors of many nematics tend to assume an orientation parallel to the direction in which an adjacent solid surface has been rubbed. Such rubbing may be done on glass with a dry cloth or a polishing material. A simple explanation of the orientation parallel to the direction of rubbing has been given (Berreman, 1972): an additional elastic energy in the nematic would occur due to distortion near the rough surface if the molecules were forced to lie against the surface with the director lying across, rather than parallel, to the grooves and ridges produced by the rubbing. If the surface is rough in both dimensions, such energy considerations explain a tendency for the molecules to align perpendicular to the surface (homeotropic condition). A perpendicular orientation of the director at a solid surface can also be obtained by coating the surface with a monolayer of material (e.g., cetyltrimethyl ammonium bromide) that is wetted by a nematic. The nematic may then be bonded in some particular orientation at the surface (Chatelain, 1954; Proust *et al.*, 1972).

Information on the elastic constants can be obtained from a number of experiments. The three most important are:

(a) observation of disclinations (Sec. V);

(b) measurement of the intensity of light scattered by the liquid crystal (Sec. VIII); and

(c) the distortion of an initially aligned structure by a magnetic field (Fredericksz transition)

Values for the elastic constants in PAA and MBBA obtained from the Fredericksz transition are given in Sec. XIX.

B. Fredericksz transition in nematics

Consider a nematic liquid crystal contained between two glass slides. The interaction between the nematic and the glass is assumed to be such that the director is constrained to lie either perpendicular or parallel to the glass at the boundaries. When a magnetic field, applied perpendicular to the director, exceeds a certain critical value, the optical properties of the system change abruptly (we assume the magnetic susceptibility anisotropy is positive in this section unless otherwise stated). The magnetic field and the boundaries both exert torques on the molecules and when the field exceeds H_c it becomes energetically favorable for the molecules in the bulk of the sample to turn in the direction of the field (see Fig. 7). This effect, first observed by Fredericksz and Zolina (1931), can be used to measure some of the elastic constants. There are several geometries in which the deformations produced by a magnetic field can be studied, of which we discuss three principal cases (Saupe, 1960b; Pieranski, Brochard, and Guyon, 1972; Rapini *et al.*, 1968). Other geometries have been considered by Dafermos (1968) and Leslie (1970a).

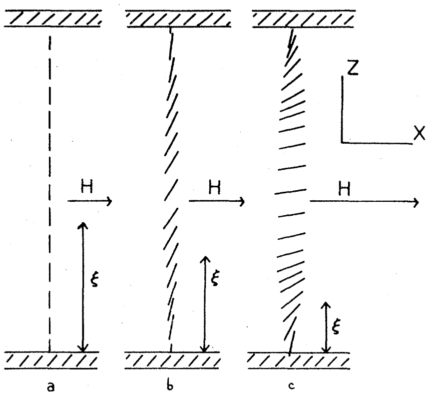

FIG. 7. Fredericksz transition, perpendicular case. The liquid crystal is constrained to be perpendicular to the boundary surfaces and a magnetic field is applied in the direction shown. (a) Below a certain critical field H_c, the alignment is not affected. (b) Slightly above H_c, deviation of the alignment sets in. Here $H = 1.07H_c$, $\theta_m = 30°$ and $\xi = 0.30d$. (c) As the field is increased further (to $1.9H_c$) the deviation increases ($\theta_m = 80°$).

1. *Perpendicular case*

In this case the director is constrained to be perpendicular to the glass surfaces. Let the z axis be perpendicular to the glass surface and the field H lie along the x direction (see Fig. 7). The director will have the form

$$n_z = \cos\theta(z), \qquad n_x = \sin\theta(z) \tag{4.2}$$

so that θ is the angle between the director and the z axis. The elastic energy per unit area g_A from Eq. (4.1) now takes the form

$$g_A = \frac{1}{2}\int_{-d/2}^{d/2} dz[(k_{11}\sin^2\theta + k_{33}\cos^2\theta)(\partial\theta/\partial z)^2 - \chi_a H^2 \sin^2\theta], \tag{4.3}$$

where d is the thickness of the sample. In the undistorted structure ($\theta = 0$) the field does not exert a torque on the molecules—they are in metastable equilibrium. We will suppose, for simplicity, that $k_{11} = k_{33} = k$ [the more general case where $k_{11} \neq k_{33}$ has been considered by Saupe (1960b) and Rapini *et al.* (1968)]. We define the length $\xi = (k/\chi_a H^2)^{1/2}$ and Eq. (4.3) becomes

$$g_A = \frac{1}{2}\frac{k}{\xi^2}\int_{-d/2}^{d/2} dz\,[\xi^2(\partial\theta/\partial z)^2 - \sin^2\theta]. \tag{4.4}$$

Minimization of the free energy leads to the differential equation

$$\xi^2(\partial^2\theta/\partial z^2) + \sin\theta\cos\theta = 0. \tag{4.5}$$

There is a trivial solution $\theta = 0$ which satisfies the boundary conditions. If the maximum distortion θ_m is small

$$\theta = \theta_m \cos(\xi^{-1}z) \tag{4.6}$$

is a good approximate solution. The boundary conditions for this solution require that $d = \xi\pi$, or, equivalently,

$$H_c = (k_{33}/\chi_a)^{1/2}(\pi/d), \tag{4.7}$$

which holds even if $k_{11} \neq k_{33}$. The distortion shown in Fig. 7b is largely "bend" with little "splay." Thus a measurement of H_c is a measurement of k_{33}, provided that χ_a is known. For fields weaker than H_c only the trivial solution exists, and there is no distortion of the nematic structure. For $k_{33} \sim 10^{-6}$ dyn, $\chi_a \sim 10^{-6}$ cgs, we find $H_c d \sim 1$ G-cm.

The general solution to Eq. (4.5) is readily found. The first integral is

$$\xi^2(d\theta/dz)^2 + \sin^2\theta = \sin^2\theta_m \tag{4.8}$$

where the constant of integration has been identified by observing that $d\theta/dz = 0$, where θ takes on its maximum value. This maximum presumably lies halfway between the glass surfaces at $z = 0$. The equation may be further integrated to give

$$\tfrac{1}{2}d - z = \xi\int_0^{\theta}\frac{d\theta'}{(\sin^2\theta_m - \sin^2\theta')^{1/2}} = \xi\csc\theta_m F(\csc\theta_m, \theta), \tag{4.9}$$

where F is the incomplete elliptic integral of the first kind, and we have used the boundary condition $\theta = 0$ at $z = \frac{1}{2}d$. The maximum distortion is found by putting $z = 0$, $\theta = \theta_m$,

$$\tfrac{1}{2}d = \xi\csc\theta_m F(\csc\theta_m, \theta_m) = \xi K(\sin\theta_m), \tag{4.10}$$

where K is the complete elliptic integral of the first kind. For fields just above H_c,

$$\theta_m \sim 2[(H/H_c) - 1]^{1/2} \tag{4.11}$$

and for large fields,

$$\sin\theta_m \sim 1 - 16\exp(-\pi H/H_c). \tag{4.12}$$

The dependence of θ_m on H is shown in Fig. 8; and Fig. 7 shows the general form of the distortion for three cases. This latter figure also makes the point that ξ can be directly interpreted as the distance which a disturbance can propagate into the liquid crystal in the presence of an ordering field. The length ξ is called the magnetic coherence length and arises in many problems involving the distortion produced by a magnetic field.

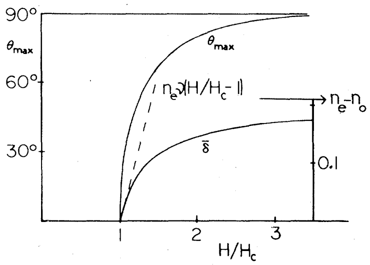

FIG. 8. Dependence of θ_m and δ on H, as given by Eqs. (4.10) and (4.15). Parameters appropriate for MBBA were chosen ($n_e = 1.75$, $n_0 = 1.54$, $\nu = 0.29$).

The distortion of the director by the field can be detected optically because there is a change in the refractive index of the material. This is the method employed by Saupe (1960b). Let the principal refractive indices of the nematic be n_0 (ordinary wave) and n_e (extraordinary wave). From Fig. 7 for a light wave polarized along z, the refractive index locally is

$$n = \frac{n_e n_0}{(n_e^2\sin^2\theta + n_0^2\cos^2\theta)^{1/2}}. \tag{4.13}$$

The average change in the refractive index is

$$\bar{\delta} = d^{-1}\int_{-d/2}^{d/2} dz(n_e - n). \tag{4.14}$$

Using Eq. (4.8), this can be put in the form

$$\begin{aligned}\frac{\bar{\delta}}{n_e} &= 1 - \frac{2\xi}{d}\int_0^{\theta_m}\frac{d\theta}{(1+\nu\sin^2\theta)^{1/2}(\sin^2\theta_m - \sin^2\theta)^{1/2}} \\ &= 1 - (2\xi/d)(1+\nu\sin^2\theta_m)^{-1/2}K\left[\left(\frac{1+\nu}{\csc^2\theta_m + \nu}\right)\right]^{1/2},\end{aligned} \tag{4.15}$$

where $\nu = (n_e^2 - n_0^2)/n_0^2$. For small deformations the change in refractive index is

$$\bar{\delta} = n_e\nu[(H - H_c)/H_c] \tag{4.16}$$

and for large fields $\bar{\delta}$ approaches $n_e - n_0$. The general behavior of $\bar{\delta}$ is also shown in Fig. 8.

An alternative method for observing the bend deformation has been used by Williams and Cladis (1972). The sample is illuminated with convergent light, and the interference figure of the uniaxial material is observed. H_c was taken to be the value of H for which the interference rings just began to be distorted.

The effects of boundary conditions on the Fredericksz transition have been discussed by Rapini and Papoular (1969). They considered both the case where the molecules make a fixed angle ϕ different from 0 or $\frac{1}{2}\pi$ with the surface and the case where the surface forces are comparable with the elastic forces, so that distortion of the alignment may take place at the surface. In both situations they find that the apparent elastic constants would be decreased.

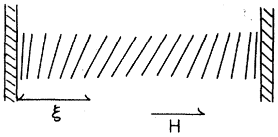

FIG. 9. Fredericksz transition, parallel case. This figure is the analog of Fig. 7b.

2. *Parallel case*

Assume instead that the molecules are constrained to be parallel to the glass at the surfaces. If a magnetic field is applied perpendicular to the surface, the structure distorts as shown in Fig. 9. This distortion is largely "splay" with only a small admixture of "bend"; the transition occurs at the field

$$H_c = (k_{11}/\chi_a)^{1/2}(\pi/d). \tag{4.17}$$

The analysis of the elastic theory with $k_{11} = k_{33}$ differs from the foregoing perpendicular case only by a rotation of axes through 90°. The change in refractive index is given by Eq. (4.15), but now refers to a wave travelling along z with polarization along x.

3. *Twist case*

A third possibility is that the field is applied in the plane of the glass, but perpendicular to the direction of the molecules which are parallel to the surface. We assume that the molecules at the surface do not twist in the direction of the field: this geometry then shows a transition to a twisted state and observation of this effect can provide information on the elastic constant k_{22}. We assume that the molecules are initially aligned along x and the field is applied in the y direction. The director has the form

$$n_x = \cos\phi(z), \qquad n_y = \sin\phi(z).$$

Substituting this form in the free energy [Eq. (4.1)], we obtain for the elastic energy per unit area

$$g_A = \tfrac{1}{2}\int_{-d/2}^{d/2} dz[k_{22}(\partial\phi/\partial z)^2 - \chi_a H^2 \sin^2\phi]. \tag{4.18}$$

This is of exactly the same form as Eq. (4.4), the only change being the substitution of k_{22} for k. Thus the critical field from Eq. (4.7) for this geometry is

$$H_c = (\pi/d)(k_{22}/\chi_a)^{1/2} \tag{4.19}$$

and observation of this effect provides information on k_{22}. This distortion can be detected optically by observing the rotation of the interference figure of a nematic (Cladis, 1972).

Twisted nematic structures can also be obtained by rotating one of the glass plates in its plane or by previously rubbing the two glass plates in different directions. These twisted structures have been discussed theoretically by Leslie (1970b). If a field is applied parallel to the twist axis, he has shown, for small values of the twist, that a critical field exists at which the molecules begin to rotate in the direction of the field. This critical field has been measured by Gerritsma *et al.* (1971) by a capacitance method (Shtrikman *et al.*, 1971). Twisted nematic and cholesteric structures have also been considered by Ericksen (1967a, 1968a, 1969a).

C. Cholesteric phase

This state is distinguished from the nematic state by the presence of enantiomorphy. The elastic free energy density takes the form in the absence of a field from Eq. (3.14)

$$g = \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2 + \tfrac{1}{2}k_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n} + t_0)^2 + \tfrac{1}{2}k_{33}(\mathbf{n}\cdot\nabla\mathbf{n})^2 \tag{4.20}$$

and the state of lowest free energy has a finite twist. There is only one structure of uniform twist: that in which $\mathbf{n}$ is constant in each of a family of parallel planes and the twist is normal to these planes (see Fig. 26). Explicitly if we choose the axis of twist to be the z axis, the cholesteric state is given by

$$n_x = \cos t_0 z, \qquad n_y = \sin t_0 z. \tag{4.21}$$

This state has the lowest free energy, $g = 0$. The pitch is given by $2\pi/t_0$, but since $\mathbf{n}$ and $-\mathbf{n}$ are indistinguishable the period of repetition is π/t_0. The pitch can be of the order of magnitude of the wavelength of visible light and is then important in the optical properties of these materials (see Sec. XVIII). It should be emphasized that the planes in which $\mathbf{n}$ is constant only exist in a geometrical sense. The molecules in the cholesteric phase do not lie in planes (in contrast with the smectic state) and the cholesteric phase is thermodynamically identical to the nematic phase.

The elastic moduli in these materials can also be studied through the effect of an applied magnetic field. We consider below the two special cases where H is perpendicular and parallel to the twist axis. The situation is simpler when the field is applied perpendicular to the twist axis—the field has the effect of unwinding the structure and there is a critical field above which the cholesteric has nematic ordering (de Gennes, 1968a; Meyer, 1968).

1. *H perpendicular to the twist axis*

In this case we can take the director in the form

$$\begin{aligned} &n_x = \cos\phi(z), \qquad n_y = \sin\phi(z), \qquad n_z = 0, \\ &H_x = H_z = 0, \qquad H_y = H. \end{aligned} \tag{4.22}$$

The elastic energy, including the magnetic energy, from Eq. (4.20) is

$$G = \tfrac{1}{2}\int_V d\mathbf{r}[k_{22}(\partial\phi/\partial z - t_0)^2 - \chi_a H^2 \sin^2\phi]. \tag{4.23}$$

The Euler–Lagrange equation which follows from minimizing G is

$$k_{22}(\partial^2\phi/\partial z^2) + \chi_a H^2 \sin\phi\cos\phi = 0 \tag{4.24}$$

which is again of the form (4.5), except that now the constant k_{22} and the characteristic length $\xi_2 = (k_{22}/\chi_a H^2)^{1/2}$

enter:

$$\xi_2^2(\partial^2\phi/\partial z^2) + \sin\phi\cos\phi = 0. \tag{4.25}$$

The first integral of this equation is

$$\xi_2^2(\partial\phi/\partial z)^2 + \sin^2\phi = 1/\kappa^2. \tag{4.26}$$

Unlike the foregoing cases, the integration constant (κ^{-2}) is greater than unity: ϕ is a periodic function in space and there is no ϕ_m. The dependence of ϕ on z is given implicitly by the integral

$$\frac{z}{\kappa\xi_2} = \int_0^{\phi} \frac{d\phi'}{(1-\kappa^2\sin^2\phi')^{1/2}}. \tag{4.27}$$

This is a definition of a Jacobian elliptic function and

$$\sin\phi = \mathrm{sn}(z/\kappa\xi_2), \qquad z = \kappa\xi_2 F(\kappa,\phi). \tag{4.28}$$

The spatial period of the structure, corresponding to a variation of ϕ by 2π, is given by

$$p = 4\kappa\xi_2 K(\kappa), \tag{4.29}$$

where $K(\kappa)$ is the complete elliptic integral of the first kind. The value of κ is determined by minimizing the free energy. The elastic energy per unit volume is

$$\begin{aligned} g &= \frac{\chi_a H^2}{2p}\int_0^p dz[\xi_2^2(\partial\phi/\partial z - t_0)^2 - \sin^2\phi] \\ &= \frac{2\chi_a H^2}{p}\int_0^{\pi/2}\frac{d\phi}{(\partial\phi/\partial z)}[\xi_2^2(\partial\phi/\partial z - t_0)^2 - \sin^2\phi]. \end{aligned} \tag{4.30}$$

Substituting from Eq. (4.26), the elastic energy density can be put in the form

$$\frac{2g}{k_{22}t_0^2} = 1 - \frac{\pi}{t_0\xi_2\kappa K(\kappa)} - \frac{1}{t_0^2\xi_2^2\kappa^2}[1 - 2E(\kappa)/K(\kappa)], \tag{4.31}$$

where E is the complete elliptic integral of the second kind. Now we calculate $\partial g/\partial\kappa$ [noting that $(\partial/\partial\kappa)(E(\kappa)/\kappa) = -K(\kappa)/\kappa^2$] and equate to zero, giving

$$E(\kappa)/\kappa = \tfrac{1}{2}\pi t_0\xi_2 \tag{4.32}$$

which determines κ as a function of ξ_2 (and hence H). Using this result, the equation for the pitch (4.29) can be written in the form

$$p/p_0 = (2/\pi)^2 K(\kappa)E(\kappa), \tag{4.33}$$

where $p_0 = 2\pi/t_0$ is the pitch in zero field. For small fields, κ is small and from Eq. (4.32) we find

$$\kappa \simeq 1/t_0\xi_2; \qquad p/p_0 = 1 + \tfrac{1}{32}(t_0\xi_2)^{-4} \tag{4.34}$$

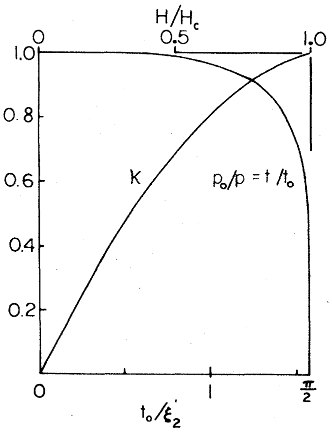

FIG. 10. Fredericksz transition in a cholesteric. As the field is increased the cholesteric unwinds and the pitch becomes infinite. The parameter κ is determined by Eq. (4.32).

and the pitch varies slowly with the fourth power of the field. There is a critical field H_c determined by [corresponding to the value $\kappa = 1$ in Eq. (4.32)]

$$1/t_0\xi_2 = \pi/2; \qquad H_c = (\pi t_0/2)(k_{22}/\chi_a)^{1/2} \tag{4.35}$$

above which the liquid crystal has nematic ordering. The measurement of this critical field can provide information on k_{22} if χ_a and t_0 are known. Typically for $k_{22} = 10^{-6}$ dyn, $\chi_a = 10^{-6}$, and $t_0 = 10^4$ cm^{-1}, we find $H_c \simeq 10^4$–10^5 G. In Fig. 10 the dependence of κ and p on field is shown. The pitch diverges logarithmically as H_c is approached:

$$\frac{p}{p_0} = \frac{4}{\pi^2}\ln\frac{4H_c}{(H_c^2 - H^2)^{1/2}}. \tag{4.36}$$

Finally from Eqs. (4.31) and (4.32) the elastic energy density can be put in the simpler form

$$g = (k_{22}t_0^2/2)[1 - 1/(t_0\xi_2\kappa)^2]. \tag{4.37}$$

The transformation from a cholesteric to a nematic structure was first observed by Wysocki *et al.* (1968) in electric fields and by Sackmann *et al.* (1967) in magnetic fields. The unwinding of the twisted structure has been confirmed by Baessler *et al.* (1969) and Kahn (1970) for electric fields and by Durand *et al.* (1969) and Meyer (1969a) for magnetic fields. Williams and Cladis (1972) have obtained k_{22}/χ_a for MBBA doped with a cholesteric from the observation of the pitch and the critical field [Eq. (4.35)].

2. *H parallel to the twist axis*

If the susceptibility anisotropy is negative, this situation is stable. For a positive anisotropy the situation can be quite complicated, and conical configurations such that

$$n_x = \sin\theta\cos\phi(z), \qquad n_y = \sin\theta\sin\phi(z), \qquad n_z = \cos\theta \tag{4.38}$$

can exist. In the absence of boundary conditions, de Gennes (1968a) and Meyer (1968) have shown that the free energy is a minimum only when $\theta = 0$ (nematic ordering parallel to H) or $\theta = \pi/2$ (cholesteric state) if $k_{33} > k_{22}$. The free energy has the value in these two cases

$$g = (k_{22}t_0^2/2)[1 - 1/(t_0\xi_2)^2], \qquad \theta = 0 \tag{4.39}$$

$$g = 0, \qquad \theta = \pi/2. \tag{4.40}$$

From these results it would appear that a discontinuous transition from the undistorted cholesteric to the nematic ordering occurs at a field

$$H_N = (k_{22}/\chi_a)^{1/2}t_0. \tag{4.41}$$

But this is below the field (4.35) so that the nematic ordered state is unstable against winding up into a cholesteric whose axis is perpendicular to the field. Even below the field (4.41) the free energy is lowered by a distortion which rotates the axis of the cholesteric to be perpendicular to the field: the free energy (4.37) is lower than (4.40).

When $k_{33} < k_{22}$ Meyer (1968) has shown that a range of fields exist for which θ and ϕ can change continuously. Solutions of this kind have also been considered by Leslie (1970b). The case where a magnetic field is applied at an angle to the twist axis has not been studied.

The $\pi/2$ rotation of the twist axis has been observed in electric fields by Kahn (1970) and Wysocki *et al.* (1969) and in magnetic fields by Rault and Cladis (1971) and Rondelez and Hulin (1972). A conical deformation has been observed in electric fields by Baessler *et al.* (1969).

Helfrich (1970a, 1971a) and Hurault (1973) have discussed a periodic, one-dimensional deformation of a cholesteric: above a field H_H, a periodic bending of the cholesteric planes with a wavelength λ is nucleated. The field H_H and λ are (Hurault, 1973)

$$H_H^2 = (6k_{22}k_{33})^{1/2}/\chi_a d, \qquad \lambda^2 = 3\pi(k_{33}/k_{22})^{1/2}(d/t_0), \tag{4.42}$$

where d is the thickness of the specimen. Thus if $dt_0 \gg 1$ the field H_H is much less than (4.41) and $\lambda t_0 \gg 1$. This deformation has been observed by Rondelez and Hulin (1972). Two-dimensional periodic deformations of a cholesteric have been observed in electric fields by Gerritsma and van Zanten (1971) and in magnetic fields by Scheffer (1972a).

D. Curvature piezoelectric effects

The symmetry of all known nematic and cholesteric liquid crystals is not compatible with ferroelectricity, and splay and polarization cannot appear spontaneously. It has been pointed out by Meyer (1969b) that it is possible to induce splay and polarization in a liquid crystal by mechanical stress or by the application of an electric field. The effects will be largest in liquid crystals whose molecules possess a large permanent dipole moment and whose shape reflects the presence of the dipole moment. Examples considered by Meyer are wedge-shaped molecules with a permanent dipole moment along the length of the molecule, and crescent-shaped molecules with the permanent dipole moment perpendicular to the long axis of the molecule. It would be expected that in the first case a splayed structure would also show polarization, and that in the second case a bent structure would show polarization.

A formal theory of these piezoelectric effects has been given by Meyer. They arise out of terms in the free energy which are bilinear in the electric field E and the curvature strains. Thus the piezoelectric part of the free energy density has the form

$$g_p = -\sum_{i,j,k} e_{ijk}(\partial n_i/\partial x_j)E_k, \tag{4.43}$$

where the e_{ijk} are the piezoelectric coefficients. The free energy must again be invariant under the symmetry operations of rotations about the director and change of sign of the director. These are sufficient to reduce e_{ijk} to just two independent coefficients; imposition of mirror symmetry produces no further relations, so that the piezoelectric effects are the same in nematic and cholesteric liquid crystals.

Written in vector form the piezoelectric part of the free energy density is

$$g_p = -e_{1z}(\boldsymbol{\nabla}\cdot\mathbf{n})\mathbf{n}\cdot\mathbf{E} - e_{3x}(\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{n})\cdot\mathbf{E}, \tag{4.44}$$

where the coefficient e_{1z} describes the interaction between splay and polarization, and e_{3x} is the interaction between bend and polarization. Either sign of the piezoelectric coefficients is possible. The electric displacement (for zero field) is given by

$$\begin{aligned}\mathbf{D} &= -4\pi(\partial g_p/\partial\mathbf{E})\\ &= 4\pi e_{1z}(\boldsymbol{\nabla}\cdot\mathbf{n})\mathbf{n} + 4\pi e_{3x}(\mathbf{n}\cdot\boldsymbol{\nabla}\mathbf{n}),\end{aligned} \tag{4.45}$$

which shows how splay and bend can induce a polarization in the liquid crystal. The sign convention on the coefficients is as follows: if they are positive, in the case of a splay locally the director seems to radiate from (or towards) a point, and the induced field is directed away from that point; in the case of a bend the director is locally tangent to a circle, and the induced field points towards the center of the circle. For a given spatially varying director $\boldsymbol{\nabla}\cdot\mathbf{D}$ is generally not zero so that the strained liquid crystal has a space charge.

The origin of the piezoelectric effects in liquid crystals is different from that occurring in solids. The strains in liquid crystals are curvature strains, whereas in a solid tensile and shearing strains are involved. Thus in a solid with a center of symmetry no piezoelectric effects can appear, while a liquid crystal with a center of symmetry (as assumed here) can be piezoelectric.

A simple geometry in which the piezoelectric effects can become manifest is that in which the liquid crystal is contained between two coaxial cylindrical electrodes. We suppose that the orientation of the molecules is determined by the boundary conditions at the electrodes. If the boundary condition is such that $\mathbf{n}$ is constrained to be perpendicular to the electrode surfaces, we have a situation in which there is pure splay. From Eq. (4.45) the electric displacement in the case of no applied field is

$$\mathbf{D} = 4\pi e_{1z}(\mathbf{r}/r^2). \tag{4.46}$$

In the other case where the molecules are constrained to lie parallel to the surface of the electrodes, we have a case of pure bend and from Eq. (4.45)

$$\mathbf{D} = -4\pi e_{3x}(\mathbf{r}/r^2). \tag{4.47}$$

In these geometries $\nabla \cdot \mathbf{D} = 0$ so that the polarization produces a surface charge only. Meyer has estimated that the surface charge is of order 10^7 electrons/cm (10^{-3} stat C/cm) length of the cylinder. This is rather small and has not been observed. Conducting impurities would easily mask this effect.

An alternative method for observing piezoelectric effects in a liquid crystal has been suggested by Helfrich (1971b). He considered a nematic confined between two glass plates separated by a distance d. The molecules are assumed to lie perpendicular to the glass. An electric field is applied parallel to the glass and the dielectric anisotropy ϵ_a is assumed to be negative so that the molecular alignment is dielectrically stable in the presence of the field. The geometry is the same as that in Fig. 7a. If piezoelectric effects are present Helfrich has shown that the structure will distort. Thus the free energy density according to Eq. (4.3) (with $k_{11} = k_{33}$ and $H = 0$) and Eq. (4.44) (with $e_{1z} = -e_{3x}$) is

$$g = \tfrac{1}{2}k(\partial\theta/\partial z)^2 - e_{3x}E(\partial\theta/\partial z), \tag{4.48}$$

where θ is the angle that the director makes with the z axis. Dielectric terms have been neglected as they may be shown to be small for thin films. In the case of perpendicular alignment as in Fig. 7a, the forces exerted on the molecules at the wall are quite weak and do not prevent a bending of the molecules at the wall. Under these circumstances the free energy is minimized by choosing

$$\partial\theta/\partial z = (e_{3x}/k)E. \tag{4.49}$$

This corresponds to a symmetrical distortion of the structure and the distortion can be detected optically as in the Fredericksz transition (Sec. IVB1). The average change in the refractive index for light propagating along z and polarized perpendicular and parallel to the field is

$$\bar{\delta} = (1/d)\int_{-d/2}^{d/2} dz(n_0 - n), \tag{4.50}$$

where n is given by Eq. (4.13). For small distortions

$$\bar{\delta} = \frac{n_0}{24}\left(\frac{n_0^2 - n_e^2}{n_e^2}\right)\left(\frac{e_{3x}E}{k}\right)^2 d^3. \tag{4.51}$$

Effects of this kind have been observed by Haas *et al.* (1970) in MBBA. The optical path difference was found to vary with the square of the voltage and no threshold was observed for the optical effects. The absence of a threshold also rules out the possibility that the observations could be due to electrohydrodynamic effects (see Sec. XVII). From the experimental values of Haas *et al.*, Helfrich has estimated that $|e_{3x}| = 7\cdot10^{-4}$ cgs. This value is in fair agreement with a theoretical estimate of e_{3x} by Helfrich (1971b).

The possibility of piezoelectric effects near disclination lines, where there are large curvatures, in bulk nematics and in droplets has been considered by Meyer (1969b) and by Dubois-Violette and Parodi (1969). Meyer has suggested that the induced space charge may serve to explain the aggregation of nematic droplets in the isotropic liquid. The piezoelectric corrections to the dielectric constant of a nematic have been considered by Derzhanski and Petrov (1971).

E. Domain walls

The stable configuration of a nematic is uniform orientation; however, there are nonuniform metastable configurations which cannot readily relax. The most important class of these are the line singularities (disclinations) to be discussed in the next section; in the presence of an orienting field, however, there is also possible a nonsingular configuration (Helfrich, 1968; de Gennes, 1971b) in which the director undergoes a 180° reversal. The phenomenology becomes even richer in the presence of orienting surfaces, as we shall show subsequently.

For the case of a uniform field in an infinite volume, it is useful to reconsider the situation discussed in Sec. IIIE: a liquid crystal constrained to have one orientation outside a sphere of radius R_2, and a differing orientation inside a concentric sphere of radius R_1 (see Fig. 6). If the angle θ_0 is increased to 180°, then a uniform magnetic field will entrain both the interior and exterior regions and prevent the configuration from untwisting. The magnetic field also affects the liquid crystal between R_1 and R_2; now rather than being distributed over the entire interval, the strain becomes restricted to a wall whose thickness is the magnetic coherence length ξ, in order to maximize the volume of liquid crystal aligned by the field.

For the case where all three elastic constants are equal, the condition for force balance is [according to Eq. (4.1)]

$$\partial^2\theta/\partial r^2 + (2/r)(\partial\theta/\partial r) + \xi^{-2}\sin\theta\cos\theta = 0, \tag{4.52}$$

where $\xi = (k/\chi_a)^{1/2}H^{-1}$; if $r \gg \xi$, the middle term may be neglected and the resulting equation can be integrated to give

$$\theta = 2\arctan\exp[(r - r_0)/\xi], \tag{4.53}$$

where r_0 determines where the wall is (arbitrary, someplace between R_1 and R_2). It is readily seen that θ takes on the values 0 and π when $|r - r_0| \gg \xi$. Thus the reorientation takes place over a short distance, especially in the limit of high fields, and the configuration may be accurately described in terms of domains of uniformly oriented material separated by reorientation walls. The walls are continuous: they may be terminated only at boundaries or by the introduction of a line singularity at the wall edge.

The nature of the reorientation varies locally. For example, in the xz plane of Fig. 6, the distortion is a mixture of splay and bend; along the y axis, the distortion is purely twist. Since the corresponding elastic constants are different, the associated wall energies (which may be regarded as "surface" tensions) differ, so that small domains will tend to have elliptical shape. These same surface tensions will cause the domains to shrink and vanish: only viscosity opposes the reorientation of the director, and hence the movement of the wall.

F. Domain walls in films

Just above the Fredericksz transition, the director is tilted slightly in the direction of the field, as shown in Figs. 7 and 9. In addition to the configurations shown ("tilted to the right"), there is also possible the mirror image ("tilted to the left"), and we can readily imagine that domains of both types can coexist, with domain walls separating them. (An experimental difficulty is that a preference for one configuration over the other will occur for non-uniform fields or fields that do not lie exactly perpendicular to the alignment of the director below the critical field.) Brochard (1972) has given the theory for this geometry.

Domain walls can occur in each of the Fredericksz geometries. The surface forces will tend to align them perpendicular to the glass slides, but their orientation is otherwise arbitrary. There are, however, the special geometries where the plane of the wall contains both **n** and **H**, which is then a pure twist wall, and a wall perpendicular to this, which is a bend-splay wall.

We will consider just the twist wall in the perpendicular geometry (Fig. 7) with the simplification $k_{11} = k_{33}$. Brochard shows that with this simplification all geometries lead to the same differential equation with the same boundary conditions, so that this is in fact a fairly general case. As before, we define θ as being the angle between the director and the z axis, but now θ depends on y as well as z and is a solution to the equation

$$\xi^2(\partial^2\theta/\partial z^2 + (k_{22}/k_{11})\partial^2\theta/\partial y^2) + \cos\theta \sin\theta = 0. \tag{4.54}$$

The boundary conditions are that θ vanishes on the planes $z = \pm\frac{1}{2}d$, and that for large y, θ approaches $\pm\theta(z)$, where $\theta(z)$ is the function found in Sec. IVA. This equation may be reduced to the case where all elastic constants are equal by rescaling the y coordinate. The equation is not particularly tractable, but Brochard observes that the function

$$\theta = \theta_\infty \cos(\pi z/d) \tanh(\beta y), \tag{4.55}$$

where $\theta^2 = 2(1 - \pi\xi^2 d^{-2})$ and $\beta = \frac{1}{2}\theta_\infty \xi^{-1}(k_{11}/k_{22})^{1/2}$, is a solution of

$$\xi^2(\partial^2\theta/\partial z^2 + (k_{22}/k_{11})\partial^2\theta/\partial y^2) + \theta - \tfrac{2}{3}\theta^3$$
$$= -\tfrac{1}{6}\theta_\infty{}^3 \cos(3\pi z/d) \tanh^3(\beta y). \tag{4.56}$$

For H only slightly larger than H_c, θ_∞ is small and the right-hand side is negligible; the left-hand side is an approximation to Eq. (4.53), again appropriate in the limit that H is only slightly larger than H_c; thus Eq. (4.54) may be regarded as an approximate solution of Eq. (4.53). We see that the width of the domain wall is $2\xi/\theta_\infty = \sqrt{2}\xi(1 - H_c{}^2/H^2)^{-1/2}$. This form has been verified experimentally by Leger (1972). For $H \gg H_c$, the surfaces affect only a thin boundary layer and the domain wall conforms to the description of the previous section.

V. DISCLINATIONS IN NEMATICS AND CHOLESTERICS

The nematic state was named for the apparent threads which can be seen in a nematic under a microscope. It was first explained by G. Friedel (1922) that these are lines on which the direction of the local preferred axis (the director) changes discontinuously. In analogy with dislocations in crystals, these line singularities have been called "disclinations" by Frank (1958). They occur in cholesteric and nematic liquid crystals. Because there is no crystal lattice in a liquid crystal, the disclinations have a line topology rather than a topology of surfaces dividing the material into domains as in a crystal. The disclination lines may have any form and generally are not constrained to be straight lines (with a few exceptions). The motion of disclination lines provides one of the mechanisms for the change of the configuration of a liquid crystal.

A disclination line L can be formed by the following operations, analogous to the Volterra process for the formation of dislocations in crystals, beginning with an unperturbed configuration (Kleman and Friedel, 1969).

(a) A cut along a surface S, limited by a line L, is made in the liquid crystal. It is assumed that the molecules are not disturbed by this cut and on the upper and lower surfaces, S_1 and S_2, of S the molecules are firmly anchored in place.

(b) The surfaces S_1 and S_2 are then rotated relative to each other about an axis $\boldsymbol{\nu}$ by an amount Ω. The symmetry of the liquid crystal requires that the rotation Ω be a multiple of π, i.e., $\Omega = m\pi$. The integer m is called the Frank index of the disclination.[6]

(c) Any empty space created by the operation (b) is filled with undistorted liquid crystal or conversely any extra material is removed. The whole structure is then allowed to relax viscously. The index m is chosen to be positive if material is removed and negative in the case that material is added.

An example of the Volterra process is shown in Fig. 14 and is discussed further after we have investigated some of the simpler types of disclination lines. Some examples of disclinations are shown in Fig. 11.

Given a single closed path through a liquid crystal, can one tell whether it encircles a disclination line just by examination of the behavior of the director along the path? The answer is that disclinations of odd index can be detected, but that no test for a disclination of even index can be given. Furthermore, the index of the odd-index disclinations cannot be resolved.

An observer travelling such a path can distinguish the preferred axis, which he can represent as a unit vector. The direction of this vector changes continuously along the path (barring the possibility that the path intersects a disclination line). After carrying the vector around the

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[6] The order of a disclination has also been defined by $S = m/2$ (Bouligand and Kleman, 1970).

path, the observer may find that the vector has returned to its original orientation, or it may have the reverse orientation. Since the sign of the director has no physical significance, this latter possibility cannot be ruled out; under these circumstances we will have to introduce a branch plane in the medium, at which the sign of the director is reversed. In this case we can definitely conclude that there must be a disclination line encircled by the path, corresponding to the edge of the branch plane.

Because the director is a vector, it is not meaningful to ask whether the director rotates through $m\pi$: the tip of the director traces out some path on the unit sphere which can always be deformed continuously into a point. Thus liquid crystals are distinct from systems with two-dimensional order parameters (such as superfluids). Although it is possible to ask whether the director rotates around the path (so that the path is knotted with the track of the tip of the director), such cases do not necessarily demonstrate the presence of disclinations; indeed, this behavior can be exhibited by some paths in a perfectly oriented nematic.

The discussion has a certain significance for the stability of disclination lines. These structures involve changes of the director over short distances, and thus large curvature strains. It would surely be energetically advantageous to eliminate the singularity and spread out the disclination into some strain pattern consistent with the boundary conditions. But as we have seen, the boundary conditions on any closed path surrounding an odd-index disclination are sufficient to require the introduction of a branch plane; the edge of the branch plane (the disclination itself) can be localized to essentially microscopic accuracy. On the other hand, the boundary conditions cannot force a disclination of even index, and Meyer (1973) has suggested that even-order disclination lines can always relax into a nonsingular strained configuration.

In nematics the rotation axis $\boldsymbol{\nu}$ (used in the Volterra construction) can be taken to be perpendicular to the preferred direction $\mathbf{n}$ of the molecules. Any rotation about an axis parallel to $\mathbf{n}$ can relax viscously back to the unperturbed configuration. Although $\boldsymbol{\nu}$ may have an arbitrary orientation relative to the disclination line, there are two special cases (the rectilinear disclinations) which are sometimes discussed:

(1) Axial disclinations. The rotation axis $\boldsymbol{\nu}$ is parallel to the disclination line (Fig. 11a, c). This type has been considered by Oseen (1933), Frank (1958), and Dzyaloshinskii (1970).

(2) Perpendicular disclinations. The rotation axis $\boldsymbol{\nu}$ is perpendicular to the disclination line (Fig. 11b, d). This type has been considered by Friedel and de Gennes (1969).

Besides these rectilinear disclinations, it is possible to have disclination lines or loops of arbitrary shape which have some of the characteristics of both the above types.

Disclination lines in cholesterics are of a richer variety. A cholesteric is essentially biaxial, since at each point in space we can define the local twist axis $\hat{\mathbf{t}}_0$ by

$$\mathbf{n}\times(\mathbf{u}\cdot\boldsymbol{\nabla})\mathbf{n} = (2\pi/p)(\mathbf{u}\cdot\hat{\mathbf{t}}_0)\hat{\mathbf{t}}_0, \qquad (5.1)$$

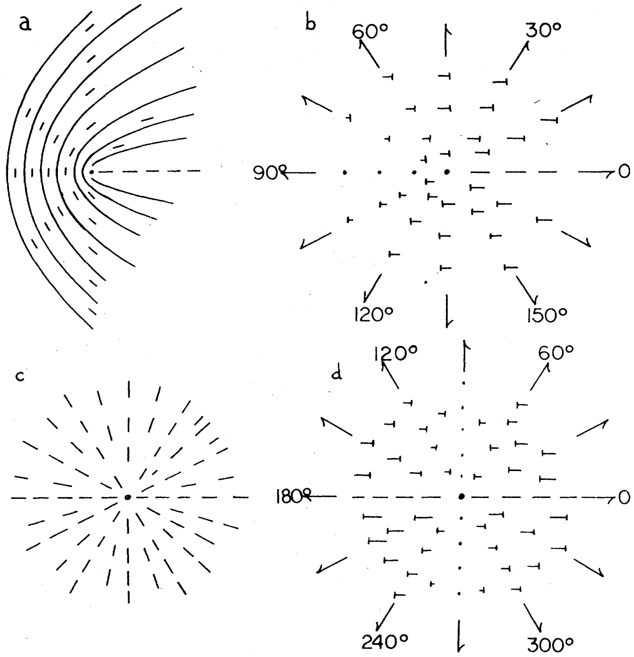

FIG. 11. Disclinations in a nematic: (a) axial disclination of index 1; (b) perpendicular disclination of index 1; (c) axial disclination of index 2; and (d) perpendicular disclination of index 2. In figures (b) and (d) the director is tilted out of the plane of the paper; this is presented by the convention that the tips of the "nails" point towards the reader, to the extent indicated by the foreshortening of the nails.

where $\mathbf{u}$ is an arbitrary vector and p is the local value of the pitch. Disclination lines in cholesterics can be singularities of the director field, the twist axis field, or both. Kleman and Friedel (1969) have given a general topological discussion of disclination lines in cholesterics. They have shown that there are essentially two types of axial disclinations in cholesterics. The first type results from a rotation (in the Volterra process) by an angle $m\pi$ about an axis parallel to the twist axis [$\chi^{(m)}$ type disclination]. The second type results from a rotation by an angle $m\pi$ about an axis perpendicular to the twist axis and parallel to the director [$\lambda^{(m)}$ type disclination] or perpendicular to the director [$\tau^{(m)}$ type disclination]. These latter types are illustrated in Fig. 12 for $m = \pm 1$.

(a) χ type disclinations. The disclination line is parallel to the twist axis and only a director field singularity occurs. These disclinations are closely similar to the axial disclinations that occur in nematics: the structure is just that of a nematic containing an axial disclination line which has been twisted about the line. This type of disclination is also equivalent to a dislocation produced by a translation: in the Volterra process the two surfaces S_1 and S_2 are translated relative to each other by the Burgers vector $b = (m/2)p$ (which is a symmetry operation of the cholesteric) (Klemand and Friedel, 1969). χ type disclinations have been discussed by Bouligand and Kleman (1970) and Rault (1971).

(b) λ and τ type disclinations. It has been shown by Kleman and Friedel (1969) that isolated λ and τ type disclination lines are necessarily rectilinear. They result from the usual Volterra process and the line is parallel to the rotation axis $\boldsymbol{\nu}$. The essential difference between the λ and τ type disclination is that the λ type disclination line is a singularity of the twist axis field but is not a singularity of the director field. The τ type disclination line is a singularity in both the twist axis and director fields. For this reason the elastic energy associated with a τ type is probably greater than that associated with a λ type.

A χ type disclination may assume any shape, but a single λ or τ must be straight. The possibility does exist that λ and τ type disclinations of opposite sign are coupled together, e.g., a λ^+ and λ^- or λ^+ and τ^-; these pairs may then take any shape. Such pairs of disclinations of opposite sign are equivalent at large distances to a multiple disclination of the χ type. Such pairs have been discussed by Kleman and Friedel (1969), Bouligand and Kleman (1970), and Cladis and Kleman (1972b).

The optical striations (Grandjean planes) observed in cholesterics in regions of variable thickness were first explained by G. Friedel (1922) as arising from a discontinuity of the molecular orientation. Observations by many authors (see Cano, 1968) have established that these striations occur when a region of m half-twists adjoins a region of $m+1$ half-twists. Jumps of two half-twists have also been observed (Orsay Group, 1969c, d). The disclination lines separating such regions have been denoted (order) 1-lines and (order) 2-lines, respectively, by the Orsay Group. The 2-lines are observed to be unstable in magnetic fields and buckle into a zigzag shape while the 1-lines are stable. The 2-lines can be explained in terms of the model of Kleman and Friedel (1969) of compensating pairs of λ and τ type disclinations. The instability in a magnetic field can be understood in terms of the different molecular configurations within the cores of the λ and τ type disclinations. The 1-lines have been explained by de Gennes (1968c) in terms of perpendicular type disclinations in cholesterics (see Sec. V.E).

Point disclinations on the surface of nematics have been discussed by de Gennes (1970b). They can be formed when a magnetic field is applied to the nematic or under suitable boundary conditions (see Sec. VD). Point disclinations at a nematic-isotropic liquid surface have been studied experimentally by Meyer (1972). The existence of point disclinations in the bulk of a nematic has been considered by Nabarro (1973). This article also contains an interesting application of Poincaré's analysis of the singularities of vector fields to nematics.

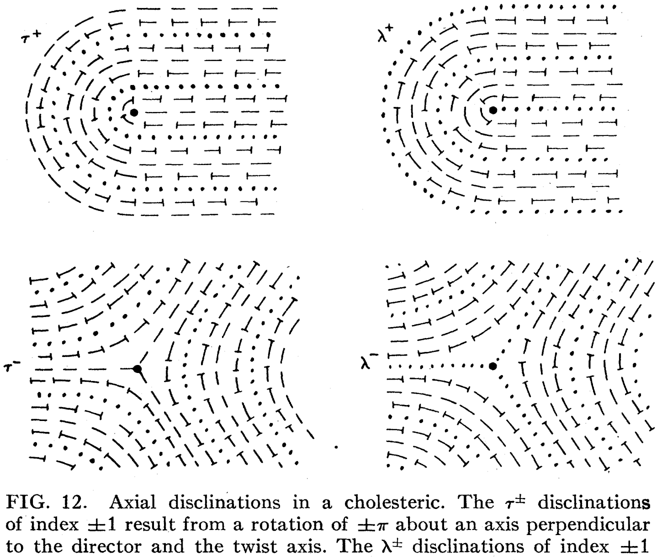

FIG. 12. Axial disclinations in a cholesteric. The $\tau^\pm$ disclinations of index ±1 result from a rotation of $\pm\pi$ about an axis perpendicular to the director and the twist axis. The $\lambda^\pm$ disclinations of index ±1 result from a rotation of $\pm\pi$ about an axis parallel to the director and perpendicular to the twist axis. The τ type disclinations are singularities in both the twist axis and director fields, and the λ type are singularities in the twist axis field.

A detailed description of the actual molecular orientation near a disclination line requires a solution of the Oseen–Frank elasticity equations of Sec. III. We now consider the solution of the elasticity equations for some of the simpler disclinations.

A. Axial disclinations

This type of disclination line was first considered by Oseen (1933), Frank (1958), and Dzyaloshinskii (1970). These disclination lines have been called axial by Friedel and de Gennes (1969) because the relative rotation of the molecules required to form the disclination line takes place about an axis parallel to the disclination. We suppose that the disclination lies along the z axis and the director $\mathbf{n}$ of the molecules then lies parallel to the x, y plane: the geometry is effectively two dimensional. The elastic energy [Eq. (4.1) with $H=0$] takes the form

$$G=\tfrac{1}{2}\int d\mathbf{r}[k_{11}(\nabla\cdot\mathbf{n})^2+k_{33}(\mathbf{n}\cdot\nabla\mathbf{n})^2]. \tag{5.2}$$

The disclinations only involve splay and bend. We will make the simplifying assumption $k_{11}=k_{33}=k$. Then letting

$$n_x=\cos\phi(x,y),\qquad n_y=\sin\phi(x,y) \tag{5.3}$$

and substituting in Eq. (5.2) we find

$$G=\tfrac{1}{2}k\int d\mathbf{r}[(\partial\phi/\partial x)^2+(\partial\phi/\partial y)^2]. \tag{5.4}$$

The elastic energy is minimized when ϕ is a solution of the two-dimensional Laplace equation

$$(\partial^2/\partial x^2+\partial^2/\partial y^2)\phi=0. \tag{5.5}$$

The constrained form (5.3) may be shown to be a solution of the Euler–Lagrange equation (3.28) in general when $k_{11}=k_{33}$. If $k_{11}\neq k_{33}$, it is only a solution if the Frank index $m=4$ or $m=2$, and in the latter case the disclination line must have cylindrical symmetry (see below) (Cladis and Kleman, 1972a; Dzyaloshinskii, 1970).

Since there are no parameters with the dimensions of length in the problem, ϕ can only depend on the azimuthal angle ψ defined by (see Fig. 13)

$$x=r\cos\psi,\qquad y=r\sin\psi. \tag{5.6}$$

The solutions of Eq. (5.5) representing disclination lines are

$$\phi=\tfrac{1}{2}m\psi+\phi_0 \tag{5.7}$$

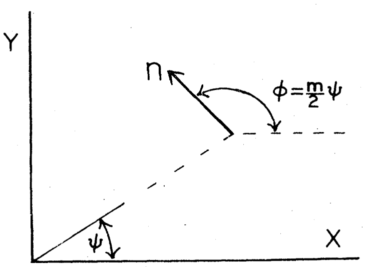

FIG. 13. Coordinate system for description of an axial disclination in a nematic. The disclination line is the z axis. The director at the point (xy) makes an angle ϕ with the x axis which is dependent only on the azimuthal angle ψ.

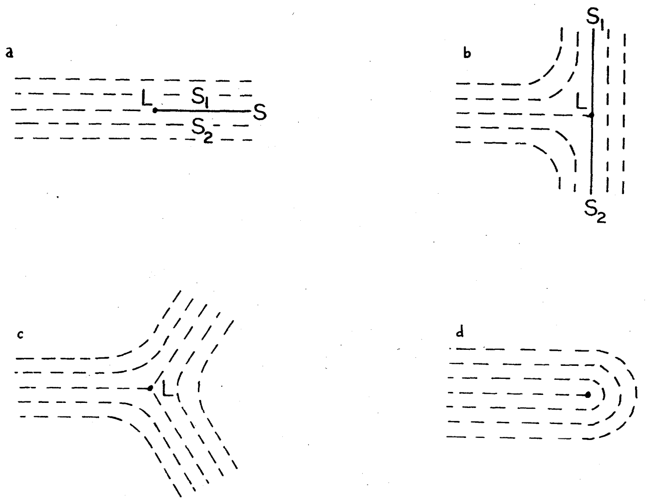

FIG. 14. Volterra process for the formation of a $m=-1$ disclination line. (a) A cut S is made terminating in the line L. (b) The two surfaces of the cut are rotated away from each other by an angle of 180°, and the void is filled with nematic material. The structure resulting is topologically equivalent to (c), which is a slightly less strained configuration. (d) A $m=+1$ disclination formed by a similar process (compare Fig. 11).

where m, the Frank index, is a positive or negative integer. As ψ varies from 0 to 2π, the angle ϕ that the director makes with the x axis varies from ϕ_0 to $\phi_0+m\pi$. ϕ_0 is a constant and in all cases except $m=2$ changing ϕ_0 merely rotates the figure.

The pattern of "flux lines," i.e., the lines which are tangent to $\mathbf{n}$, is given by the solutions of

$$dy/dx=n_y/n_x. \tag{5.8}$$

In the polar coordinates (5.6) this equation is

$$d/d\psi \ln r=\cot(\phi-\psi). \tag{5.9}$$

It follows from this equation that there exist singular flux lines which are radial and whose direction is determined by

$$\phi-\psi=\nu\pi;\qquad \psi=[2/(m-2)](\nu\pi-\phi_0),\quad m\neq 2 \tag{5.10}$$

where ν is an integer. The second result follows from Eq. (5.7). The number of such lines is $(m-2)$. In the special case $m=2$, Eq. (5.9) has the solution

$$\nu=c\exp(\psi\cot\phi_0), \tag{5.11}$$

where c is a constant. The form of the disclination now depends on ϕ_0. It has been shown by Dzyaloshinskii (1970) that if $k_{11}\neq k_{33}$ only the two solutions $\phi_0=0$, $\pi/2$ are allowed. Disclination lines with $m=1$ and $m=2(\phi_0=0)$ are shown in Fig. 11.

The elastic energy per unit length associated with a disclination, obtained by substituting Eq. (5.7) in Eq. (5.4), is

$$g_L=(\pi/4)km^2\ln R/r_0, \tag{5.12}$$

when R is the size of the sample and r_0 is a lower cutoff radius (the core size). The elastic energy increases as m^2 so that the formation of disclinations with large m is energetically unfavorable.

The nature of the core of a disclination line has been discussed by a number of authors. Fan (1971) included the order parameter S in the description of a disclination and S decreased to zero at the core (isotropic liquid core). It has been shown by Cladis and Kleman (1972a) and Meyer (1973) in the case of $m=2$ disclinations that the elastic energy is reduced if the molecules are allowed to relax out of the plane perpendicular to the disclination line. This solution has no singularity on the axis. Irregularities have been observed on disclination lines by Rault (1972a) and interpreted as arising from the tendency of molecules to lie parallel to the line in order to reduce the core energy.

The Volterra process for the formation of a disclination $(m=-1)$ is shown in Fig. 14. The two surfaces, S_1 and S_2 of the cut S, are rotated by $\pi/2$ (counterclockwise) and $-\pi/2$ (clockwise) about an axis perpendicular to the paper, respectively. The net effect is a rotation by π which is a symmetry operation of a nematic. The space formed by this deformation is then filled with nematic (Fig. 14b) and the whole structure is allowed to relax viscously (Fig. 14c). A disclination with $m=+1$ is obtained if we rotate S_1 and S_2 by $-\pi/2$ and $\pi/2$, respectively. The material is then joined along the cut S and the excess material is removed (Fig. 14d). In general the formation of a disclination of negative index requires the addition of material, and of positive index requires the removal of excess material.

The χ type disclinations in cholesterics (parallel to the twist axis) are closely similar to the above disclinations in nematics. In the case $k_{11}=k_{33}$ the solution of the elasticity equations representing a χ disclination line is obtained by superposing the cholesteric twist on the deformation due to the disclination, i.e., from Eq. (5.7)

$$\phi=\tfrac{1}{2}m\psi+t_0z+\phi_0. \tag{5.13}$$

B. Perpendicular disclinations

The perpendicular type of disclination has been discussed by de Gennes (1968c). The relative rotation of the molecules required to form this type of disclination is about an axis perpendicular to the disclination line. Assume as before that the z axis is the axis of rotation and that the disclination line lies along the y axis (see Fig. 15). The director is

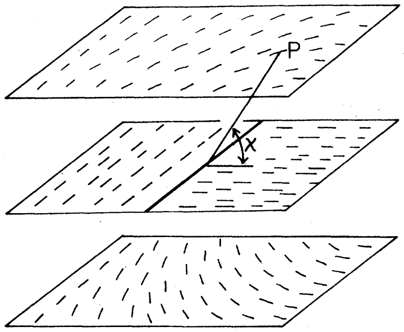

FIG. 15. The coordinate system for description of a perpendicular disclination in a nematic.

parallel to the x, y plane and is taken in the form

$$n_x = \cos\phi(x, z), \qquad n_y = \sin\phi(x, z). \tag{5.14}$$

The elastic energy [Eq. (4.1) with $H = 0$] is (for nematics)

$$G = \tfrac{1}{2} \int d\mathbf{r}[(k_{11} \sin^2\phi + k_{33} \cos^2\phi)(\partial\phi/\partial x)^2 + k_{22}(\partial\phi/\partial z)^2]. \tag{5.15}$$

The disclination in this case also involves twist. In the case $k_{11} = k_{22} = k_{33} = k$ the energy is minimized if ϕ satisfies the two-dimensional Laplace equation

$$(\partial^2/\partial x^2 + \partial^2/\partial z^2)\phi = 0. \tag{5.16}$$

The solutions representing disclinations are

$$\phi = \tfrac{1}{2}m\chi + \phi_0, \tag{5.17}$$

where m is a positive or negative integer and χ is the angle between the x axis and a line from the origin to the point x, z. In the plane $z = 0$ the configuration is simple (with $\phi_0 = 0$):

$$\begin{array}{ll} \phi = 0, & x > 0; \\ \phi = (\pi/2)(\mathrm{mod}\,\pi), & x < 0(\mathrm{m\ odd}) \\ \phi = 0(\mathrm{mod}\ \pi) & (m\ \mathrm{even}). \end{array} \tag{5.18}$$

Disclinations with $\pm m$ are obtained from each other by reflection in the x, y plane. Perpendicular disclinations are shown in Figs. 11b, 11d, and 15. The elastic energy per unit length of this type of disclination is also given by Eq. (5.12).

This type of disclination can also exist in cholesterics and is important in the interpretation of the Grandjean planes (see Sec. VE). In the case $k_{11} = k_{33}$ the solution is again obtained from the nematic case [Eq. (5.17)] by superposing the cholesteric twist. The case of a small anisotropy ($k_{11} \neq k_{33}$) has been considered by Caroli and DuBois-Violette (1969).

C. Disclination loops in nematics

The properties of disclination loops in nematics have been investigated by Friedel and de Gennes (1969). A situation in which such loops may arise is the following: a nematic is confined between parallel glass slides and the boundary conditions at the glass are that the molecules lie in the surface. The upper slide is then turned through an angle qd (d is the distance between the slides); when this angle is sufficiently large, it will be advantageous to relax the torsion by forming a disclination loop.

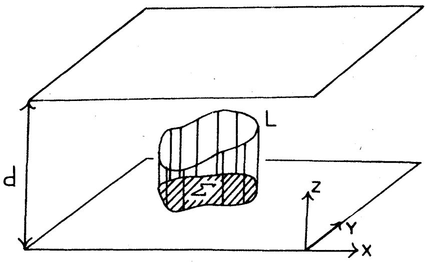

FIG. 16. A disclination loop L between glass slides a distance d apart. Σ is the area of the projection of the loop onto the xy plane

Suppose that the disclination loop is parallel to the glass slides which are parallel to the x, y plane (see Fig. 16) and that the director has the form

$$n_x = \cos\phi(x, y, z), \qquad n_y = \sin\phi(x, y, z). \tag{5.19}$$

In the case $k_{11} = k_{22} = k_{33} = k$ the elastic energy [Eq. (4.1) with $H = 0$] is minimized if ϕ satisfies the three-dimensional Laplace equation, $\nabla^2\phi = 0$, everywhere except on the loop itself (branch surfaces where ϕ changes discontinuously by $m\pi$ are also allowed). A comparable problem arises in the magnetic field of a current loop; the solution at the point $P = x, y, z$ is known to be

$$\phi(x, y, z) = (m/4)\Omega_P + qz + c, \tag{5.20}$$

where Ω_P is the solid angle subtended by the loop at P, m is the Frank index, and c is a constant. The solid angle Ω_P changes by 4π on passing through the loop and thus ϕ changes by $m\pi$. If the size of the loop is small compared with d and the loop is far removed from both surfaces, we may ignore the images of the loop which otherwise would have to be included to satisfy the boundary conditions. The second term in Eq. (5.20) is the uniform twist imposed on the nematic.

The elastic energy of the loop is

$$G_L = (k/32) \int d\mathbf{r}[m^2(\nabla\Omega_P)^2 + 8qm(\partial\Omega_P/\partial z)], \tag{5.21}$$

where the first term is the elastic energy of the strain field of the loop and the second term is the interaction between the uniform twist and the loop (the elastic energy of the uniform twist has been omitted). Using the equivalence between the disclination loop and a current loop, the elastic energy (5.21) is

$$G_L = (\pi k/8)(m^2 L_i - 8mq\Sigma), \tag{5.22}$$

where L_i is the self-inductance of the equivalent current loop and Σ is the area of the projection of the loop on the

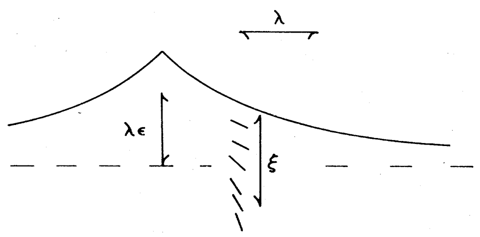

FIG. 17. A point disclination on the surface of a liquid. The liquid surface is represented by the solid line; the dashed line is the equilibrium position of the surface. The molecules lie parallel to the surface at the surface, but are perpendicular to the surface far from it. The scale of the boundary layer is the coherence length ξ. The disclination causes a dimple on the surface of the liquid, whose dimensions are characterized by the lengths λ and $\epsilon\lambda$, as shown. This figure is not to scale in the sense that the lengths ξ, λ, and $\epsilon\lambda$ are not generally of comparable size.

x, y plane. In the special case of a circular loop of radius R parallel to the x, y plane $L_i = 4\pi R \ln 8R/r_0$.

From the condition $(\partial/\partial R)G_L = 0$ we determine a critical radius $R_c = (m/4q) \ln (2/qr_0)$; loops with $R > R_c$ will tend to grow. The elastic energy required for the formation of a loop of critical radius is

$$G_L(R = R_c) = (\pi^2 k m^2/16q)(\ln 2/qr_0)^2. \tag{5.23}$$

Taking $q^{-1} = d = 1$ cm, $m = 1$, $k = 10^{-6}$ dyn, this energy is 10^{-6} ergs which is large compared with thermal energies, and spontaneous nucleation of loops in the bulk is improbable (more probable is the nucleation on surfaces). From Eq. (5.22) the elastic energy is lowered by the formation of a loop of radius R when $qR > -\ln 8R/r_0$; this determines the angle of twist for which it is energetically favorable to form a loop. This result is only approximate as we have not considered the boundary conditions. A detailed investigation of disclination loops in nematics has been made by Nehring (1973).

Disclination loops in cholesterics have been considered by Friedel and de Gennes (1969). Suppose the nematic state has been produced by applying a magnetic field exceeding the critical field H_c [Eq. (4.35)]. As the field is decreased through H_c, the aligned state becomes metastable, and it was suggested by Friedel and de Gennes (1969) that the nucleation of the cholesteric state proceeds via the formation of disclination loops.

The energy of the disclination loop (with $k_{11} = k_{22} = k_{33} = k$) is

$$G_L^{(c)} = (k/2) \int d\mathbf{r}[(\boldsymbol{\nabla}\phi)^2 - 2t_0(\partial\phi/\partial z) + 1/\xi^2 \cos^2\phi], \tag{5.24}$$

where ξ is the magnetic coherence length and the energy of the completely aligned state has been omitted. The first two terms are the elastic energy of the loop, and the third term is the magnetic energy. We estimate this latter term approximately by replacing $\cos\phi$ by unity in a region of volume $4\pi R^2\xi$. From Eq. (5.22) for a circular loop of radius R we have

$$G_L^{(c)} = \tfrac{1}{2}k\pi^2 R[\ln 8R/r_0 - 2Rt_0(1 - H/H_c)]. \tag{5.25}$$

The critical radius for stability of the loop is approximately

$$R_c = \frac{1}{4t_0}\left(\frac{H_c}{H - H_c}\right)\ln\frac{8\xi}{r_0}. \tag{5.26}$$

The energy of a loop of this radius is

$$G_L^{(c)}(R = R_c) = \frac{k\pi^2}{16t_0}\left(\frac{H_c}{H_c - H}\right)\left(\ln\frac{8\xi}{r_0}\right)^2. \tag{5.27}$$

Using $k = 10^{-6}$ dyn and $t_0 = 10^5$ cm^{-1}, this energy is 10^{-12} $(H_c/H_c - H)$ ergs; it is much larger than thermal energies and nucleation would be expected to take place only on surfaces. Observations of nucleation in cholesterics near H_c have been made by Durand *et al.* (1969).

D. Point disclinations in nematics

Consider a free surface of a nematic at which the director is free to orient itself in any direction lying in the surface (below we consider the case where the molecules lie parallel to the surface). A magnetic field is now applied perpendicular to the surface, tending to orient the molecules in this direction. De Gennes (1970b) has shown that, in the presence of these opposing forces, it is energetically favorable for the surface to distort and break up into a domain structure with a regular array of point disclinations.

A similar situation has been achieved experimentally by Meyer (1972) by arranging that the molecules align perpendicular to all other surfaces except the free surface. The boundary conditions replace the magnetic field. Isolated point singularities were observed by Meyer but no domain structure.

We assume that the undisturbed surface of the nematic is the plane $z = 0$ with the nematic occupying the half-space $z < 0$. The boundary condition is that the molecules are parallel to the field for $z \ll 0$ (see Fig. 17). The small displacement of the surface in the z direction is $\zeta(x, y)$. The elastic energy including the magnetic field energy is (with $k_{11} = k_{22} = k_{33} = k$)

$$G = \tfrac{1}{2} \int d\mathbf{r}[k \sum_{i,j} (\nabla_i n_j)^2 - \chi_a(\mathbf{n}\cdot\mathbf{H})^2]. \tag{5.28}$$

We take the director in the form

$$n_z = \cos\theta, \qquad n_\perp = \sin\theta \tag{5.29}$$

and substituting in Eq. (5.28) gives the elastic energy per unit area

$$g_A = \frac{k}{2\xi^2}\int_{-\infty}^{\zeta} dz[\xi_i(\partial\theta/\partial z)^2 + \sin^2\theta]. \tag{5.30}$$

The elastic energy associated with variations in the x, y

directions and a constant term have been omitted, and ξ is the magnetic coherence length. The elastic energy is a minimum when θ satisfies the equation

$$\xi^2(\partial^2\theta/\partial z^2) - \sin\theta \cos\theta = 0 \tag{5.31}$$

which has a first integral satisfying the boundary condition $\theta = 0$ at $z = -\infty$:

$$\xi^2(\partial\theta/\partial z)^2 - \sin^2\theta = 0. \tag{5.32}$$

At the free surface the surface tension forces require that **n** be parallel to the surface and thus, at the surface $z = \zeta$, θ takes the value $\theta_m = (\pi/2) - |\nabla\zeta|$. Substituting Eq. (5.32) in Eq. (5.30), the elastic energy per unit area is

$$\begin{aligned} g_A &= \frac{k}{\xi}\int_0^{\theta_m} d\theta \sin\theta \\ &= \frac{k}{\xi}(1 - |\nabla\zeta|). \end{aligned} \tag{5.33}$$

The first term in Eq. (5.33) is the elastic energy associated with a flat surface; we will subtract it out and measure energies relative to a flat surface. The second term depends on the form of the surface.

The equilibrium form of the surface is determined by minimizing the total surface energy

$$G_A = \tfrac{1}{2}\int dx\, dy[\sigma(\nabla\zeta)^2 - (2k/\xi)\,|\nabla\zeta| + \rho g\zeta^2], \tag{5.34}$$

where σ is the surface tension, ρ the density, and g the acceleration of gravity.

Owing to the structure of the integrand, $-\zeta$ gives a minimum free energy if $+\zeta$ does. Thus both dimples and pimples appear as possible structures. We will assume $\zeta(\rho)$ radially symmetric and positive, and $\partial\zeta/\partial\rho < 0$. Then the surface free energy is

$$G_A = \pi\sigma\int \rho d\rho[(\partial\zeta/\partial\rho)^2 + 2\epsilon(\partial\zeta/\partial\rho) + (1/\lambda^2)\zeta^2], \tag{5.35}$$

where $\lambda = (\sigma/\rho g)^{1/2}$ and $\epsilon = k/\xi\sigma$. ϵ is the angle the surface makes with the horizontal at the point singularity. Minimizing this equation with respect to variations in ζ leads to the Euler–Lagrange equation and the boundary condition

$$\begin{aligned} &\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial\zeta}{\partial\rho}\right) - \frac{1}{\lambda^2}\zeta = -\epsilon/\rho \\ &(\partial\zeta/\partial\rho)_{\rho=0} = -\epsilon. \end{aligned} \tag{5.36}$$

The solution of this equation is

$$\zeta(\rho) = \lambda\epsilon\int_0^{\pi/2} d\theta \exp[-(\rho/\lambda)\cos\theta] \tag{5.37}$$

and is shown in Fig. 17. The fluid displacement at the point singularity is $\zeta(0) = \pi\lambda\epsilon/2$ and at large distances ($\rho \gg \lambda$) $\zeta(\rho) = \epsilon\lambda^2/\rho$.

The total energy associated with a single point singularity from Eqs. (5.33) and (5.34) is approximately

$$G_p = ck\xi - \pi\sigma\epsilon^2\lambda^2 \ln R/\lambda. \tag{5.38}$$

The second term is the surface energy (5.35) and the first term is the elastic energy of the singularity assumed to extend a depth ξ in the nematic. The constant c is of order $(\pi/4)\ln(R/r_0)$ [see Eq. (5.12)], where R is the distance separating the singularities. It becomes energetically favorable to form such a singularity when the magnetic field exceeds

$$H_p = \left(\frac{k}{\chi_a}\right)^{1/2}\left[\frac{c\rho g}{2\pi k \ln(R/\lambda)}\right]^{1/3}. \tag{5.39}$$

Using $k = 10^{-6}$ dyn, $\chi_a = 10^{-6}$ cgs, $\rho = 1$ g cm^{-3}, and $\sigma = 10$ cgs, we find $H_p = 10^3$ G, $\lambda = 0.1$ cm, and $\zeta(0) = 10^{-3}$ cm.

The case of line singularities lying along the surface has been discussed by de Gennes (1970b) with the conclusion that they are less stable than the point singularities. For fields $H > H_p$ we would expect to obtain some two-dimensional lattice arrangement of point singularities. The slope of the liquid surface near a point singularity ϵ is small ($\sim 10^{-3}$) and difficult to detect. However, the neighborhood of the singularity is optically distinct from the bulk of the material in that the direction of the optical axis changes rapidly (Meyer, 1972).

E. Grandjean planes

When a cholesteric is confined between glass slides, which form a wedge of small angle, a succession of dark and light regions (Grandjean planes) is observable in polarized light. It was first suggested by G. Friedel (1922) that these planes result from discontinuities in the twisted cholesteric texture. If the molecules at the glass surfaces are constrained to lie in a particular direction parallel to the surface, then as the distance between the slides increases it becomes possible to accommodate a greater number of turns of the twisted structure (see Fig. 18).

It was suggested by de Gennes (1968c) that a perpendicular type of disclination line separates adjoining regions of m and $m + 1$ half-twists. An alternative explanation, based on compensating pairs of λ and τ type disclinations, has been suggested by Kleman and Friedel (1969). Two types of disclination lines, separating regions where the number of half-twists jumps by one and two, have been observed (Orsay Group, 1969c, d). They appear to be well accounted for by the de Gennes and Kleman–Friedel type disclinations, respectively.

Following de Gennes we analyze the situation in Fig. 18. The perpendicular disclination is along the y axis in Fig. 18, and the director is taken in the form

$$n_x = \cos[\phi(x, z) + tz], \qquad n_y = \sin[\phi(x, z) + tz]. \tag{5.40}$$

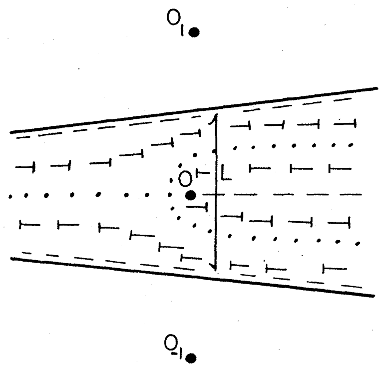

FIG. 18. Structure of a Grand-jean plane. To the left of 0 the cholesteric makes one half-twist; to the right, two half-twists. The disclination line at 0 this possible.

The boundary conditions are that the cholesteric has $m+1$ half-twists well to the right and m half-twists well to the left in Fig. 18. The equilibrium state is determined by minimizing the elastic energy

$$G=\tfrac{1}{2}k\int d\mathbf{r}[(\partial\phi/\partial x)^2+(\partial\phi/\partial z+t-t_0)^2]. \qquad (5.41)$$

This leads to the condition $t=t_0$ and the equation

$$(\partial^2/\partial x^2+\partial^2/\partial z^2)\phi=0.$$

The solutions of this equation representing disclination lines have been discussed in Sec. V.B. In the present case the disclination line has index $m=1$. The boundary conditions at $z=\pm d/2$ can be satisfied by the method of images: We suppose that a series of identical disclination lines are obtained by multiple reflection of the line at $x=z=0$ in the boundary planes $z=\pm d/2$. This leads to a series of disclination lines at $x=0$, $z=0$, $\pm d$, $\pm 2d, \ldots$. These points are denoted by 0, $0_{\pm 1}, \ldots$ in Fig. 18. The solution is thus

$$\phi=\tfrac{1}{2}\sum_n \chi_n, \qquad (5.42)$$

where χ_n is the angle between the x axis and the line from O_n to the point $x, z, y=0$. The structure is shown in Fig. 18. These disclination lines are probably responsible for the optical striations or discontinuities observed in the wedge-shaped geometry. A detailed analysis of the structure and energy of these disclinations has been given by Scheffer (1972b).

A similar phenomenon to that occurring in the wedge geometry has been observed in cholesteric drops with a free surface placed in a magnetic field (Rault, 1972b). For zero field no lines of discontinuity are observed. When the field is applied perpendicular to the pitch axis, the surface molecules are forced to align parallel to the field. Above a critical field a lattice of disclination lines forms, analogous to that observed in the Grandjean wedge geometry.

A different type of optical striped texture has been observed by Cladis and Kleman (1972b) in cholesterics with large pitch held between parallel glass slides. The distance between the stripes is approximately $p/2$. These observations were explained by assuming that the molecules lie in planes perpendicular to the glass and twist uniformly in the interior of the sample. The boundary conditions can be satisfied by including a lattice of $\chi^{(2)}$ disclinations at the surface. A more stable situation results if the $\chi^{(2)}$ disclinations split into λ and τ pairs.

VI. HYDRODYNAMIC EQUATIONS FOR NEMATIC LIQUID CRYSTALS

The anisotropy of a liquid crystal has some interesting implications for its hydrodynamic behavior. For example, a new hydrodynamic mode (not present in normal liquids) associated with fluctuations in the director occurs (in addition to shear wave and sound wave modes). There are a number of distinct geometries for Poiseuille flow of a nematic in a capillary—in fact five independent viscosity constants are required to describe the general behavior of the system. The thermal conductivity of a nematic is also anisotropic and requires two constants for its description.

Discussion of the hydrodynamics of liquid crystals proceeds on two levels. It is first necessary to derive a set of hydrodynamic equations consistent with the conservation laws. Then these equations must be solved for geometries relevant to experiment.

In the first subsection of this section we present and describe a practical set of hydrodynamic equations due to Ericksen (1959, 1961, 1966a, 1967b, 1969b) and Leslie (1966, 1968a, b). The remaining subsections present alternate derivations of such equations and discuss their domain of validity. Applications of these equations are deferred to later sections.

A. Hydrodynamics

Most disturbances in many-body systems take place and damp out in very short times. An exception to this generalization is a local variation in a quantity which is subject to a conservation law: such a perturbation can persist for a relatively long time because the conservation requirement effectively hinders its dispersal. Hydrodynamical equations describe the propagation of disturbances in the local densities and currents which correspond to conserved quantities.

This prescription has to be altered slightly in the case of liquid crystals because there is no locally conserved quantity corresponding to rotations of the director (Straley, 1971), so that a Bogoliubov inequality treatment of the dynamics cannot be given (Forster *et al.*, 1971).

We have followed the method of Ericksen and Leslie, who introduce an equation of motion for the director. The procedure is subject to challenge (Forster *et al.*, 1971) since some of the terms thus introduced are not of truly hydrodynamical character (i.e., they give finite rate constants for infinitely long wavelength disturbances). We will assure the reader, however, that within the limitations that we impose the description we give below is in agreement with the alternate descriptions.

A number of alternate descriptions of the hydrodynamics of nematic liquid crystals have been given (Stephen, 1970; Forster *et al.*, 1971; Huang, 1971; Jahnig and Schmidt, 1971; Martin *et al.*, 1972; and Lee and Eringen, 1971). All these formulations of the hydrodynamics are in essential agreement with the present formulation in the interesting case of disturbances which vary slowly on space and time, i.e., the truly hydrodynamic modes of the system. The advantages of the formulation of Forster *et al.* (1971) and Martin *et al.* (1972) are discussed in Sec. VI.H.

B. Hydrodynamic equations

The hydrodynamic equations relate the density ρ, the fluid velocity $\mathbf{v}$, the director $\mathbf{n}$, the temperature T, and their time and space derivatives. In formulating these equations, it is convenient to define the quantities

$$\dot{n}_i = (\partial/\partial t)n_i + \mathbf{v}\cdot\nabla n_i, \tag{6.1}$$

the time derivative of $\mathbf{n}$ in a frame moving with the liquid;

$$\boldsymbol{\omega} = \tfrac{1}{2}\,\mathrm{curl}\,\mathbf{v}, \tag{6.2}$$

the local angular velocity of the fluid;

$$\mathbf{N} = \dot{\mathbf{n}} - \boldsymbol{\omega}\times\mathbf{n}, \tag{6.3}$$

the rate of change of the director relative to the moving fluid;

$$\mathbf{J} = \rho\mathbf{v}, \tag{6.4}$$

the momentum density; and

$$d_{ij} = \tfrac{1}{2}(\partial v_i/\partial x_j + \partial v_j/\partial x_i), \tag{6.5}$$

which is the strain rate tensor for an *isotropic* fluid.

We will assume here that the liquid is incompressible. This is a realistic assumption since the bulk modulus of liquid crystals is so large compared with the curvature strain constants that in circumstances in which the latter are relevant, the density must be very nearly uniform. Thus the continuity equation (conservation of mass) has the form

$$\mathrm{div}\mathbf{v} = 0. \tag{6.6}$$

We shall now display a set of hydrodynamic equations. A derivation of these equations is given in Secs. VI.E–VI.G; it is shown there how the various conservation laws and symmetries to which the system is subject enforce the form given here.

The hydrodynamics of a nematic liquid crystal is determined by the equations for momentum transport[7]

$$(\partial/\partial t)J_i + (\partial/\partial x_j)T_{ij} + (\partial/\partial x_j)t_{ij} = 0 \tag{6.7}$$

and equation for the director

$$(\partial/\partial x_j)\Pi_{ij} + f_i + f_i' = \gamma n_i \tag{6.8}$$

and an equation describing entropy transport

$$(\partial/\partial t)(\rho s) + \nabla\cdot(\rho s\mathbf{v} + T^{-1}\mathbf{q}) = R, \tag{6.9}$$

where s is the entropy per unit mass. The hitherto undefined quantities which enter into these equations are:

— the part of the momentum flux tensor independent of dissipative effects

$$T_{ij} = \rho v_i v_j + P\delta_{ij} - \Pi_{kj}(\partial/\partial x_i)n_k, \tag{6.10}$$

where P is the pressure and Π_{ij} is the stress tensor (3.21);

— the part of the momentum flux tensor involving dissipative effects

$$\begin{aligned} t_{ij} = &-\alpha_1 n_k n_h d_{kh} n_i n_j - \alpha_2 n_j N_i - \alpha_3 n_i N_j - \alpha_4 d_{ij} \\ &- \alpha_5 n_i n_k d_{kj} - \alpha_6 d_{ik} n_k n_j, \end{aligned} \tag{6.11}$$

where the α_i are temperature- and pressure-dependent parameters having the dimensions of viscosity (g cm^{-1}$\cdot$sec^{-1}).

— the heat current

$$q_i = -\beta_1 n_i n_j(\partial/\partial x_j)T - \beta_2(\partial/\partial x_i)T, \tag{6.12}$$

where the β are thermal conductivity coefficients and T is the temperature;

— the entropy production $R(=ds/dt)$

$$TR = -t_{ij}d_{ij} + f_i'N_i - T^{-1}q_i(\partial T/\partial x_i); \tag{6.13}$$

— the part of the body force associated with the presence of velocity gradients

$$f_i' = (\alpha_3 - \alpha_2)N_i + (\alpha_3 + \alpha_2)d_{ij}n_j. \tag{6.14}$$

The body force f_i is defined in Eq. (3.24).

C. Some comments on these equations

Equation (6.7) relates the change in momentum density to the local forces. The conservative forces are contained in T_{ij}; they arise from gradients in kinetic energy density (the Bernoulli effect), pressure, and curvature stress density. The conservative forces are generally negligible in the examples we shall consider: the first term is of second order in the velocity, the pressure plays the role of a Lagrangian multiplier (conjugate to the incompressible fluid condition), and the third term is second order in the gradients of the director. The nonconservative (viscous) forces are contained in t_{ij}. Six different tensors of the correct symmetry can be formed from the director and the derivatives of the velocity; an Onsager relation

$$\alpha_6 = \alpha_2 + \alpha_3 + \alpha_5 \tag{6.15}$$

allows one to be eliminated (Parodi, 1970). There are a number of different conventions for expressing the viscosity

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[7] We use a Cartesian tensor notation; repeated indices are to be summed over.

TABLE I. Combination of viscosity coefficients common in the literature.

$\mu_i \equiv \alpha_i$	generally (not in this chapter)
$\gamma_1 = \alpha_3 - \alpha_2$	Leslie (1966), Parodi (1970)
$\gamma_2 = \alpha_6 - \alpha_5 = \alpha_3 + \alpha_2$	Forster *et al.* (1971)
$\eta_1 = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)$	Miesowicz (1936)
$\eta_2 = \frac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2)$	Parodi (1970), Sec. VII
$\eta_3 = \frac{1}{2}\alpha_4$	
$\nu_1 = \frac{1}{2}(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + 2\alpha_5)$	Forster *et al.* (1971)
$\nu_2 = \frac{1}{2}\alpha_4$	
$\nu_3 = \frac{1}{2}(\alpha_4 + \alpha_5 - \gamma_2\alpha_2/\gamma_1)$	
$\lambda = -\gamma_2/\gamma_1$	
$\eta_1^{(H)} = \eta_2$	Helfrich (1969a, 1970b)
$\eta_2^{(H)} = \eta_1$	
$\eta_{12}^{(H)} = \alpha_1$	
$\lambda_1 = \alpha_2 - \alpha_3 = -\gamma_1$	Atkin and Leslie (1969)
$\lambda_2 = -(\alpha_2 + \alpha_3) = -\gamma_2$	
$\tan^2\theta_0 = -\alpha_3/\alpha_2$ Sec. VII	

Typical numerical values for the viscosity coefficients are given in Sec. XIX.

coefficients (and various combinations of them) which are summarized in Table I. The origins of these definitions are explained below or elsewhere, as indicated in the table. The condition that entropy production (and all friction constants that can be measured in a real experiment) be positive restricts the possible values of the α_i as explained in Sec. VI.F.

The director equation expresses the balance of curvature stress and torques due to shear flow. We will frequently use in Eq. (6.14) $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_3 + \alpha_2$; these parameters with the dimensions of viscosity determine the relaxation time for the director, and the torque exerted on the director by a shear flow, respectively. Forster *et al.* have pointed out that γ_2 is not an independent dissipative coefficient, but that the ratio γ_2/γ_1 is a reactive coefficient which determines the response of the director to a local shear (see Sec. VI.H). The inertial terms that might be expected in an equation of motion have been deleted because the observable motions are always overdamped, so that the kinetic energy of rotation of a molecule about its center of mass of very small. In the static case and absence of gradients of the velocity field, f_i' vanishes, and Eq. (6.8) reduces to Eq. (3.28) for static equilibrium. The right-hand side of Eq. (6.8) is a Lagrange multiplier term; γ is to be determined by the condition that $\mathbf{n}$ is normalized to unity.

Equation (6.9) equates the time derivative of the local entropy density plus the transport of entropy by the flow of the liquid and thermal conductivity to the local rate of entropy production. Equation (6.12) predicts anisotropy of the thermal conductivity.

D. Reversible hydrodynamics

In the remaining subsections of this section, we shall give derivations of the equations presented in Sec. VI.B and some defense of the statements made there.

Initially we shall not consider dissipative processes. The flow is assumed reversible; entropy is conserved. We therefore write the conservation laws

$$(\partial/\partial t)\rho + \nabla\cdot\mathbf{J} = 0, \tag{6.16}$$

$$(\partial/\partial t)(\rho s) + \nabla\cdot(\rho s\mathbf{v}) = 0, \tag{6.17}$$

and

$$(\partial/\partial t)J_i + (\partial/\partial x_j)T_{ij} = 0. \tag{6.18}$$

For the purposes of this section, inertial terms will be added to Eq. (6.8) for the director so that it now reads

$$(\partial/\partial t)(I\dot{n}_i) + (\partial/\partial x_j)(\dot{n}_i v_j) + (\partial/\partial x_j)\Pi_{ij} + f_i = 0, \tag{6.19}$$

where I is the moment of inertia per unit volume: $I = \rho a^2$, where a is the typical dimension of a molecule.[8]

Equations (6.16) through (6.19) represent a complete system of hydrodynamic equations of a liquid crystal, but T_{ij} is as yet unknown. In order to determine its form we use the law of conservation of energy

$$(\partial E/\partial t) + \nabla\cdot\mathbf{Q} = 0, \tag{6.20}$$

where E is the energy per unit volume of the liquid and $\mathbf{Q}$ is the energy flux. The tensor T_{ij} should have the property that this equation is satisfied automatically. This is not in itself sufficient to determine T_{ij}, but we may further use the principle of Galilean relativity[9] in the following way. If we transform to a coordinate system moving with the fluid, i.e., with velocity $\mathbf{v}$ and angular velocity $\boldsymbol{\omega} = \frac{1}{2}\operatorname{curl}\mathbf{v}$, the only motion remaining is the rotation of the molecules relative to the moving coordinate system. The rate of change of the director relative to the moving fluid is given by $\mathbf{N}$ [Eq. (6.3)]. The Galilean relativity principle allows us to determine the dependence of all quantities (in particular the stress tensor T_{ij}, the energy E, and the energy current $\mathbf{Q}$) on the velocity $\mathbf{v}$ for a given value of $\mathbf{N}$ by use of the transformation laws for mechanical quantities from a stationary coordinate system to a moving coordinate system. Then the consistency of Eq. (6.20) with Eqs. (6.16)–(6.19) determines the remaining dependence of T_{ij} and $\mathbf{Q}$ on $\mathbf{N}$ uniquely.

We now investigate how the stress tensor T_{ij}, the energy E, and the energy current $\mathbf{Q}$ in the stationary coordinate system are related to their values in the moving coordinate system (which we denote by a subscript 0). The stress

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[8] The inertial terms are included only for convenience in the derivation of the hydrodynamic equations. These terms are negligible in all the applications to low-frequency phenomena in the following sections (see Sec. VIII). At higher frequencies the inertial terms can be important, but then Eq. (6.19), which contains a single relaxation time, would not be expected to provide an accurate description. Several relaxation processes could be important.

[9] The method was introduced by Landau (1941) and Landau and Lifshitz (1959) and has been used extensively by them to discuss the hydrodynamics of superfluids. The application to liquid crystals has been given by Stephen (1970).

tensor T_{ij} will transform as for an ordinary fluid:

$$T_{ij} = \rho v_i v_j + T_{0ij}. \tag{6.21}$$

In order to investigate how quantities like E and $\mathbf{Q}$ in Eq. (6.20) transform, we take a simple model in which the liquid is composed of dumbbell-like molecules. Each molecule consists of two masses M_1 and M_2 rigidly connected. We focus attention on one molecule where M_1 is at $\mathbf{r}_1$ and M_2 at $\mathbf{r}_2$. The center of mass $\mathbf{R}$ and the director $\mathbf{n}$ of this molecule are given by

$$\mathbf{R} = M^{-1}(M_1\mathbf{r}_1 + M_2\mathbf{r}_2), \qquad \mathbf{n} = (\mathbf{r}_1 - \mathbf{r}_2)/a, \tag{6.22}$$

where $M = M_1 + M_2$ is the total mass, and a is the length of the molecule. The energy of this molecule is

$$e = \tfrac{1}{2}M\dot{\mathbf{R}}^2 + \tfrac{1}{2}I_0\dot{\mathbf{n}}^2 + U, \tag{6.23}$$

where $I_0 = (M_1M_2/M)a^2$ is the moment of inertia and U is the potential energy. We now transform to a coordinate system moving with velocity $\mathbf{v}$ and angular velocity $\boldsymbol{\omega}$. The energy e_0 measured by an observer in this coordinate system, is

$$e_0 = \tfrac{1}{2}M(\dot{\mathbf{R}} - \mathbf{v})^2 + \tfrac{1}{2}I_0(\dot{\mathbf{n}} - \boldsymbol{\omega} \times \mathbf{n})^2 + U. \tag{6.24}$$

The kinetic energy vanishes, as it should, if the coordinate system is rigidly fixed to the molecule. In the case where $\dot{\mathbf{R}} = \mathbf{v}$ and $\boldsymbol{\omega} = \frac{1}{2}$ curl $\mathbf{v}$, e_0 is the intrinsic rotational energy of a molecule excluding that part produced by the fluid flow. From Eqs. (6.23) and (6.24) we find

$$\begin{aligned} e = {} & \tfrac{1}{2}Mv^2 + I_0(\boldsymbol{\omega} \times \mathbf{n})\cdot(\dot{\mathbf{n}} - \boldsymbol{\omega} \times \mathbf{n}) \\ & + \tfrac{1}{2}I_0(\boldsymbol{\omega} \times \mathbf{n})^2 + e_0. \end{aligned} \tag{6.25}$$

When we generalize this to the case of a fluid, the energy E per unit volume will transform as follows:

$$E = \tfrac{1}{2}\rho\mathbf{v}^2 + I(\boldsymbol{\omega} \times \mathbf{n})\cdot\mathbf{N} + \tfrac{1}{2}I(\boldsymbol{\omega} \times \mathbf{n})^2 + E_0, \tag{6.26}$$

where I is the moment of inertia/unit volume, and E_0 is to be identified with the thermodynamic internal energy which satisfies the thermodynamic identity

$$dE_0 = \mu d\rho + Td(\rho s) + f_i dn_i - \Pi_{ij} dn_{i,j} + N_i d(IN_i). \tag{6.27}$$

Here μ is the chemical potential per unit mass, and the last term of Eq. (6.27) simply expresses the fact that the relative angular velocity $\mathbf{N}$ is the derivative of the energy with respect to the relative angular momentum.

By using similar arguments we can show that the energy current Q_j is related to its value Q_{0j} in the moving coordinate system by

$$\begin{aligned} Q_j = {} & [\tfrac{1}{2}\rho\mathbf{v}^2 + I(\boldsymbol{\omega} \times \mathbf{n})\cdot\mathbf{N} + \tfrac{1}{2}I(\boldsymbol{\omega} \times \mathbf{n})^2 + E_0]v_j \\ & + v_i T_{0ij} + (\boldsymbol{\omega} \times \mathbf{n})_i \Pi_{ij} + Q_{0j}. \end{aligned} \tag{6.28}$$

The quantities T_{0ij}, E_0, and Q_{0j} in Eqs. (6.21), (6.26), and (6.28) will depend only on $\mathbf{N}$ and other thermodynamic variables, but not explicitly on $\mathbf{v}$. T_{0ij} and Q_{0j} are now determined uniquely from the consistency of Eqs. (6.16)–(6.20). The details of this calculation are similar to those of Landau (1941) and Landau and Lifshitz (1959) in the superfluid case, so we will only give the general outline. In the equation of conservation of energy (6.20), we substitute for E and Q from Eqs. (6.26) and (6.28) and calculate the time derivative of E_0 from Eq. (6.27). All the time derivatives are eliminated using Eqs. (6.16)–(6.19). The resultant equation, after some rearrangement, has the form

$$\begin{aligned} 0 = \partial E/\partial t + \nabla\cdot\mathbf{Q} = {} & (\partial/\partial x_j)(\mathbf{Q}_{0j} - N_i\Pi_{ij}) \\ & + (E_0 - \mu\rho - T\rho s - I\mathbf{N}^2)\nabla\cdot\mathbf{v} + T_{0ij}v_{i,j} \\ & + \Pi_{kj}n_{k,i}v_{i,j}. \end{aligned} \tag{6.29}$$

The terms not containing $\mathbf{v}$ and terms linear in $\mathbf{v}$ are independent. This uniquely determines T_{0ij} and Q_{0j} as

$$T_{0ij} = (-E_0 + \mu\rho + T\rho s + IN^2)\delta_{ij} - \Pi_{kj}n_{k,i} \tag{6.30}$$

$$Q_{0j} = N_i\Pi_{ij}. \tag{6.31}$$

With these definitions, the hydrodynamic Eqs. (6.14)–(6.17) and (6.20) are completely determined.

In the stationary case, when all time derivatives vanish from Eqs. (6.16) and (6.18), we have

$$(\partial/\partial x_j)T_{0ij} = 0 \tag{6.32}$$

$$(\partial/\partial x_j)\Pi_{ij} + f_i = 0. \tag{6.33}$$

From Eq. (6.27) Eq. (6.33) can be written in the form

$$(\partial/\partial x_j)(\partial E_0/\partial n_{i,j}) - (\partial E_0/\partial n_i) = 0 \tag{6.34}$$

where the derivatives with respect to n_i and $n_{i,j}$ are taken at constant density and entropy. When we impose the condition $\mathbf{n}^2 = 1$, this equation is just the Euler–Lagrange equation (3.29). We now turn to Eq. (6.32) which from (6.30) can be written

$$\begin{aligned} & \rho(\partial\mu/\partial x_i) + \rho s(\partial T/\partial x_i) - f_k n_{k,i} + \Pi_{kl}n_{k,li} \\ & \quad - (\partial/\partial x_j)(\Pi_{kj}n_{k,i}) = 0. \end{aligned} \tag{6.35}$$

Using Eq. (6.33) to eliminate f_k, this reduces to

$$\rho(\partial\mu/\partial x_i) + \rho s(\partial T/\partial x_i) = 0 \tag{6.36}$$

which is the usual condition for the hydrostatic equilibrium of an ordinary fluid, and in that case is equivalent to the pressure being constant.

E. Conservation of angular momentum

The conservation of angular momentum puts a restriction on the symmetry properties of the quantities T_{0ij},

Π_{ij}, and g_i. We define the angular momentum tensor density by

$$\rho M_{ij} = \tfrac{1}{2}\rho(x_i v_j - x_j v_i) + \tfrac{1}{2}I(n_i \dot{n}_j - n_j \dot{n}_i) \tag{6.37}$$

and it must satisfy the conservation relation

$$(\partial/\partial t)(\rho M_{ij}) + (\partial/\partial x_k)(\rho M_{ij} v_k) + \tfrac{1}{2}(\partial/\partial x_k)[(x_i T_{0jk} - x_j T_{0ik}) + (n_i \Pi_{jk} - n_j \Pi_{ik})] = 0. \tag{6.38}$$

Substituting Eq. (6.37) in (6.38) and eliminating the time derivatives by means of Eqs. (6.16) and (6.18) gives

$$T_{0ij} - T_{0ji} + \Pi_{ik} n_{j,k} - \Pi_{jk} n_{i,k} + n_i f_j - n_j f_i = 0. \tag{6.39}$$

This is a symmetry requirement that the stresses must satisfy in order that angular momentum be conserved. This equation has already been verified in Sec. III [Eq. (3.40)].

F. Irreversible hydrodynamics

In the presence of dissipative effects, the hydrodynamic equations (6.17)–(6.20) are generalized to

$$\partial J_i/\partial t + (\partial/\partial x_j)(T_{ij} + t_{ij}) = 0, \tag{6.40}$$

$$(\partial/\partial t)(\rho s) + \nabla \cdot (\rho s \mathbf{v} + \mathbf{q}/T) = R, \tag{6.41}$$

$$(\partial/\partial t)(I\dot{n}_i) + (\partial/\partial x_j)(I\dot{n}_i v_j) + (\partial/\partial x_j)(\Pi_{ij} + \pi_{ij}) + f_i + f_i' = \gamma n_i, \tag{6.42}$$

$$(\partial E/\partial t) + \nabla \cdot (\mathbf{Q} + \mathbf{Q}') = 0. \tag{6.43}$$

We shall show below that π_{ij} vanishes to the accuracy to which we are working. The inertial terms in Eq. (6.42) are only important at high frequencies which are outside the hydrodynamic regime and will be dropped in what follows. The extra fluxes and forces in Eqs. (6.40) through (6.43) are subject to the restrictions

(i) that they vanish in the steady-state condition,
(ii) that they also satisfy the symmetry property (6.39),
(iii) that the entropy production R be positive.

The quantities Q' and R are determined as before by substituting Eqs. (6.26) and (6.27) into (6.43), the time derivatives being eliminated by means of Eqs. (6.16) and (6.40)–(6.42). It is found that

$$Q_j' = q_j + v_i t_{ij} + \dot{n}_i \pi_{ij} \tag{6.44}$$

$$TR = -t_{ij} v_{i,j} - \pi_{ij} \dot{n}_{i,j} + f_i' \dot{n}_i - T^{-1} q_i T_{,i}, \tag{6.45}$$

where $v_{i,j} = \partial v_i/\partial x_j$ and $T_{,i} = \partial T/\partial x_i$. Using the symmetry property (6.39), we can write TR in a more convenient form. Thus

$$t_{ij} v_{i,j} = t_{ij} d_{ij} + t_{ij}\omega_{ij} = t_{ij} d_{ij} + \tfrac{1}{2}(t_{ij} - t_{ji})\omega_{ij}, \tag{6.46}$$

where

$$\omega_{ij} = \tfrac{1}{2}(v_{i,j} - v_{j,i}). \tag{6.47}$$

Using Eq. (6.39) to eliminate $t_{ij} - t_{ji}$ in Eq. (6.46), we find

$$t_{ij} v_{i,j} = t_{ij} d_{ij} - \pi_{ij}\omega_{ik} n_{k,j} + f_i' \omega_{ij} n_j \tag{6.48}$$

and on substituting this result in Eq. (6.45)

$$TR = -t_{ij} d_{ij} - \pi_{ij} N_{ij} + f_i' N_i - T^{-1} q_i T_{,i}, \tag{6.49}$$

where $N_{ij} = \dot{n}_{i,j} - \omega_{ik} n_{k,j}$ and is the change of the director gradient relative to the moving fluid.

1. *Nematics*

In order to develop the theory further it is necessary to have constitutive equations for the quantities t_{ij}, π_{ij}, f_i', and q_i. We first consider the case of nematic liquid crystals and make the assumption that the fluid has a center of symmetry and that $\mathbf{n}$ and $-\mathbf{n}$ are indistinguishable. Thus t_{ij} and q_i must be unaltered when $\mathbf{n}$ is replaced by $-\mathbf{n}$, and f_i' and π_{ij} must change sign. We will confine ourselves to constitutive relations which are linear in the quantities d_{ij}, N_i, and $T_{,i}$ and neglect terms involving the gradient of the director. We also note that terms like $n_i N_i$ cannot appear owing to the condition $\mathbf{n}^2 = 1$. The most general equations which meet these requirements have been given by Leslie and are

$$t_{ij} = -(\mu_1 d_{kk} + \mu_2 n_k n_p d_{kp})\delta_{ij} - (\mu_3 d_{kk} + \mu_4 n_k n_p d_{kp}) n_i n_j - \mu_5 N_i n_j - \mu_6 n_i N_j - \mu_7 d_{ij} - \mu_8 d_{ik} n_k n_j - \mu_9 n_i n_k d_{kj}, \tag{6.50}$$

$$f_i' = (\lambda_2 d_{kk} + \lambda_3 n_k n_p d_{kp}) n_i + \lambda_4 N_i + \lambda_5 d_{ij} n_j, \tag{6.51}$$

$$q_i = -\beta_1 n_i n_j T_{,j} - \beta_2 T_{,i}, \tag{6.52}$$

$$\pi_{ij} = 0. \tag{6.53}$$

The coefficients μ_i, λ_i, and β_i depend on p and T. The symmetry relation (6.39) requires that

$$\lambda_4 = \mu_6 - \mu_5; \qquad \lambda_5 = \mu_9 - \mu_8.$$

These constitutive relations are consistent with the general symmetry relations for nematics discussed in Sec. III in that they transform as vectors and tensors for rotations about the director or for reflections in a plane containing the director.

In the case of an incompressible nematic liquid crystal, we have the extra relation $d_{kk} = 0$, and the constitutive relations may be taken in the simpler form

$$t_{ij} = -\alpha_1 n_k n_p d_{kp} n_i n_j - \alpha_2 N_i n_j - \alpha_3 n_i N_j - \alpha_4 d_{ij} - \alpha_5 d_{ik} n_k n_j - \alpha_6 n_i n_k d_{kj}, \tag{6.55}$$

$$f_i' = \gamma_1 N_i + \gamma_2 d_{ij} n_j, \tag{6.56}$$

$$q_i = -\beta_1 n_i n_j T_{,j} - \beta_2 T_{,i}, \tag{6.57}$$

where the coefficients α_i, γ_i, and β_i depend on T. The symmetry relation (6.39) requires that

$$\gamma_1 = \alpha_3 - \alpha_2, \qquad \gamma_2 = \alpha_6 - \alpha_5. \tag{6.58}$$

The dissipative coefficients α_i and γ_i in Eqs. (6.55)–(6.57) [or the μ_i and λ_i in Eqs. (6.50)–(6.52)] all have the dimensions of a viscosity. The constitutive relations are somewhat different from those usually considered in hydrodynamics. In the hydrodynamics of ordinary fluids the dissipative fluxes are expanded only in the spatial gradients of velocity, temperature, etc. Here it is necessary to include the quantity N_i which describes the rotation of the director relative to the fluid. Thus in Eq. (6.56) the coefficient γ_1 determines the rate of relaxation of the director relative to the fluid motion. The equilibrium state in a rotating fluid is where the director rotates with the fluid corresponding to $\mathbf{N} = 0$. The term γ_2 in Eq. (6.56) leads to a coupling between the orientation of the director and shear flow.

In Eq. (6.55) there are six viscosity coefficients α_i. It will be shown in Sec. VI.G that invariance under microscopic time reversal leads to the relation

$$\gamma_2 = \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \tag{6.59}$$

leaving a total of five. The viscosity of the fluid naturally depends on the relative orientation of the director and the flow. This is discussed further in Sec. VII.

Upon substitution of Eqs. (6.55)–(6.57) into (6.49), the entropy production is expressed in terms of the tensor d_{ij} and the vectors $\mathbf{n}$, $\mathbf{N}$, and ∇T:

$$\begin{aligned} TR = {} & \alpha_1(n_i d_{ij} n_j)^2 + 2\gamma_2 n_i d_{ij} N_j + \alpha_4 d_{ij} d_{ij} \\ & + (\alpha_5 + \alpha_6) n_i d_{ik} d_{kj} n_j + \gamma_1 (\mathbf{N})^2 \\ & + \frac{\beta_1}{T} (\mathbf{n}\cdot\nabla T)^2 + \frac{\beta_2}{T} (\nabla T)^2. \end{aligned} \tag{6.60}$$

For all physical processes, the entropy production must be positive. This implies certain conditions on the viscosity coefficients, which can be derived from Eq. (6.60) by consideration of the range of possible values for $\mathbf{n}$, $\mathbf{N}$, ∇T, and d_{ij} (except for the fact that d_{ij} is symmetric and traceless, the components of all these quantities can vary independently). These are

$$\begin{aligned} &\alpha_4 > 0, && 2\alpha_1 + 3\alpha_4 + 2\alpha_5 + 2\alpha_6 > 0, \\ &\gamma_1 > 0, && \gamma_1(2\alpha_4 + \alpha_5 + \alpha_6) > \gamma_2^2, \\ &\beta_2 > 0, && \beta_1 + \beta_2 > 0. \end{aligned} \tag{6.61}$$

2. *Cholesterics*

In the case of incompressible cholesteric liquid crystals, some additional terms consistent with the symmetry are possible in Eqs. (6.55)–(6.57). For cholesterics it is not necessary that the constitutive relations be invariant under reflections in planes containing the director. We again assume that $\mathbf{n}$ and $-\mathbf{n}$ are equivalent. Now the following additional terms $t_{ij}^{(c)}$, $f_i^{(c)}$, and $q_i^{(c)}$ should be included in Eqs. (6.55)–(6.57):

$$t_{ij}^{(c)} = -\alpha_7 n_j e_{ikl} n_k T_{,l} - \alpha_8 n_i e_{jkl} n_k T_{,l} \tag{6.62}$$

$$f_i'^{(c)} = \gamma_3 e_{ijk} n_j T_{,k} \tag{6.63}$$

$$q_i^{(c)} = -\beta_3 e_{ijk} n_j N_k - \beta_4 e_{ijk} n_j d_{kl} n_l. \tag{6.64}$$

From Eq. (6.39) we require that $\gamma_3 = \alpha_8 - \alpha_7$. The Onsager reciprocal relations (Prost, 1972, and Section VI.G) give the additional relations $\gamma_3 = -\beta_3$ and $\alpha_7 + \alpha_8 = -\beta_4$. These equations show that a temperature gradient in a cholesteric will exert a torque on the fluid and the director. Conversely, according to Eq. (6.64) a heat current is induced if the director rotates relative to the fluid. These terms are consistent with an observation by Lehmann (reported by Oseen, 1933) that in certain cases drops of a cholesteric, spread out between glass surfaces, were put into violent rotation when heated from below. The theory of this effect has been discussed by Leslie (1968b).

G. Onsager reciprocal relations

When deriving the constitutive relations (6.50)–(6.52) and (6.55)–(6.57), the spatial symmetry properties of the liquid crystal were taken into account. The conservation of angular momentum led to the relations (6.54) and (6.58). We now consider the Onsager reciprocal relations which reflect the time reversal invariance of the microscopic equations of motion of the individual particles. This has been discussed by Parodi (1970). We will show that this invariance leads to the relations

$$\begin{aligned} \lambda_5 &= \mu_5 + \mu_6 = \mu_9 - \mu_8 \\ \gamma_2 &= \alpha_3 + \alpha_2 = \alpha_6 - \alpha_5 \end{aligned} \tag{6.65}$$

and, in Eqs. (6.62)–(6.64),

$$\begin{aligned} \gamma_3 &= -\beta_3 \\ \alpha_7 + \alpha_8 &= -\beta_4. \end{aligned} \tag{6.66}$$

In order to obtain the reciprocal relations we must identify the independent thermodynamic fluxes and forces. The entropy production (6.49) is given by

$$TR = -t_{ij} d_{ij} + f_i' N_i - (q_i/T) T_{,i}. \tag{6.67}$$

From this form it is not clear that t_{ij} and f_i' are independent. For the present purposes R is more conveniently written in the following way. We introduce the angular velocity of the director $\mathbf{\Omega}$ which is given by

$$\dot{\mathbf{n}} = (\mathbf{\Omega} \times \mathbf{n}), \tag{6.68}$$

and introduce an antisymmetric tensor Ω_{ij} such that

$$\Omega_{ij} = -\Omega_k, \tag{6.69}$$

where (i, j, k) is a cyclic permutation of (x, y, z). The rate of change of the director relative to the fluid is now given by

$$\begin{aligned} N_i &= (\Omega_{ik} - \omega_{ik}) n_k \\ &= \bar{\Omega}_{ik} n_k, \end{aligned} \tag{6.70}$$

where the last relation defines the antisymmetric tensor $\bar{\Omega}_{ik}$. We also introduce the symmetric and antisymmetric parts of the stress tensor

$$t_{ij}^{(s)} = \tfrac{1}{2}(t_{ij} + t_{ji}) \tag{6.71}$$

$$t_{ij}^{(a)} = \tfrac{1}{2}(t_{ij} - t_{ji}) = \tfrac{1}{2}(f_i' n_j - n_i f_j'). \tag{6.72}$$

The last relation follows from Eq. (6.39). The entropy production (6.67) can now be written

$$TR = -t_{ij}^{(s)} d_{ij} + t_{ij}^{(a)} \bar{\Omega}_{ij} - (q_i/T) T_{,i}. \tag{6.73}$$

We can now identify the three independent thermodynamic forces

$$x_{ij}^{(1)} = d_{ij}, \qquad x_{ij}^{(2)} = \bar{\Omega}_{ij}, \qquad x_i^{(3)} = (1/T) T_{,i}. \tag{6.74}$$

The corresponding fluxes are

$$J_{ij}^{(1)} = -t_{ij}^{(s)}, \qquad J_{ij}^{(2)} = t_{ij}^{(a)}, \qquad J_i^{(3)} = -q_i. \tag{6.75}$$

The constitutive relations (6.55)–(6.57) and (6.62)–(6.64) can now be written as relations between the fluxes (6.75) and the forces (6.74):

$$\begin{aligned} J_{ij}^{(1)} &= L_{ij,kl}^{(11)} d_{kl} + L_{ij,kl}^{(12)} \bar{\Omega}_{kl} + L_{ij,k}^{(13)} (1/T) T_{,k}, \\ J_{ij}^{(2)} &= L_{ij,kl}^{(21)} d_{kl} + L_{ij,kl}^{(22)} \bar{\Omega}_{kl} + L_{ij,k}^{(23)} (1/T) T_{,k}, \\ J_i^{(3)} &= L_{i,jk}^{(31)} d_{jk} + L_{i,jk}^{(32)} \bar{\Omega}_{jk} + L_{ij}^{(33)} (1/T) T_{,j}. \end{aligned} \tag{6.76}$$

The Onsager reciprocal relations state that

$$L_{ij,kl}^{(12)} = L_{kl,ij}^{(21)}, \tag{6.77}$$

$$L_{ij,k}^{(13)} = L_{k,ij}^{(31)}, \tag{6.78}$$

$$L_{ij,k}^{(23)} = L_{k,ij}^{(32)}. \tag{6.79}$$

For example, from Eqs. (6.55) and (6.56) we find that

$$\begin{aligned} L_{ij,kl}^{(12)} &= \tfrac{1}{2}(\alpha_2 + \alpha_3)(\delta_{ik} n_j n_l - n_i n_k \delta_{jl}) \\ L_{kl,ij}^{(21)} &= \tfrac{1}{2}\gamma_2 (\delta_{ik} n_j n_l - n_i n_k \delta_{jl}) \end{aligned} \tag{6.80}$$

which from Eq. (6.77) leads to the second result of Eq. (6.65). The first result of Eq. (6.65) is obtained by applying Eq. (6.79) to the constitutive relations (6.50) and (6.51). In a similar way Eqs. (6.78) and (6.79) lead to the identities (6.66).

H. Alternative form of the hydrodynamic equations

Another form of the linearized hydrodynamic equations for an incompressible nematic has been given by Forster *et al.* (1971) and Martin *et al.* (1972). In this section we demonstrate that these equations are identical with the linearized equations of Ericksen and Leslie given in previous sections. In Eq. (6.8) for the director we retain only terms linear in the curvature strains:

$$(\alpha_3 - \alpha_2) N_i + (\alpha_2 + \alpha_3) d_{ij} n_j + (\partial/\partial x_j) \Pi_{ij} = \gamma n_i. \tag{6.81}$$

We now use this equation to eliminate N_i in the stress tensor [Eq. (6.11)] and the relations (6.58) and (6.59). The stress tensor for an incompressible fluid can then be written

$$t_{ij} = t_{ij}^{(d)} + t_{ij}^{(r)}, \tag{6.82}$$

where

$$\begin{aligned} t_{ij}^{(d)} = &-\alpha_1 n_k n_p d_{kp} n_i n_j - \alpha_4 d_{ij} \\ &- [(\alpha_3\alpha_5 - \alpha_2\alpha_6)/\gamma_1](d_{ik} n_k n_j + d_{jk} n_k n_i) \end{aligned} \tag{6.83}$$

$$\begin{aligned} t_{ij}^{(r)} = &(\gamma_2/2\gamma_1)(n_j \Pi_{ik,k} + n_i \Pi_{jk,k}) \\ &+ \tfrac{1}{2} n_i \Pi_{jk,k} - \tfrac{1}{2} n_j \Pi_{ik,k}. \end{aligned} \tag{6.84}$$

We can interpret those two parts of the stress tensor as the dissipative and reactive parts. The dissipative part (6.83) is symmetric and (for an incompressible fluid) contains three viscosity coefficients. The reactive part arises from the reaction of the director back on the fluid flow. It is not symmetric in Eq. (6.84), but it can also be written in a symmetric form

$$\begin{aligned} \bar{t}_{ij}^{(r)} = &(\gamma_2/2\gamma_1)(n_j \Pi_{ik,k} + n_i \Pi_{jk,k}) - \tfrac{1}{2} n_k (\Pi_{ij,k} + \Pi_{ji,k}) \\ &+ \tfrac{1}{2} n_i \Pi_{kj,k} + \tfrac{1}{2} n_j \Pi_{ki,k}. \end{aligned} \tag{6.85}$$

It is easily verified that

$$\bar{t}_{ij,j}^{(r)} = t_{ij,j}^{(r)} \tag{6.87}$$

so that the equations of motion are unchanged whether we use $t_{ij}^{(r)}$ or $\bar{t}_{ij}^{(r)}$. The hydrodynamic equations of Forster *et al.* (1971) are given by Eq. (6.81) together with the conservation relations (6.6), (6.7), and (6.9). The advantage in using a symmetric form for the stress tensor is that angular momentum is automatically conserved.

These equations (for an incompressible fluid) contain four dissipative coefficients; the three viscosity coefficients appearing in Eq. (6.83) and $\gamma_1 = \alpha_3 - \alpha_2$ in Eq. (6.81) which determines the relaxation time for the director. The ratio $\gamma_2/\gamma_1 = (\alpha_3 + \alpha_2)/(\alpha_3 - \alpha_2)$ appearing in Eqs. (6.81) and (6.84) is a reactive coefficient determining the response of the director to the local shear and the reaction of the director back on the fluid.

VII. STEADY STATE AND SLOWLY VARYING FLOW

We now consider applications of the hydrodynamic equations set forth in the previous section to several simple problems.

A. Orientation of the director by a velocity shear

We consider the case of a fluid flowing in the x direction with a velocity gradient along y so that

$$v_x = u(y), \qquad v_y = v_z = 0. \tag{7.1}$$

A magnetic field in the xy plane is also imposed. The director will have the form

$$\mathbf{n} = \mathbf{x}\cos\phi(y) + \mathbf{y}\sin\phi(y). \tag{7.2}$$

The two components of the director Eq. (6.8) are

$$\begin{aligned}&[(\alpha_3-\alpha_2)(\partial/\partial t) - k(\partial^2/\partial y^2) - H_x{}^2\chi_a]\cos\phi\\ &\quad + (u'\alpha_2 - H_xH_y\chi_a)\sin\phi = \gamma\cos\phi\\ &[(\alpha_3-\alpha_2)(\partial/\partial t) - k(\partial^2/\partial y^2) - H_y{}^2\chi_a]\sin\phi\\ &\quad + (u'\alpha_3 - H_xH_y\chi_a)\cos\phi = \gamma\sin\phi,\end{aligned} \tag{7.3}$$

where the Frank elastic constants have been taken all equal to k, and where $u' = \partial u/\partial y$. The unknown γ is determined by the condition $n_x{}^2 + n_y{}^2 = 1$. It may be eliminated from Eq. (7.3) to give

$$\begin{aligned}&[(\alpha_3-\alpha_2)(\partial/\partial t) - k(\partial^2/\partial y^2)]\phi\\ &\quad + \chi_a(H_x{}^2 - H_y{}^2)\sin\phi\cos\phi + (u'\alpha_3 - H_xH_y\chi_a)\cos^2\phi\\ &\quad - (u'\alpha_2 - H_xH_y\chi_a)\sin^2\phi = 0.\end{aligned} \tag{7.4}$$

Let us consider first the uniform solution. The first term is discarded; the remainder can be written as an equation for $\tan\phi$ by dividing by $\cos^2\phi$. Introduce further $H^2 = H_x{}^2 + H_y{}^2$, $\tan\phi_H = H_y/H_x$ and Eq. (7.4) becomes

$$\begin{aligned}&\chi_aH^2\cos2\phi_H\tan\phi + (u'\alpha_3 - \tfrac{1}{2}\chi_aH^2\sin2\phi_H)\\ &\quad -(u'\alpha_2 - \tfrac{1}{2}\chi_aH^2\sin2\phi_H)\tan^2\phi = 0\end{aligned} \tag{7.5}$$

whose solution for $\tan\phi$ is

$$\tan\phi_0 = [\chi_aH^2\cos2\phi_H \pm Q][2u'\alpha_2 - \chi_aH^2\sin2\phi_H]^{-1}, \tag{7.6}$$

where

$$Q = [\chi_a{}^2H^4 + 4u'^2\alpha_2\alpha_3 - 2u'H^2\chi_a\sin2\phi_H(\alpha_2+\alpha_3)]^{1/2}. \tag{7.7}$$

We will argue below that only the lower sign solution is stable against small oscillations. The high and low field limits of Eq. (7.6) are

$$\tan\phi_0 \sim (\cos2\phi_H - 1)/\sin2\phi_H = \tan\phi_H, \qquad H\to\infty \tag{7.8}$$

(so that the director is aligned by the field) and

$$\tan\phi_0 \sim -(\alpha_2\alpha_3)^{1/2}\,|\,u'\,|/\alpha_2u' = \tan\phi_u, \qquad H = 0. \tag{7.9}$$

Thus a velocity gradient also aligns the director, at an angle ϕ_u to the direction of flow.

In order that ϕ_u be a physical angle it is necessary that α_2 and α_3 have the same sign. This condition can also be written $|\,\gamma_2\,| > \gamma_1$ and seems to be always found experimentally [the opposite case $|\,\gamma_2\,| < \gamma_1$ has been considered theoretically by Ericksen (1966b, 1969b)].

Since $\gamma_1 = \alpha_3 - \alpha_2$ must be positive [see Eq. (6.61)], the possible choices are $\alpha_2 < \alpha_3 < 0$ and $\alpha_3 > \alpha_2 > 0$. The former gives alignment of the director roughly in the direction of the flow with a small component in the direction of positive u'; the latter gives alignment nearly perpendicular to the flow direction. The former is the expected behavior of long molecules and is the behavior observed experimentally. Molecular models to explain the flow alignment in nematics have been discussed by Helfrich (1969b, 1970b, 1972). Shear orientation of liquid crystals has been studied experimentally by Porter and Johnson (1962, 1966) and Meiboom and Hewitt (1973). Typical measured values of ϕ_u are 18° for MBBA.

Crossover between orientation near ϕ_H and orientation near ϕ_u occurs when χ_aH^2 and $(\alpha_2\alpha_3)^{1/2}u'$ are comparable. For typical parameters this implies that a Kilogauss and a 1 cm/sec per cm flow gradient are equally effective in aligning the director.

We now consider the stability of the solution (7.6) against small oscillations. Expand Eq. (7.4) to linear order in $\delta\phi = \phi - \phi_0$:

$$\begin{aligned}&(\alpha_3-\alpha_2)(\partial/\partial t)\delta\phi - k(\partial^2/\partial y^2)\delta\phi = -\chi_aH^2\cos\ \phi_H\delta\phi\\ &\quad + (2u'\alpha - \chi_aH^2\sin2\phi_H)\tan\phi_0\delta\phi = \pm\delta\phi Q.\end{aligned} \tag{7.10}$$

In order that the amplitude of $\delta\phi$ decrease in time, the coefficient of $\delta\phi$ on the right-hand side must be negative, confirming our choice of sign in the solution (7.6).

We may also study the effect of surfaces and disclinations which introduce perturbations of the orientation from ϕ_0. According to Eq. (7.10) these die out in a length ξ given by

$$\xi^2 = k/Q \tag{7.11}$$

which reduces to the magnetic coherence length in the limit of large fields. For a 1 kG field or a 1 cm/sec per cm flow gradient ξ is of order 10^{-3} cm: the boundaries will have no effect except in the smallest samples. Boundary effects have been discussed by Leslie (1968a) and Ericksen (1968b).

B. Viscosity of an oriented flow

An incompressible nematic or cholesteric liquid crystal has five viscosity coefficients in Eq. (6.11) when we take into account the relation (6.15). We now investigate how these viscosity coefficients are related to the viscosity that would be measured in a shear flow experiment. We suppose that the liquid is flowing steadily in the x direction while a linear velocity gradient exists along the y axis so that $v_x = u'y$ and that a magnetic field is applied which is sufficiently strong to suppress boundary and shear flow aligning effects. Then the tangential shearing stress on a plane of unit area perpendicular to y is

$$-t_{xy} = \tfrac{1}{2}u'[\alpha_4 + (\alpha_3 + \alpha_6)n_x^2 + (\alpha_5 - \alpha_2)n_y^2 + 2\alpha_1 n_x^2 n_y^2], \tag{7.12}$$

where n_x and n_y are the components of the director along x and y, respectively. The effective viscosity is then

$$\eta = -t_{xy}/u'. \tag{7.13}$$

We see that the effective viscosity coefficient depends on the orientation of the molecules. Miesowicz (1936, 1946) [see also Parodi (1970)] has defined three principle viscosity coefficients corresponding to the cases where the director is

(1) parallel to the flow
(2) parallel to the velocity gradient
(3) perpendicular to both the flow and velocity gradient.

The corresponding viscosity coefficients are:

$$\begin{aligned} \eta_1 &= \tfrac{1}{2}(\alpha_4 + \alpha_6 + \alpha_3), \\ \eta_2 &= \tfrac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2), \\ \eta_3 &= \tfrac{1}{2}\alpha_4. \end{aligned} \tag{7.14}$$

These are necessarily positive [as can be shown from Eq. (6.61)]; furthermore, if $\alpha_2 \ll \alpha_3 < 0$, as required for shear orientation, $\eta_1 < \eta_2$; experimentally $0 < \eta_1 < \eta_3 < \eta_2$. This inequality was demonstrated by Miesowicz (1946) for PAA. By a measurement of the flow orientation and the three principle viscosity coefficients, it is possible to determine α_2, α_3, α_4, and α_5. The determination of α_1 would require a measurement of the viscosity when the director lies in the plane containing the direction of flow and the velocity gradient and at some angle to each. In most cases α_1 is small (see Table II).

In the absence of the aligning magnetic field the director field is oriented by the shear, as discussed in the previous subsection. Since the alignment angle ϕ_u is small, the effective viscosity measured in this geometry is nearly the same as η_1. Tseng, Silver, and Finlayson (1972) have given a detailed discussion of the actual velocity profile under these conditions. They also point out that the effective viscosity will be velocity dependent, since the size of the regions near the walls and near the center of a tube where the shear orienting effect must compete with the elastic forces depends on the magnitude of the shear. Several other flow problems and the effects of boundaries on the flow have been considered in the literature. Atkin (1970) has considered Poiseuille flow of nematics and Atkin and Leslie (1970) and Currie (1970) have considered Couette flow.

C. Torque due to rotation in a magnetic field

Let a container of liquid crystal be placed in a strong magnetic field, whose direction changes in time at a constant rate (or equivalently, have the container rotate uniformly relative to the field). The molecules in maintaining their alignment with the field encounter a viscous force opposing their motion relative to the fluid.

We assume that the boundary conditions at the container walls are $v = 0$ (no slip), but that the molecules at the walls may rotate freely. Since the director is constant in space, the director Eq. (6.8) becomes

$$(\alpha_3 - \alpha_2)N_i + (\alpha_2 + \alpha_3)d_{ij}n_j + \chi_a H_i H_j n_j = \gamma n_i. \tag{7.15}$$

The torque on a volume element dV due to the magnetic field is

$$d\boldsymbol{\tau} = \chi_a(\mathbf{n} \times \mathbf{H})(\mathbf{n}\cdot\mathbf{H})\, dV \tag{7.16}$$

and so the corresponding total torque on the liquid in the container is

$$\begin{aligned} \boldsymbol{\tau} = &-\int (\alpha_3 - \alpha_2)\mathbf{n} \times (\partial\mathbf{n}/\partial t - \boldsymbol{\omega} \times \mathbf{n})\, dV \\ &- \int (\alpha_2 + \alpha_3)(\mathbf{n} \times \mathbf{d}\cdot\mathbf{n})\, dV. \end{aligned} \tag{7.17}$$

The terms involving derivatives of the velocity field actually make no contribution to the integral. They all have the form $A\, dv_i/dx_j$, where the prefactor involves the components of $\mathbf{n}$, which are constant throughout the volume at a given time. When the integral over x_j has been performed, these terms can be expressed in terms of the value of v_i at the boundary, which is by hypothesis zero for the case of the stationary container. Thus the nonvanishing part of Eq. (7.16) is

$$\tau = -(\alpha_3 - \alpha_2)[\mathbf{n} \times (\partial/\partial t)\mathbf{n}]_z V = \gamma_1 \omega_H V, \tag{7.18}$$

where ω_H is the angular velocity of the magnetic field.

Extension to the case of a rotating container is readily made. The velocity field is divided into the velocity field of a rotating solid body and an arbitrary field which vanishes at the boundaries; again the latter gives no contribution to $\boldsymbol{\tau}$. The resultant torque is

$$\begin{aligned} \tau &= (\alpha_2 - \alpha_3)\{\mathbf{n} \times [(\partial/\partial t)\mathbf{n} - \boldsymbol{\omega} \times \mathbf{n}]\}_z V \\ &= \gamma_1(\omega_H - \omega_0)V \end{aligned} \tag{7.19}$$

if the axes of rotation of the field (ω_H) and the container (ω_0) are the same. Thus all such experiments are a measure of $\gamma_1 = \alpha_2 - \alpha_3$; they have been performed by Zwetkoff (1939a, 1939b), Prost and Gasparoux (1971), and Meiboom and Hewitt (1973).

In the case of steady-state flow the torque applied by the field (which is what we have calculated) is the same as the torque which acts on the container walls. Alternate derivations of this torque from this point of view can also be given (Prost and Gasparoux, 1971). The steady-state flow field is just solid body rotation ($\mathbf{v} = 0$ for the stationary container) (Jenkins, 1971).

In the derivation of Eq. (7.17) it is assumed that $\omega_H < \omega_C = \chi_a H^2/2\gamma_1$. In this case it can be shown from Eq. (7.14) that the director rigidly follows the rotating field and makes an angle δ with the field given by $\sin 2\delta = \omega_H/\omega_C$. The case of high rotation speeds $\omega_H > \omega_C$ has been considered by Leslie, Luckhurst, and Smith (1972). The director now lags behind the field and can be shown to rotate with a mean angular velocity $\omega_H - (\omega_H^2 - \omega_C^2)^{1/2}$. The effects of boundary conditions have also been considered by Leslie, Luckhurst, and Smith and found to be small when $\omega_H < \omega_C$.

A related problem has been considered by de Gennes (1971b) in which the orientation of the molecules in a nematic slab is fixed on the lower boundary but free to rotate on the upper boundary (free surface). A rotating field is applied in the plane of the slab and de Gennes discusses the appearance and migration of 180° walls in the slab.

Other methods of obtaining the coefficient γ_1 include a study of the dynamics of the orientation of nematics by a variable magnetic field (Brochard, Pieranski, and Guyon, 1972; Pieranski, Brochard, and Guyon, 1973) and studies of cholesteric liquid crystals in variable magnetic fields near the aligning field H_c (Wysocki, 1971; Parsons and Hayes, 1973).

D. Capillary flow in a cholesteric

The viscosity measured for a cholesteric forced through a capillary is much larger than for similar nematic and nonordered liquids (Porter, Barrall, and Johnson, 1966). The explanation for this effect lies in the fact that as the molecules move along the twist axis they must rotate (to maintain their orientation with the local director) which, similarly to the case of the previous section, implies a large viscous force (Helfrich, 1969c).

Let the capillary be a circular tube of radius a. It is assumed that the twist axis of the cholesteric coincides with that of the tube (which is taken to be the z axis)

$$\mathbf{n}(z) = \mathbf{x}\cos(2\pi z/p) + \mathbf{y}\sin(2\pi z/p) \tag{7.20}$$

and that this orientation pattern is firmly fixed at the walls of the capillary so that its distortion due to the flow may be neglected. Even with these simplifications, the hydrodynamic equations yield rather formidable equations for the velocity field. We will then proceed by assuming a simple form for the velocity field $\mathbf{v}(\mathbf{r})$, and evaluate the entropy production [Eq. (6.13)] for this choice. In steady state this entropy production is balanced by the work done by the pressure gradient

$$TR = (dP/dz)\langle v_z\rangle,$$

where $\langle v_z\rangle$ is the z component of the velocity averaged over the cross section of the capillary. The result for dP/dz will depend on our choice for $\mathbf{v}(\mathbf{r})$, but the essence of our argument will be that no matter how $\mathbf{v}(\mathbf{r})$ is chosen,

$$dP/dz \sim \eta\langle v_z\rangle p^{-2}, \tag{7.21}$$

where η is some average of the viscosity coefficients. In contrast, ordinary Poiseuille flow would replace the p^{-2} by a^{-2}. Since these quantities differ by a factor of 10^6 for typical experiments, this implies a large apparent viscosity for the cholesteric. Equation (7.21) also implies that the total rate of flow out of the capillary (for given pressure head) varies as a^2, whereas in ordinary Poiseuille flow it varies as a^4.

First consider a velocity field of the form

$$\mathbf{v} = \mathbf{z}u(\mathbf{r}), \tag{7.22}$$

where u is an arbitrary function except that it must vanish at $r = a$, the walls of the tube. The only nonvanishing terms of Eq. (6.13) are

$$RT = \alpha_4 d_{ij}d_{ji} + (\alpha_3 - \alpha_2)N^2. \tag{7.23}$$

Since the director is time-independent,

$$RT = \alpha_4(\nabla u)^2 + \tfrac{1}{4}(\alpha_3 - \alpha_2)(\mathbf{n}\cdot\nabla\mathbf{v})^2 + (\alpha_3 - \alpha_2)(2\pi u/p)^2. \tag{7.24}$$

The first term is the usual Poiseuille term. The first two terms are of order $(v_z/a)^2$ which is negligible compared to the last term ($\sim(v_z/p)^2$). The latter implies

$$dP/dz = \gamma_1 4\pi^2\langle v_z^2\rangle p^{-2}/\langle v_z\rangle \tag{7.25}$$

which is comparable to Eq. (7.21).

The velocity field (7.22) is much too simple; in particular we might expect the liquid to rotate about the z axis. This "backflow" will have the effect of reducing the N^2 term, since now

$$N^2 = [(2\pi v_z/p) - \tfrac{1}{2}(\operatorname{curl}\mathbf{v})_z]^2 + [(\mathbf{v}\cdot\nabla)\mathbf{n}]^2. \tag{7.26}$$

Choice of a velocity field with a large rotation about the z axis [$(\operatorname{curl}\mathbf{v})_z \sim v_z/p$] could cause the first term of Eq. (7.26) to cancel in whole or in part. The actual velocity field undoubtedly does have such character; however, other terms in R involving the rotational part of $\mathbf{v}$ arise which guarantee that the pressure gradient has the order of magnitude indicated by Eq. (7.21). An approximate solution to this problem has also been given by Lubensky (1972b).

E. Force on a disclination line and domain walls

An argument similar to that of the previous section can be used to estimate the viscous drag force per unit length acting on a disclination line moving relative to the fluid (Imura and Okano, 1973a). For simplicity, we assume a stationary axial disclination line along the z axis, which is not being disturbed by the flow of the liquid:

$$\mathbf{n}(\mathbf{r}) = \mathbf{x}\cos\tfrac{1}{2}m\phi(\mathbf{r}) + \mathbf{y}\sin\tfrac{1}{2}m\phi(\mathbf{r}), \tag{7.27}$$

where m is the index of the disclination line and $\phi = \arctan(y/x)$ is the angle defined in Fig. 13. We also assume the liquid is flowing at constant velocity v in the x direction. Then the entropy production is

$$TR = \int_V (\alpha_3 - \alpha_2)^2[(\partial/\partial x)\mathbf{n}(\mathbf{r})]^2\, d\mathbf{r} \tag{7.28}$$

according to Eq. (6.13), which leads to

$$\begin{aligned} TR &= (\alpha_3 - \alpha_2)v^2\tfrac{1}{4}m^2 \int_V [(\partial/\partial x)\phi(\mathbf{r})]^2\, d\mathbf{r} \\ &= \tfrac{1}{4}(\alpha_3 - \alpha_2)m^2v^2L \int \frac{y^2}{(x^2+y^2)^2}\, dxdy \\ &= \tfrac{1}{4}\pi(\alpha_3 - \alpha_2)m^2v^2L\ln(R/r_0), \end{aligned} \tag{7.29}$$

where L is the length of the line, and the integral has been cut off at the radius R of the container and the radius r_0 of the core of the disclination line. The entropy production is balanced by the rate at which work is done to maintain the flow

$$vf = TR, \tag{7.30}$$

where f is the force on the disclination line. Then

$$f/L = \tfrac{1}{4}\pi(\alpha_3 - \alpha_2)m^2v\ln(R/r_0) \tag{7.31}$$

is the force per unit length.

Similarly, for an infinite planar domain wall we may write [from Eq. (4.53)]

$$\mathbf{n}(\mathbf{r}) = \mathbf{z}\tanh(\mathbf{u}\cdot\mathbf{r}/\xi) + \mathbf{y}\,\mathrm{sech}(\mathbf{u}\cdot\mathbf{r}/\xi),$$

where $\mathbf{z}$ is the direction of the uniform magnetic field, $\mathbf{u}$ is a unit vector normal to the wall, and the y direction is chosen arbitrarily. We assume a uniform velocity field parallel to $\mathbf{u}$ which does not distort the wall and is not affected by the wall. Then the rate of entropy production is

$$\begin{aligned} TR &= \int_V (\alpha_3 - \alpha_2)v^2[\mathbf{u}\cdot\nabla\mathbf{n}(\mathbf{r})]^2\, d^3\mathbf{r} \\ &= (\alpha_3 - \alpha_2)v^2\xi^{-2}\iint dx'dy' \int dz'\,\mathrm{sech}^2\left(\frac{z'}{\xi}\right), \end{aligned} \tag{7.32}$$

where $z' = \mathbf{u}\cdot\mathbf{r}$ and the x', y' axes lie in the plane of the wall. Thus the force per unit area acting on the wall is

$$F = (\alpha_3 - \alpha_2)\xi^2 \int dz'\,\mathrm{sech}^2(z'/\xi) = \pi[(\alpha_3 - \alpha_2)/\xi]. \tag{7.33}$$

Brochard (1972) discusses the case of the thin film geometry taking some account of the deflection of the velocity field by the wall. It proves to be a small correction ($\sim$10%).

VIII. FLUCTUATIONS IN NEMATIC LIQUID CRYSTALS

In a nematic liquid crystal the molecules tend to be aligned along a constant direction. However, there are thermal fluctuations around this equilibrium configuration. This section is devoted to an investigation of the amplitudes and time dependence of these fluctuations. The low frequency normal modes of a nematic liquid crystal are a combination of orientational and shear wave motion. In addition, it is possible to propagate compressional waves (sound waves) in the liquid. The frequency of these sound waves is high compared to the relaxation rates of the orientational and shear waves, however, and so we can neglect the coupling between the sound waves and these latter waves; in this section we regard the nematic as incompressible. Sound waves in nematics are discussed in Sec. XII.

Since the polarizability of a molecule and of the ordered medium is very anisotropic, the orientational fluctuations give rise to fluctuations in the dielectric constant of a nematic which scatter light strongly. The scattered light is strongly depolarized. According to the elastic theory of Sec. III, the energy required to create an orientational disturbance of wave vector q is proportional to kq^2 where k is an elastic constant. This vanishes for long wavelengths corresponding to the fact that it takes no energy to rigidly rotate the director. It is thus easy to create long wavelength fluctuations. The turbid or milky appearance of nematics is a result of the strong light scattering at long wavelengths. If the nematic is heated above the transition temperature, these long wavelength, low-frequency modes no longer exist, and a clear liquid results. For this reason the transition temperature is sometimes called the clearing temperature.

The first measurements on light scattering from nematics were made by Chatelain (1948), who measured the intensity and angular distribution of the scattered light. More recently, with the advent of lasers, it has been possible to measure the spectral distribution of the scattered light. Such measurements have been made by the Orsay Liquid Crystal Group (1969b) on the nematic PAA and by Haller and Litster (1970a) on MBBA. Measurements of the intensity of the scattered light gives information on the elastic constants, and the spectral distribution gives information on the viscosity coefficients. The normal modes of an incompressible nematic have been considered by de Gennes (1968b) and the Orsay Group (1969a) using the Ericksen–Leslie hydrodynamic equations.

A. Basic formulas of light scattering

In this subsection we give the basic formulas for the scattering of light by the fluctuations of the dielectric constant of a medium.

In the case of interest to us the fundamental fluctuating quantity is the director

$$\mathbf{n}(\mathbf{r},t) = \mathbf{n}_0 + \delta\mathbf{n}(\mathbf{r},t), \tag{8.1}$$

where $\mathbf{n}_0$ is the equilibrium director. The small fluctuation $\delta\mathbf{n}$ must be perpendicular to $\mathbf{n}_0$ because both $\mathbf{n}$ and $\mathbf{n}_0$ are unit vectors. Thus $\delta\mathbf{n}$ has but two independent components. When discussing a fluctuation of particular wave vector $\mathbf{q}$, we will use the coordinate system of Fig. 19. The component δn_x, which lies in the plane of $\mathbf{q}$ and $\mathbf{n}_0$, and δn_y, which is perpendicular to this plane, will prove to be uncorrelated, and thus define the polarizations of the two independent fluctuation modes.

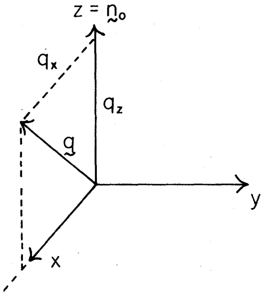

FIG. 19. Geometry to describe a single plane-wave disturbance in a nematic. The z axis is chosen to lie along the director $\mathbf{n}_0$ and the wave vector $\mathbf{q}$ of the disturbance lies in the xz plane.

Each point in the medium is described by a dielectric tensor $\epsilon_{ij}(\mathbf{r}, t)$, whose dependence on space and time is determined by the fluctuations taking place. We will suppose that these fluctuations are small so that

$$\epsilon_{ij}(\mathbf{r}, t) = \epsilon_{ij} + \delta\epsilon_{ij}(\mathbf{r}, t), \tag{8.2}$$

where ϵ_{ij} is the average dielectric tensor. In the case of the fluctuating director, the fluctuation in the dielectric tensor arising from $\delta\mathbf{n}$ is [see Eq. (3.17)]

$$\delta\epsilon_{ij} = \epsilon_a(\delta n_i n_{0j} + n_{0i}\delta n_j), \tag{8.3}$$

where $\epsilon_a = \epsilon_{\|} - \epsilon_{\perp}$ is the anisotropy in the dielectric constant.

We consider an incident light wave of frequency ω_0, wave vector $\mathbf{k}_0$, and polarization along the unit vector $\mathbf{p}_0$ and a scattered light wave of frequency ω_1, wave vector $\mathbf{k}_1$, and polarization $\mathbf{p}_1$. The frequency and wave vector transfer are

$$\begin{aligned} \omega &= \omega_0 - \omega_1 \qquad (\omega \ll \omega_0) \\ \mathbf{q} &= \mathbf{k}_0 - \mathbf{k}_1. \end{aligned} \tag{8.4}$$

As $\omega \ll \omega_0$, the wave vector transfer $q = 2(\omega_0/c)\sin(\theta/2)$, where θ is the angle of scattering. In terms of these quantities the differential scattering cross section, per unit volume, per unit solid angle $d\Omega$, and per unit angular frequency $d\omega$ is given by

$$d\sigma/d\Omega d\omega = (1/32\pi^3)(\omega_1/c)^4 I(\mathbf{q}, \omega), \tag{8.5}$$

where

$$I(\mathbf{q}, \omega) = \int_V d\mathbf{r}_{12} \int_{-\infty}^{\infty} dt_{12} \exp(i\mathbf{q}\cdot\mathbf{r}_{12} - i\omega t_{12}) \cdot \langle \delta\epsilon(\mathbf{r}_1 t_1)\,\delta\epsilon(\mathbf{r}_2 t_2)\rangle, \tag{8.6}$$

where the angular brackets indicate a thermal average and $\delta\epsilon = \mathbf{p}_1\cdot\delta\boldsymbol{\epsilon}\cdot\mathbf{p}_0$. For the case of a fluctuating director we substitute Eq. (8.3) for $\delta\boldsymbol{\epsilon}$, with the result

$$I(\mathbf{q}, \omega) = \epsilon_a^2 \sum_{\alpha=x,y} (\mathbf{p}_0\cdot\mathbf{n}_0\,\mathbf{p}_1\cdot\hat{\boldsymbol{\alpha}} + \mathbf{p}_0\cdot\hat{\boldsymbol{\alpha}}\,\mathbf{p}_1\cdot\mathbf{n}_0)^2 I_\alpha(\mathbf{q}, \omega), \tag{8.7}$$

where the sum is over the two dynamically independent components of $\delta\mathbf{n}$, δn_x and δn_y, and $I_\alpha(q, \omega)$ is the correlation function

$$I_\alpha(\mathbf{q}, \omega) = \int d\mathbf{r}_{12} \int_{-\infty}^{\infty} dt_{12} \exp(i\mathbf{q}\cdot\mathbf{r}_{12} - i\omega t_{12}) \cdot \langle \delta n_\alpha(\mathbf{r}_1 t_1)\,\delta n_\alpha(\mathbf{r}_2 t_2)\rangle. \tag{8.8}$$

Apart from the slowly varying factor $(\omega_1/c)^4$ in Eq. (8.5), all the spectral information is contained in the correlation functions $I_\alpha(\mathbf{q}, \omega)$. The total intensity of the light scattered per unit volume, per unit solid angle is obtained by integrating Eq. (8.5) over all frequencies. Using Eqs. (8.7) and (8.8), we find

$$d\sigma/d\Omega = (\epsilon_a^2/16\pi^2)(\omega_0/c)^4 \sum_{\alpha=x,y} (\mathbf{p}_0\cdot\mathbf{n}_0\,\mathbf{p}_1\cdot\hat{\boldsymbol{\alpha}} + \mathbf{p}_0\cdot\hat{\boldsymbol{\alpha}}\,\mathbf{p}_1\cdot\mathbf{n}_0)^2 I_\alpha(\mathbf{q}) \tag{8.9}$$

where we replaced ω_1 by ω_0 in the factor $(\omega_1/c)^4$ and

$$I_\alpha(\mathbf{q}) = \int_V d\mathbf{r}_{12} \exp(i\mathbf{q}\cdot\mathbf{r}_{12})\langle \delta n_\alpha(\mathbf{r}_1)\,\delta n_\alpha(\mathbf{r}_2)\rangle. \tag{8.10}$$

The total intensity is thus proportional to the mean square fluctuations of wave vector $\mathbf{q}$ of the director.

B. Amplitude of the fluctuations

Thermal fluctuations in orientation of the director give rise to corresponding fluctuations in the dielectric tensor of a liquid crystal. The amplitudes of these fluctuations are determined by the elastic constants discussed in Sec. III, as will be shown presently. It will be shown in the next subsection that the fluctuations are greatly damped by the viscous terms, so that the hydrodynamics of the substance are important to the dynamics of the fluctuations.

We will treat the simple case of small oscillations about a uniformly oriented liquid crystal. The equilibrium director $\mathbf{n}_0$ is oriented along the z axis by a field having that direction. The general disturbance $\delta\mathbf{n}$ can be regarded as a superposition of the plane-wave disturbances

$$\delta\mathbf{n}(\mathbf{r}, t) = V^{-1/2}\,\mathrm{Re}[\delta\mathbf{n}_{\mathbf{q}} \exp(i\mathbf{q}\cdot\mathbf{r})], \tag{8.11}$$

where $\delta\mathbf{n}_{\mathbf{q}}$ is a complex number containing both amplitude and phase. The increase in free energy due to this disturbance is given by Eq. (3.21). Keeping just the quadratic terms, there results

$$\begin{aligned} \delta G = {} & \tfrac{1}{2}\,|\,\delta n_{qx}\,|^2(k_{11}q_x^2 + k_{33}q_z^2 + \chi_a H^2) \\ & + \tfrac{1}{2}\,|\,\delta n_{qy}\,|^2(k_{22}q_x^2 + k_{33}q_z^2 + \chi_a H^2). \end{aligned} \tag{8.12}$$

(In the coordinate system defined by Fig. 19, $\mathbf{q}$ does not have a y component.) Application of the equipartition theorem of classical statistical mechanics gives

$$\begin{aligned} I_x(\mathbf{q}) &= k_B T[k_{11}q_x^2 + k_{33}q_z^2 + \chi_a H^2]^{-1} \\ I_y(\mathbf{q}) &= k_B T[k_{22}q_x^2 + k_{33}q_z^2 + \chi_a H^2]^{-1}. \end{aligned} \tag{8.13}$$

The combinations of elastic constants entering here arise from the fact that the fluctuations are combinations of splay and bend for δn_x and twist and bend for δn_y.

We may now use Eq. (8.9) to obtain the intensity of scattered light as a weighted combination of the $I_\alpha(\mathbf{q})$. It should be noted that for $H = 0$ the I_α diverge for small q, indicating that the energy required to create a fluctuation gets smaller the longer the wavelength of the fluctuation. This implies that light will be scattered very strongly close to the forward direction, where q is small. Thus a nematic liquid crystal is always critically opalescent in the absence of a field. This accounts for the turbidity of these materials.

Magnetic fields can suppress the fluctuations of orientation, but only wavelengths longer than $k^{1/2}\chi_a^{-1/2}H^{-1}$ (where k is one of the curvature elastic constants) are affected; since χ_a and k are of order 10^{-6} cgs units, only large fields ($H > 10^3$ G) will have any effect on the scattering of light except in the extreme forward direction.

Measurements of the intensity of the scattered light can provide information about the elastic constants of nematics. The temperature dependence of the light scattering in the absence of a field is determined by $\epsilon_a^2 k^{-1}$ [apart from the slowly varying factor k_BT in Eq. (8.13)]. It will be shown in Sec. XIII that ϵ_a varies like the order parameter S and k varies with the square of the order parameter. Thus the ratio ϵ_a^2/k is independent of S and the intensity of light scattering should vary slowly with temperature, in agreement with the experimental results of Haller and Litster (1970).

C. Dynamics of the fluctuations

The spectrum of the scattered light is determined by the dynamics of the fluctuations. The orientation fluctuations of the director are coupled to the fluid velocity by viscous effects, and in fact are overdamped: the modes which the elastic theory of the previous section predicts do not propagate.

We now consider the linearized hydrodynamic equations for the coupled motion of the director and the fluid velocity, both of which are regarded as small. We will assume that the nematic is incompressible, thus neglecting a small coupling between the sound wave modes and the director fluctuations; we also ignore temperature variations. The two equations we shall need are the equation for the director

$$I(\partial^2/\partial t^2)\delta n_i + \nabla_j \Pi_{ij} + f_i + f_i' = 0 \tag{8.14}$$

which is Eq. (6.42) with a term of order $\delta\mathbf{n} \times \mathbf{v}$ omitted, and Eq. (6.40) for the fluid velocity

$$\rho(\partial v_i/\partial t) + \nabla_i P + \nabla_j t_{ij} = 0. \tag{8.15}$$

The quantities $\mathbf{f}$, $\mathbf{f}'$, Π_{ij}, P, and t_{ij} must also be given linear form. All that survives of $\mathbf{f} + \mathbf{f}'$ is

$$f_i + f_i' = -\chi_a H_i(\mathbf{n}\cdot\mathbf{H}) + \gamma n_i + \gamma_1 N_i + \gamma_2 d_{ij} n_{0j}. \tag{8.16}$$

The Lagrange multiplier γ serves to guarantee the condition that $\mathbf{n}$ be a unit vector, or equivalently, that $\mathbf{n}_0\cdot\delta\mathbf{n} = 0$. It may be determined by constructing the z component of Eq. (8.14) (the coordinate system is again that of Fig. 19). However, since γ enters into the nontrivial x and y components of Eq. (8.14) only as a coefficient of $\delta\mathbf{n}$, it is sufficient to evaluate it just to zero order in $\mathbf{v}$ and $\delta\mathbf{n}$, which gives just

$$\gamma = \chi_a H^2. \tag{8.17}$$

We are assuming that the liquid crystal is incompressible, so that

$$\nabla\cdot\mathbf{v}(\mathbf{r}, t) = 0, \tag{8.18}$$

or, introducing a plane-wave representation for $\mathbf{v}$ similar to Eq. (8.11),

$$q_x v_x(\mathbf{q}, t) + q_z v_z(\mathbf{q}, t) = 0. \tag{8.19}$$

The pressure P is essentially a Lagrange multiplier which ensures that this condition holds. Thus taking the divergence of Eq. (8.15) gives

$$\nabla^2 P + \nabla_i\nabla_j t_{ij} = 0; \tag{8.20}$$

or, in terms of the Fourier transforms of P and t_{ij},

$$q^2 P = -q_i q_j t_{ij}. \tag{8.21}$$

We will use Eq. (8.19) to eliminate v_z wherever it occurs. Thus for a plane-wave disturbance

$$\begin{aligned} N_x &= (\partial/\partial t)\delta n_x - \tfrac{1}{2}i(q^2/q_z)v_x, & N_y &= (\partial/\partial t)\delta n_y - \tfrac{1}{2}iq_z v_y \\ d_{xz} &= (i/2q_z)(q_z^2 - q_x^2)v_x, & d_{yz} &= \tfrac{1}{2}iq_z v_y \end{aligned} \tag{8.22}$$

and from Eq. (6.55)

$$\begin{aligned} t_{xx} &= -i\alpha_4 q_x v_x, \\ t_{yx} &= -\tfrac{1}{2}i\alpha_4 q_x v_y, \\ t_{yz} &= -\alpha_2(\partial/\partial t)\delta n_y + \tfrac{1}{2}iq_z v_y(\alpha_2 - \alpha_4 - \alpha_5), \\ t_{zz} &= iq_x v_x(\alpha_1 + \alpha_4 + \alpha_5 + \alpha_6), \\ t_{zx} &= -\alpha_3(\partial/\partial t)\delta n_x + (i/2q_z)v_x(\alpha_3 q^2 \\ &\quad + (\alpha_4 + \alpha_6)(q_x^2 - q_z^2)), \\ t_{xz} &= -\alpha_2(\partial/\partial t)\delta n_x + (i/2q_z)v_x(\alpha_2 q^2 \\ &\quad + (\alpha_4 + \alpha_5)(q_x^2 - q_z^2)). \end{aligned} \tag{8.23}$$

The elements of Π_{ij} needed are found from Eq. (3.22):

$$\begin{aligned} \Pi_{xx} &= -ik_{11}q_x\delta n_x, & \Pi_{yx} &= -ik_{22}q_x\delta n_y, \\ \Pi_{xz} &= -ik_{33}q_z\delta n_x, & \Pi_{yz} &= -ik_{33}q_z\delta n_y. \end{aligned} \tag{8.24}$$

Combining these results, Eq. (8.14) comes to have the form

$$[I(\partial^2/\partial t^2) + \gamma_1(\partial/\partial t) + K^{(\alpha)}(q)]\delta n_\alpha + iC^{(\alpha)}(q)v_\alpha = 0 \tag{8.25}$$

where $\alpha = x, y$, repeated indices are not summed, and

$$\begin{aligned} K^{(x)} &= k_{11}q_x^2 + k_{33}q_z^2 + \chi_a H^2, \\ C^{(x)} &= -(1/2q_z)[\gamma_1 q^2 + \gamma_2(q_x^2 - q_z^2)] \\ K^{(y)} &= k_{22}q_x^2 + k_{33}q_z^2 + \chi_a H^2, \\ C^{(y)} &= \tfrac{1}{2}(\gamma_2 - \gamma_1)q_z \end{aligned} \tag{8.26}$$

and Eq. (8.15) becomes

$$[\rho(\partial/\partial t) + P^{(\alpha)}(q)]v_\alpha - iQ^{(\alpha)}(q)(\partial/\partial t)\delta n_\alpha = 0, \tag{8.27}$$

where

$$\begin{aligned} P^{(x)} &= \tfrac{1}{2}q^{-2}(2\eta_1 q_x^4 + 2\eta_2 q_z^4 + \alpha_m q_x^2 q_z^2), \\ P^{(y)} &= \tfrac{1}{2}(\alpha_4 q_x^2 + 2\eta_2 q_z^2), \\ Q^{(x)} &= q_z q^{-2}(\alpha_3 q_x^2 - \alpha_2 q_z^2), \\ Q^{(y)} &= \alpha_2 q_z. \end{aligned} \tag{8.28}$$

We have introduced the abbreviations

$$\begin{aligned} \eta_1 &= \tfrac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6), \\ \eta_2 &= \tfrac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2), \\ \alpha_m &= 2(\alpha_1 + \alpha_4) + \alpha_5 + \alpha_6 + \alpha_3 - \alpha_2, \end{aligned} \tag{8.29}$$

where η_1 and η_2 are the Miesowicz viscosity coefficients [Eq. (7.13)].

The normal modes are now determined from Eqs. (8.25) and (8.27). As promised, these equations separate into two sets involving the pairs n_x, v_x and n_y, v_y. To determine the modes, we suppose all these quantities have a time dependence $e^{-i\omega t}$. Further, at low frequencies we may neglect the first inertial term in each of (8.25). This approximation will be discussed further below. The equations for δn_x, v_x are then

$$\begin{aligned} (-i\omega\gamma_1 + K^{(x)})\delta n_x + iC^{(x)}v_x &= 0 \\ (-i\omega\rho + P^{(x)})v_x - \omega Q^{(x)}\delta n_x &= 0 \end{aligned} \tag{8.30}$$

with a similar set of equations for δn_y, v_y. In each case we get the secular equation for the normal mode frequencies

$$\omega^2\rho\gamma_1 + i\omega(\rho K^{(\alpha)} + \gamma_1 P^{(\alpha)} - C^{(\alpha)}Q^{(\alpha)}) - K^{(\alpha)}P^{(\alpha)} = 0. \tag{8.31}$$

We first consider the case where the magnetic field is zero. Let us first estimate the orders of magnitude of the various terms in Eq. (8.31). We assume that the six viscosity coefficients α are all of order 0.1 poise and that the three elastic constants have comparable magnitudes $k \simeq 10^{-6}$ dynes. Then the various functions that enter into Eq. (8.31) are approximately

$$\begin{aligned} P^{(\alpha)} &\sim \eta q^2, \\ C^{(\alpha)} &\sim Q^{(\alpha)} \sim \eta q, \\ K^{(\alpha)} &\sim kq^2. \end{aligned} \tag{8.32}$$

The form of the modes depends on the value of the dimensionless parameter

$$\mu = k\rho/\eta^2; \tag{8.33}$$

using the above values of k, α, and $\rho = 1$ g/cm^3, we find $\mu \simeq 10^{-4}$. The smallness of this parameter allows us to simplify Eq. (8.31); in the limit $\mu \ll 1$ the two solutions are

$$\begin{aligned} \omega_S^{(\alpha)} &= -i\frac{K^{(\alpha)}P^{(\alpha)}}{\gamma_1 P^{(\alpha)} - C^{(\alpha)}Q^{(\alpha)}} = -i\Gamma_S^{(\alpha)} \\ \omega_F^{(\alpha)} &= -(i/\rho\gamma_1)(\gamma_1 P^{(\alpha)} - C^{(\alpha)}P^{(\alpha)}) = -i\Gamma_F^{(\alpha)}. \end{aligned} \tag{8.34}$$

We have defined the damping constants Γ of the two modes, both of which are overdamped. The modes are a mixture of hydrodynamic and director motion and the suffixes S and F stand for slow and fast relaxation behavior. Thus

$$\Gamma_S^\alpha \sim kq^2/\eta, \qquad \Gamma_F^\alpha \sim \eta q^2/\rho. \tag{8.35}$$

The slow mode corresponds to a slow relaxation of a curved nematic structure with the torques due to curvature being opposed by frictional effects. In the fast mode, inertial effects of the fluid are important and the relaxation rate is characteristic of a shear wave in a fluid. These shear modes are discussed further in the next section. In both modes the rotation velocity of the molecules $\omega\delta n_\alpha$ is comparable with the velocity gradient qv. The relaxation rates are proportional to q^2 which is characteristic of hydrodynamic modes. In the special case where the modes propagate along the z axis, the two types $\alpha = x, y$ become identical, and the damping constants are

$$\begin{aligned} \Gamma_S &= k_{33}q^2[\gamma_1 + (\alpha_2/2\eta_2)(\gamma_1 - \gamma_2)]^{-1} \\ \Gamma_F &= (q^2/2\rho)[2\eta_2 + (\alpha_2/\gamma_1)(\gamma_1 - \gamma_2)]. \end{aligned} \tag{8.36}$$

We now examine the modes in the high field limit, which corresponds to

$$\chi_a H^2 \gg \eta^2 q^2/\rho. \tag{8.37}$$

This inequality can only be achieved with the strongest fields and small-angle scattering: with $H = 10^4$ G, $\chi_a = 10^{-5}$, $\eta = 0.1$ P it requires $q < 10^2$ cm^{-1}. In this limit we find one orientational mode with relaxation rate

$$\Gamma_1^{(\alpha)} = \chi_a H^2/\gamma_1 \tag{8.38}$$

and one shear wave hydrodynamic mode with relaxation rate

$$\Gamma_2^{(\alpha)} = P^\alpha/\rho. \tag{8.39}$$

The effective viscosity coefficients which enter these shear wave modes are just those that would be measured by the technique of Miesowicz: for $q_z = 0$, $P^{(x)}$ involves η_1 and $P^{(y)}$ involves $\eta_3 = \alpha_4/2$, and for $q_x = 0$, $P^{(x)}$ involves η_2 only. The orientational mode has the greater relaxation rate in this case.

We have neglected the inertial term $I(\partial^2/\partial t^2)\delta n$ in the equations of motion (8.25). We must compare $I\omega^2$ with the elastic restoring force kq^2. The moment of inertia I per unit volume is of order ρa^2 where a is a molecular dimension. The ratio of these terms is then

$$I\omega^2/kq^2 \simeq \rho a^2\omega^2/kq^2. \tag{8.40}$$

For the slow mode in the small μ limit this ratio is $\mu(qa)^2$ and thus always negligible. For the fast mode it is $(qa)^2/\mu$ and thus becomes important for $qa > \mu^{1/2}$. However, we will show below that the light scattering is dominated by the slow mode so that the neglect of inertia in this context is satisfactory. The opposite limit of high frequencies has been investigated by Ericksen (1969), and there the normal modes have a very different character.

D. Correlation functions

To determine the spectrum of the scattered light, we require the Fourier transforms (8.8). These can be obtained from the hydrodynamic equations (8.25) and (8.27). Consider, for example, the δn_x, v_x mode. It is more convenient now to take the Laplace transform in time of these equations. Thus we define

$$\delta n_x(s) = \int_0^\infty dt \exp(-st)\,\delta n_x(t)$$

$$v_x(s) = \int_0^\infty dt \exp(-st)\,v_x(t). \tag{8.41}$$

Then multiplying Eqs. (8.25) and (8.27) on the left by e^{-st} and integrating over t gives the two equations [again omitting the inertial terms in Eq. (8.25)]

$$\begin{aligned}(\gamma_1 s + K^{(x)})\,\delta n_x(s) + iC^{(x)}v_x(s) &= \gamma_1\delta n_\alpha(0)\\ (\rho s + P^{(x)})\,v_x(s) - isQ^{(x)}\delta n_x(s) &= \rho v_x(0) - iQ^{(x)}\delta n_x(0),\end{aligned} \tag{8.42}$$

where $\delta n_x(0)$ and $v_x(0)$ are the initial values of δn_x and v_x at $t = 0$. Solving these equations for $\delta n_x(s)$, we find

$$\delta n_x(s) = \frac{(\gamma_1 s\rho + \gamma_1 P^{(x)} - C^{(x)}Q^{(x)})\,\delta n_x(0) - i\rho C^{(x)}v_x(0)}{D^{(x)}(s)}, \tag{8.43}$$

where

$$\begin{aligned}D^{(x)}(s) = {}& s^2\rho\gamma_1 + s(\rho K^{(x)} + \gamma_1 P^{(x)} - C^{(x)}Q^{(x)})\\ &+ K^{(x)}P^{(x)}.\end{aligned} \tag{8.44}$$

The calculation of the Laplace transforms of the correlation functions is now reduced to a determination of equal time correlation functions. Hence

$$I_\alpha(\mathbf{q}, s) = \frac{\gamma_1 s\rho + \gamma_1 P_\alpha{}^{(\alpha)} - C_\alpha{}^{(\alpha)}Q_\alpha{}^{(\alpha)}}{D_\alpha{}^{(\alpha)}(s)}\,I_\alpha(q), \tag{8.45}$$

where $\alpha = x$, y and $I_\alpha(q)$ is given by Eq. (8.13). In the limit $\mu \ll 1$ we have

$$D_\alpha{}^{(\alpha)}(s) = \rho\gamma_1(s + \Gamma_{S\alpha}{}^{(\alpha)})(s + \Gamma_{F\alpha}{}^{(\alpha)}), \tag{8.46}$$

where the relaxation rates Γ are given in Eq. (8.34). Substituting Eq. (8.46) in (8.45), we obtain the simple result

$$I_\alpha(\mathbf{q}, s) = I_\alpha(\mathbf{q})/(s + \Gamma_S{}^{(\alpha)}) \tag{8.47}$$

in which only the slow mode contributes. The Fourier transform $I_\alpha(\mathbf{q}, \omega)$ is related to the Laplace transform by

$$\begin{aligned}I_\alpha(\mathbf{q}, \omega) &= 2\,\mathrm{Re}\,I_\alpha(\mathbf{q}, s = i\omega)\\ &= I_\alpha(\mathbf{q})[2\Gamma_{S\alpha}/(\omega^2 + \Gamma_{S\alpha}{}^2)]\end{aligned} \tag{8.48}$$

which gives rise to a Lorentzian line shape. The scattered light in general is the sum of two Lorentzians [Eq. (8.7)]. It is possible to separate the two modes by arranging that the polarization of the incident and scattered light is perpendicular to x or to y.

We can summarize the results of these calculations on the light scattering by orientation fluctuations in nematics as follows. The light scattering is dominated by the slow modes in which a distorted molecular configuration relaxes exponentially to equilibrium. In the slow modes the deflection $\delta\mathbf{n}$ of the director is larger than the amplitude of the velocity fluctuation ($\delta n \sim vq/\Gamma_S$), and this is the reason that the slow modes dominate the light scattering. Measurement of the linewidths of the scattered light gives information on the ratio of elastic constants to certain viscosity coefficients. Measurements of the intensity of light scattering gives information on the elastic constants.

Measurements on the spectral distribution of light scattered from PAA have been made by the Orsay Liquid Crystal Group (1969b, 1971a). Using Zwetkoff (1937, 1943) measurements of the elastic constants, they were able to determine the viscosity coefficients α_2, α_3, α_4, α_5, γ_1, and γ_2, generally in good agreement with the measurements of Miesowicz (1946). Forster *et al.* (1971) have also made a comparison between the predictions of the hydrodynamic theory and the Orsay light scattering data and shown that the agreement is satisfactory.

The application of a magnetic (or electric) field leads to a decrease in the intensity [Eq. (8.13)] and an increase in the linewidth [Eq. (8.34)] of the Rayleigh scattering. These effects have been observed by Martinand and Durand (1972) and used to determine the bend elastic constant.

IX. SHEAR WAVES IN NEMATIC LIQUID CRYSTALS

In the previous section we showed that there are two types of normal modes of nematic liquid crystals. There is a "slow" mode, which is chiefly responsible for the Rayleigh scattering of light by nematics, and a "fast" mode, which is predominantly a shear wave, similar to the shear wave modes which occur in normal liquids.

The shear wave modes are nonpropagating and damp out in a short distance; however, they can be observed by

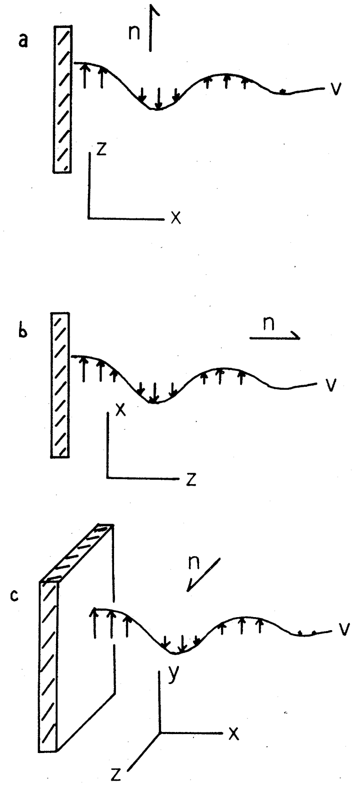

FIG. 20. Three geometries for shear waves. The arrows give the direction of the flow velocity **v** and the half-arrow gives the orientation of the director **n**. In each case the z axis is taken parallel to **n**. (a) The director is parallel to the flow; (b) the director is parallel to the direction of propagation of the wave; (c) the director is perpendicular to both the flow and the direction of propagation.

using a reflectance technique, in which a shear wave in a solid is reflected from a solid–nematic interface. Measurement of the coefficient of reflection in this experiment gives an effective viscosity coefficient, and thus provides another useful way in which some of the viscosity coefficients of a nematic liquid crystal may be determined. This technique was first used by Martinoty and Candau (1971) for the nematic MBBA. They have also considered the relations between the coefficient of reflection, the effective viscosity coefficient, and the Ericksen–Leslie viscosity coefficients.

We will consider the three different geometries shown in Fig. 20 for the propagation of shear waves relative to orientation of the director of the molecules. In (a) the director **n** is parallel to the flow velocity; in (b) **n** is parallel to the direction of propagation of the shear wave; and in (c) **n** is perpendicular to both the flow velocity and direction of propagation of the shear wave. In the case where there is a strong magnetic field applied to the nematic so that the director is fixed, the effective viscosity coefficients which determine the shear wave damping in these three geometries are exactly those defined by Miesowicz (see Sec. VII,B). When there is no magnetic field, or it is small, the fast modes are a combination of shear and orientational motions, and the effective viscosity coefficients are changed.

The shear wave modes are driven by the motion of the solid surface, which is oscillating with a given frequency ω. The complex wave vector of the shear wave is found by solving the dispersion relation (8.31). Making the approximation that $\mu \ll 1$ [Eq. (8.33)], we find that the propagation constants of the slow and fast modes in the three geometries of Fig. 20 are (in the absence of an external field)

$$\begin{aligned} q_{Sa} &= (1+i)(\eta_a\gamma_1\omega/2k_{11}\eta_1)^{1/2},\\ q_{Fa} &= (1+i)(\rho\omega/2\eta_a)^{1/2}, \end{aligned} \tag{9.1}$$

$$\begin{aligned} q_{Sb} &= (1+i)(\eta_b\gamma_1\omega/2k_{33}\eta_2)^{1/2},\\ q_{Fb} &= (1+i)(\rho\omega/2\eta_b)^{1/2}, \end{aligned} \tag{9.2}$$

$$\begin{aligned} q_{Sc} &= (1+i)(\gamma_1\omega/2k_{22})^{1/2},\\ q_{Fc} &= (1+i)(\rho\omega/\alpha_4)^{1/2}, \end{aligned} \tag{9.3}$$

where

$$\begin{aligned} \eta_a &= \eta_1 - (\alpha_3/2)[1+(\gamma_2/\gamma_1)]\\ \eta_b &= \eta_2 + (\alpha_2/2)[1-(\gamma_2/\gamma_1)]. \end{aligned} \tag{9.4}$$

In Eqs. (9.1)–(9.3) the subscripts S and F indicate the slow and fast modes, respectively, and the subscripts a, b, or c indicate that the geometry is either that of Fig. 20a, 20b, or 20c. In case (c) the slow mode is purely orientational and the fast mode is a pure shear wave, as is easily seen by examining the equations of motion (8.30) for this case. The effective viscosity coefficients η_a and η_b which determine the damping of the fast shear wave modes in cases (a) and (b) are given by Eq. (9.4). Using the two identities $\gamma_1 = \alpha_3 - \alpha_2$, $\gamma_2 = \alpha_6 - \alpha_5$, it may be shown that $\eta_a = \eta_b$. This is a consequence of the fact that the stress tensor can be written in a symmetric form (see Sec. VI,H). If we choose the fluid velocity v along x in Fig. 20b, then the equality $t_{zx} = t_{xz}$ is equivalent to $\eta_a = \eta_b$.

In the case of a strong magnetic field the director motion is prevented, and the modes are pure shear wave modes. The damping constants are given by Eq. (8.39), and the corresponding propagation constants are given by

$$\begin{aligned} q_{Fa} &= (1+i)(\rho\omega/2\eta_1)^{1/2},\\ q_{Fb} &= (1+i)(\rho\omega/2\eta_2)^{1/2},\\ q_{Fc} &= (1+i)(\rho\omega/\alpha_4)^{1/2}. \end{aligned} \tag{9.5}$$

As remarked above, only the principal viscosity coefficients of Miesowicz η_1, η_2, and $\eta_3 = \frac{1}{2}\alpha_4$ enter here. The fast (a) and (b) modes have different damping constants as we no longer have the symmetry $t_{xz} = t_{zx}$.

As discussed in Sec. VII,A, the relation $\gamma_2 \sim -\gamma_1$ is approximately obeyed. Physically this corresponds to the fact that the molecules prefer to lie approximately along the direction of the flow velocity in shear flow. Under these circumstances $\eta_a \simeq \eta_1$. Thus the damping of the shear flow modes in cases (a) and (c) is determined almost entirely by the Miesowicz viscosities η_1 and η_3: the director motion is small. On the other hand, in case (b) the director motion is important, and η_b can be considerably different from η_2. This mode will also be sensitive to the application of a magnetic field.

A. Reflection of shear waves at an interface

We consider a shear wave being reflected at normal incidence to a solid-nematic interface.[10] At the surface the boundary conditions are:

(i) the tangential components of the velocity must be continuous;

(ii) the tangential stresses on the two sides of the interface must be equal. We consider the cases (a), (b), and (c) separately.

(a) We suppose that the solid-nematic interface is the plane $x = 0$ and that shear waves are incident normally on the interface from the solid which occupies the region $x < 0$. In the solid we have an incident and a reflected wave. The velocity fields associated with these waves are, respectively,

$$v_z = A_i \exp(iqx - i\omega t)$$

$$v_z = A_r \exp(-iqx - i\omega t), \tag{9.6}$$

where $q = (\rho_s/\mu_s)^{1/2}\omega$ and μ_s is the shear modulus in the solid and ρ_s is the density. In the nematic liquid we have a transmitted wave which in general is a linear combination of the slow and fast modes,

$$v_z = A_S \exp(iq_{Sa}x - i\omega t) + A_F \exp(iq_{Fa}x - i\omega t). \tag{9.7}$$

The continuity of the velocity at $x = 0$ gives

$$A_i + A_r = A_S + A_F. \tag{9.8}$$

In the solid the stress on the interface in the z direction, T_{zx}, is given by

$$T_{zx} = -(i\mu_s/\omega)(\partial v_z/\partial x). \tag{9.9}$$

From Eq. (9.6)

$$T_{zx} = Z(A_i - A_r), \tag{9.10}$$

where Z is the mechanical impedance of the solid, $Z = (\rho_s\mu_s)^{1/2}$. In the liquid from Eq. (6.55) the surface stress is

$$t_{zx} = -\alpha_3(\partial/\partial t)\delta n_x - \eta_1(\partial v_z/\partial x). \tag{9.11}$$

We assume that at the surface the orientation of the molecules is fixed owing to the strong surface forces. Thus in Eq. (9.11) we take $\delta n_x = 0$ and then for Eq. (9.7) at $x = 0$

$$t_{zx} = -i\eta_1(q_{Sa}A_S + q_{Fa}A_F). \tag{9.12}$$

The equality of the stresses now gives the second condition

$$Z(A_i - A_r) = -i\eta(q_{Sa}A_S + q_{Fa}A_F). \tag{9.13}$$

From Eqs. (9.8) and (9.13) the reflection coefficient R is given by

$$R = A_r/A_i = (Z - Z_a)/(Z + Z_a), \tag{9.14}$$

where Z_a, the mechanical impedance of the nematic, is given by

$$Z_a = -i\eta_1 q_{Fa}\frac{[1 + (q_{Sa}A_S/q_{Fa}A_F)]}{[1 + (A_S/A_F)]}. \tag{9.15}$$

The ratio of the amplitudes A_S and A_F is determined by the equation of motion of the director (8.25). For the particular geometry of Fig. 20a it becomes

$$[-i\omega\gamma_1 - k_{11}(\partial^2/\partial x^2)]\delta n_x + \tfrac{1}{2}(\gamma_1 + \gamma_2)(\partial v_z/\partial x) = 0. \tag{9.16}$$

Using the condition that $n_x = 0$ at the surface and Eq. (9.7), we find

$$\frac{A_S}{A_F} = -\frac{q_{Fa}}{q_{Sa}}\frac{(\omega\gamma_1 + ik_{11}q_{Sa}^2)}{(\omega\gamma_1 + ik_{11}q_{Fa}^2)}. \tag{9.17}$$

Substituting for q_{Sa} and q_{Fa} from Eq. (9.1), we find

$$\frac{A_S}{A_F} = -\left(\frac{\rho\eta_1 k_{11}}{2\gamma_1\eta_a^2}\right)^{1/2}\left[\frac{1 - (2\eta_a/\eta_1)}{1 - (\rho k_{11}/\gamma_1\eta_a)}\right]. \tag{9.18}$$

The prefactor is $\mu^{1/2}$; thus $A_S/A_F \ll 1$ and it can be neglected in Eq. (9.15). In the same way we find

$$1 + (q_{Sa}A_S/q_{Fa}A_F) = 2\eta_a/\eta_1. \tag{9.19}$$

Substituting into Eq. (9.15), we find the mechanical impedance of the nematic is

$$Z_a = (1 - i)(\rho\omega\eta_a/2)^{1/2}. \tag{9.20}$$

The resistance R_a and the reactance X_a, defined by $Z_a = R_a - iX_a$, are thus equal. The real and imaginary parts of the dynamic viscosity are defined by

$$\eta_a^{1} = 2R_aX_a/\rho\omega, \qquad \eta_a^{11} = (R_a^2 - X_a^2)/\rho\omega. \tag{9.21}$$

Thus from Eq. (9.20)

$$\eta_a^{1} = \eta_a, \qquad \eta_a^{11} = 0. \tag{9.22}$$

In the case of a strong magnetic field η_a is replaced by η_1 [Eq. (9.5)].

(b) The solid-nematic interface is the plane $z = 0$. Proceeding as above, we find that the surface stress in the nematic is now given by Eq. (6.55) (with $\delta n_y = 0$)

$$t_{yz} = -\eta_2(\partial v_y/\partial z); \tag{9.23}$$

the mechanical impedance of the nematic is

$$Z_b = (1 - i)(\rho\omega\eta_b/2)^{1/2}; \tag{9.24}$$

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[10] The case of oblique incidence has been considered by Martinoty and Candau (1971).

and the real and imaginary parts of the dynamic viscosity are

$$\eta_b{}^1 = \eta_b, \qquad \eta_b{}^{11} = 0. \tag{9.25}$$

In a strong magnetic field η_b is replaced by η_2.

(c) In this case we only need consider the single shear mode in the liquid. We take the plane $x = 0$ to be the solid–nematic interface. From Eq. (6.55) the surface stress in the liquid is

$$t_{yx} = -(\alpha_4/2)(\partial v_y/\partial x). \tag{9.26}$$

As above we find the mechanical impedance of the nematic is

$$Z_c = \tfrac{1}{2}(1 - i)(\rho\omega\alpha_4)^{1/2} \tag{9.27}$$

and the dynamic viscosities are

$$\eta_c{}^1 = \alpha_4/2, \qquad \eta_c{}^{11} = 0. \tag{9.28}$$

An applied field has no effect in this case.

B. Discussion of the reflection coefficient

If the mechanical impedance Z of the solid is known, the mechanical impedance of the nematic at the interface can be determined from a measurement of the reflection coefficient R. From Eq. (9.14)

$$Z_\alpha = Z[(1 - R_\alpha)/(1 + R_\alpha)], \tag{9.29}$$

where $\alpha = a$, b, or c. The complex reflection coefficient can be written

$$R_\alpha = | R_\alpha | \exp(i\theta_\alpha) \tag{9.30}$$

and then

$$Z_\alpha = Z \frac{1 - | R_\alpha |^2 - 2i | R_\alpha | \sin\theta_\alpha}{1 + | R_\alpha |^2 + 2 | R_\alpha | \cos\theta_\alpha}. \tag{9.31}$$

In all the cases considered the real and imaginary parts of Z_α are equal, and so

$$\sin\theta_\alpha = (1 - | R_\alpha |^2)/2 | R_\alpha |. \tag{9.32}$$

Thus it is only necessary to determine $| R_\alpha |$.

The penetration depths λ of the wave into the nematic are determined by Eqs. (9.1) through (9.3). In case (b), for example, these are

$$\begin{aligned} \lambda_{Sb} &= (2k_{33}\eta_2/\eta_b\gamma_1\omega)^{1/2} \\ \lambda_{Fb} &= (2\eta_b/\rho\omega)^{1/2}. \end{aligned} \tag{9.33}$$

For ω in the range 10–100 MHz, $k_{33} \simeq 10^{-6}$ dyn, $\eta \simeq 0.1$ P, and $\rho = 1$ g/cm^3, we find

$$\begin{aligned} 10^{-6}\ \text{cm} &< \lambda_{Sb} < 3.10^{-7}\ \text{cm} \\ 10^{-4}\ \text{cm} &< \lambda_{Fb} < 4.10^{-5}\ \text{cm}. \end{aligned} \tag{9.34}$$

The orientation mode is thus attenuated in a very short distance, several molecular lengths. The shear wave hydrodynamic mode propagates about 10^{-4} cm into the liquid, and it may be possible to perform transmission experiments on thin samples.

As discussed above, for most nematics $\gamma_2 \simeq -\gamma_1$ and then the viscosity coefficient $\eta_a \simeq \eta_1$. Also in case (c) only the Miesowicz viscosity $\eta_3 = \frac{1}{2}\alpha_4$ enters. The most interesting case is (b) where the director motion is important. The viscosity coefficient η_b in this case will differ appreciably from η_2 and will also be sensitive to an applied field.

The viscosity coefficients in cases (a) and (c) have been measured by Martinoty and Candau (1971) for MBBA. Far from the phase transition the values obtained by the shear wave technique and those obtained from conventional viscometry are in good agreement.

Similar studies have also been made in cholesteric liquid crystals (Martinoty and Candau, 1972a,b). Propagation of shear waves in cholesterics has been considered theoretically by Brochard (1971). The behavior of the impedance depends on the relative magnitudes of the pitch p and the penetration depth λ_F for shear waves. From Eq. (9.34) we see that these lengths can be comparable. Brochard considered the two geometries (a) and (c) above, where the pitch axis is normal to the solid–liquid crystal interface and the molecules at the surface are parallel or perpendicular to the shear wave velocity, respectively. The impedance depends on the ratio p/λ_F: for $p \ll \lambda_F$, $Z_a = Z_c$ and the impedance is isotropic as it is averaged over many turns of cholesteric structure; for $p \gg \lambda_F$, $Z_a \neq Z_c$ and Z_a and Z_c are close to their values for nematics. The calculated pitch dependence of Z_a and Z_c is in good agreement with the dependence found experimentally by Martinoty and Candau if the pitch is not too small.

X. FLUCTUATIONS IN CHOLESTERICS

The spiral structure of a cholesteric alters the nature of the fluctuations about equilibrium. In an *infinite* cholesteric the phase fluctuations diverge (the phase determines the origin of twist) (Lubensky, 1972a)—but as we shall see, this has no significance for the laboratory materials. Some of the modes found in nematics no longer have a hydrodynamical character in cholesterics; that is, the damping is not proportional to q^2. The modes of cholesterics have been investigated by Fan *et al.* (1970) and Lubensky (1972b).

We choose the axis of the cholesteric to be the z axis of a Cartesian coordinate system. In equilibrium the directors $\mathbf{n}_0$ of the molecules lie in planes normal to this axis and have the form

$$n_{0x} = \cos\phi_0, \quad n_{0y} = \sin\phi_0, \quad \phi_0 = t_0 z. \tag{10.1}$$

The arbitrary phase has been chosen so that $\mathbf{n}_0$ is along the x axis at $z = 0$.

A. Fluctuations of the director

We can describe the fluctuations of the director by writing it in the form

$$\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}, \tag{10.2}$$

where $\delta\mathbf{n}$ represents the small fluctuations. The condition that $\mathbf{n}$ is a unit vector requires $\mathbf{n}_0 \cdot \delta\mathbf{n} = 0$, and is automatically satisfied by

$$\delta n_x = -\phi \sin\phi_0, \qquad \delta n_y = \phi \cos\phi_0. \tag{10.3}$$

Physically ϕ corresponds to the fluctuations in the phase of the twisted cholesteric. The other independent component, δn_z, represents a tilting of the cholesteric axis and is a combination of splay and bend.

We assume, for simplicity, that $k_{11} = k_{22} = k$, and introduce Eqs. (10.1)–(10.3) in the Oseen–Frank elastic energy equation (3.16). Retaining only terms quadratic in the small fluctuations, the elastic energy is

$$\Delta G = \tfrac{1}{2}k \int_V d\mathbf{r}[(\nabla\phi)^2 + 4t_0\delta n_z[\cos\phi_0(\partial\phi/\partial x) + \sin\phi_0(\partial\phi/\partial y)] + t_0^2\delta n_z^2 + (\nabla\delta n_z)^2], \tag{10.4}$$

where surface energies have been neglected. This quadratic form can be partially diagonalized by introducing

$$w = \delta n_z + t_0^{-1}[\cos\phi_0(\partial\phi/\partial x) + \sin\phi_0(\partial\phi/\partial y)]. \tag{10.5}$$

Substituting in Eq. (10.4), we find

$$\Delta G = \tfrac{1}{2}k \int dr\{t_0^2 w^2 + (\nabla w)^2 + (\partial\phi/\partial z)^2 + 4(\partial\phi/\partial z)[\sin\phi_0(\partial w/\partial x) - \cos\phi_0(\partial w/\partial y)] + \cdots\}, \tag{10.6}$$

where terms involving higher-order derivatives have been omitted temporarily. This form indicates that fluctuations for which $w = 0$ have a restoring force proportional to q_z^2 for wave vectors along the z axis. For wave vector $q_\perp$, perpendicular to the pitch axis, the restoring force is proportional to a higher power of $q_\perp$ than $q_\perp^2$. To investigate further the long wavelength fluctuations (with wavelength greater than the pitch), we assume w and ϕ in Eq. (10.6) vary slowly compared with the pitch. We may then average Eq. (10.6) over many pitch lengths and, now including terms involving higher derivatives, we find

$$\langle\Delta G\rangle_{\text{av}} = \tfrac{1}{2}k \int_V d\mathbf{r}\left[t_0^2 w^2 + (\nabla w)^2 + \left(\frac{\partial\phi}{\partial z}\right)^2 + \tfrac{1}{2}t_0^{-2}\frac{\partial^2\phi}{\partial z^2}\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right) + \tfrac{1}{2}t_0^{-2}\left(\frac{\partial^2\phi}{\partial x^2} + \frac{\partial^2\phi}{\partial y^2}\right)^2\right]. \tag{10.7}$$

Introducing Fourier transforms gives us

$$\langle\Delta G\rangle_{\text{av}} = \tfrac{1}{2}k \sum_{\mathbf{q}} \{(t_0^2 + q^2) \mid w_{\mathbf{q}} \mid^2 + [q_z^2 + \tfrac{1}{2}t_0^{-2}(q_z^2 q_\perp^2 + q_\perp^4)] \mid \phi_{\mathbf{q}} \mid^2\}. \tag{10.8}$$

The mean square fluctuations in $w_{\mathbf{q}}$ and $\phi_{\mathbf{q}}$ are then

$$\langle \mid w_{\mathbf{q}} \mid^2 \rangle = I_z(\mathbf{q}) = \frac{k_B T}{k(t_0^2 + q^2)} \tag{10.9}$$

$$\langle \mid \phi_{\mathbf{q}} \mid^2 \rangle = I_\phi(\mathbf{q}) = \frac{2t_0^2 k_B T}{k(2t_0^2 q_z^2 + q_z^2 q_\perp^2 + q_\perp^4)}. \tag{10.10}$$

Equation (10.9) shows that fluctuations in $w_{\mathbf{q}}$, and hence $\delta n_{z\mathbf{q}}$, do not diverge as $q \rightarrow 0$. This indicates that this variable is not a hydrodynamic variable (it is also shown below that the relaxation frequency for fluctuations in $\delta n_{z\mathbf{q}}$ does not vanish as $q \rightarrow 0$). On the other hand, the fluctuations in the phase $\phi_{\mathbf{q}}$ do diverge as $q \rightarrow 0$ and in the case $q_z = 0$ behave as $q_\perp^{-4}$. This has the consequence that the mean square fluctuations in ϕ diverge for an infinite cholesteric. It also has the consequence that the phase of a cholesteric is not correlated over arbitrarily large distances so that the pitch of a cholesteric is not a true order parameter. The arguments are very similar to those used by Landau and Lifshitz (1958, Chap. 13) to show that an extended three-dimensional body with crystalline order in one direction cannot exist. The correlation function for the phase is $\exp[-\Phi(r)]$ where

$$\Phi(\mathbf{r}) = \tfrac{1}{2}\langle(\phi(\mathbf{r}) - \phi(0))^2\rangle = \tfrac{1}{2}(2\pi)^{-3} \int d\mathbf{q}[1 - \exp(i\mathbf{q}\cdot\mathbf{r})]\langle \mid \phi_{\mathbf{q}} \mid^2 \rangle. \tag{10.11}$$

This function has been evaluated by Lubensky (1972a). In the interesting case when $\mathbf{r}$ is along the z axis, we have

$$\Phi(z) = (k_B T t_0/4\sqrt{2}\pi k) \log(z q_m^2/\sqrt{2}t_0), \tag{10.12}$$

where q_m is the maximum wave vector for fluctuations for which Eq. (10.10) applies ($q_m \sim t_0$). This function diverges as $z \rightarrow \infty$ indicating the absence of true long-range order in the phase angle ϕ. Using $T = 300$°K, $t_0 = 3 \times 10^5$ cm^{-1}, and $k = 10^{-6}$ dyn, we have $\Phi(z) \sim 10^{-3} \log z t_0$ which shows that distance at which correlations become small is extremely large. The presence of boundaries or a magnetic field perpendicular to the axis has the effect of stabilizing the structure. These arguments are thus not relevant to samples used in the laboratory.

B. Light scattering from cholesterics

The differential scattering cross section for light is given by Eqs. (8.5) and (8.6). We again assume that the fluctuations in the dielectric constant arise from the director fluctuations and are given by Eq. (8.3). From Eqs. (10.1) and (10.3) the fluctuations in the dielectric constant are given by

$$\delta\epsilon = \mathbf{p}_1 \cdot \delta\boldsymbol{\varepsilon} \cdot \mathbf{p}_0 = \epsilon_a[(\mathbf{p}_0 \cdot \mathbf{n}_0)\mathbf{z} \cdot (\mathbf{n}_0 \times \mathbf{p}_1) + (\mathbf{p}_1 \cdot \mathbf{n}_0)\mathbf{z} \cdot (\mathbf{n}_0 \times \mathbf{p}_0)]\phi + \epsilon_a[(\mathbf{p}_0 \cdot \mathbf{n}_0)(\mathbf{p}_1 \cdot \mathbf{z}) + (\mathbf{p}_1 \cdot \mathbf{n}_0)(\mathbf{p}_0 \cdot \mathbf{z})]\delta n_z. \tag{10.13}$$

Note that $\delta\epsilon$ depends on position both through the fluctuations ϕ and δn_z and $\mathbf{n}_0$. The correlation function for the dielectric fluctuations in Eq. (8.6) can now be expressed in terms of the correlation functions for the director fluctuations defined by

$$I_\phi(\mathbf{r},t) = \langle \phi(\mathbf{r},t)\phi(0,0)\rangle$$
$$I_z(\mathbf{r},t) = \langle \delta n_z(\mathbf{r},t)\delta n_z(0,0)\rangle. \tag{10.14}$$

The differential scattering cross section is again given by Eq. (8.5) with

$$I(\mathbf{q},\omega) = A[I_\phi(\mathbf{q}+2\mathbf{t}_0,\omega) + I_\phi(\mathbf{q}-2\mathbf{t}_0,\omega)] + B[I_z(\mathbf{q}+\mathbf{t}_0,\omega) + I_z(\mathbf{q}-\mathbf{t}_0,\omega)] \tag{10.15}$$

where

$$A = \tfrac{1}{4}\epsilon_a^2(p_{0x}^2+p_{0y}^2)(p_{1x}^2+p_{1y}^2)$$
$$B = \tfrac{1}{4}\epsilon_a^2[(p_{0x}p_{1z}+p_{1x}p_{0z})^2 + (p_{0y}p_{1z}+p_{1y}p_{0z})^2], \tag{10.16}$$

$\mathbf{t}_0$ is a vector of magnitude t_0 along the twist axis, and we have introduced the Fourier transforms of the correlation functions (10.14). In evaluating Eq. (10.15), we have supposed that the dimensions of the scattering region in the cholesteric are much larger than the pitch $2\pi/t_0$. Terms which vary like $\exp[\pm it_0(z_1+z_2)]$ have been neglected because they average to zero.

The total intensity of the scattered light is obtained by integrating Eq. (10.15) over all frequencies and is proportional to

$$I(q) = A[I_\phi(\mathbf{q}+2\mathbf{t}_0) + I_\phi(\mathbf{q}-2\mathbf{t}_0)] + B[I_z(\mathbf{q}+\mathbf{t}_0) + I_z(\mathbf{q}-\mathbf{t}_0)] \tag{10.17}$$

where the correlation functions are given by Eqs. (10.9) and (10.10). The scattering of light by the phase fluctuations diverges at $\mathbf{q} = \pm 2\mathbf{t}_0$, i.e., at exactly those wave vector transfers which lead to first-order Bragg scattering. The light scattering by the splay bend mode is a maximum for $\mathbf{q} = \pm\mathbf{t}_0$, but does not diverge. Only the first order of Bragg scattering enters Eq. (10.17) because we have not considered multiple scattering of the light, i.e., we have stopped at the first Born approximation. This is valid provided ϵ_a is small. The results (10.17) were first given by Pincus (1969c) in the special case where $\mathbf{q}$ is along the pitch axis.

It should be noted that the results of this section are for the case of a perfect cholesteric containing many twists. The wave vector transfer along the pitch axis q_z is assumed less than or comparable with t_0. A cholesteric of very long pitch, i.e., $q_z \gg t_0$ will essentially behave as a nematic.

C. Dynamics of the fluctuations

The dynamics of the fluctuations are described by the linearized hydrodynamic equations for the coupled motion of the director and the fluid velocity. We will again make use of the Ericksen–Leslie hydrodynamic equations of Sec. VI. A different set of hydrodynamic equations for cholesterics has been given by Lubensky (1972b). The orientational modes of hydrodynamical character (which are of greatest interest in light scattering) are almost identical in the two versions of the hydrodynamics. We will assume that the cholesteric is incompressible and ignore any temperature fluctuations.

In the special case where the wave vector of the fluctuation is along the pitch axis, the linearized hydrodynamic equations are particularly simple. The linearized director Eq. (8.14) for the phase fluctuations is (neglecting inertial terms)

$$[\gamma_1(\partial/\partial t) + k_{22}(\partial^2/\partial z^2)]\phi = 0 \tag{10.18}$$

and is not coupled with the fluid velocity. This mode is analogous to the δn_y mode (Eq. 8.25) in nematics. From Eq. (10.18) the phase fluctuations of wave vector q_z are damped with a damping constant

$$\Gamma_{\phi q} = k_{22}q_z^2/\gamma_1. \tag{10.19}$$

The case where the wave vector q is perpendicular to the twist axis has been investigated by Lubensky (1972b) and an overdamped mode very similar to Eq. (10.19) was found. The correlation function in Eq. (10.15) for either mode is given by

$$I_\phi(\mathbf{q},\omega) = [2\Gamma_{\phi q}/(\omega^2+\Gamma_{\phi q}^2)]I_\phi(\mathbf{q}). \tag{10.20}$$

In the light scattering this function is evaluated at $\mathbf{q}+2\mathbf{t}_0$, and thus the linewidth remains finite as $q\to 0$.

The δn_z mode has been investigated by Fan *et al.* (1970) for q along the pitch axis. They showed that this mode is overdamped with a damping constant

$$\Gamma_{zq} = \frac{(k_{33}t_0^2 + k_{11}q_z^2)(\alpha_3+\alpha_4+\alpha_6)}{\gamma_1(\alpha_4+\alpha_6) - \gamma_2\alpha_3}. \tag{10.21}$$

This mode is not strictly a hydrodynamic mode as Γ_{zq} does not vanish as $q\to 0$.

Rapidly damped shear wave modes also exist in cholesterics and have been investigated by Fan *et al.* (1970), Lubensky (1972b), and Brochard (1971), and have a similar character to those in nematics. Shear wave reflectance measurements on cholesterics have been made by Martinoty and Candau (1972a,b).

XI. SURFACE WAVES ON NEMATICS

The surface (or capillary) waves on nematics provide a further application of the hydrodynamic equations of Sec. VI. These waves have been observed by Langevin (1972) in PAA and MBBA by light scattering from the free surface. The spectral distribution of the scattered light gives information on the surface tension and viscosity coefficients. The dispersion relation for surface waves in nematics has been determined from the hydrodynamic equations by Papoular (1969a), Papoular and Rapini (1969), and by Langevin and Bouchiat (1972). The form of this dispersion relation depends on (a) the boundary conditions at the surface; (b) the orientation of the molecules at the surface. We will assume that the surface is a free surface, i.e., nematic liquid-vapor. The orientation of the molecules in PAA and MBBA at a free surface has been investigated, using light reflection techniques, by Bouchiat and Langevin-Cruchon (1971). They found that in PAA the preferred direction of the molecules lies in the plane of the surface, while in MBBA the preferred direction makes an angle ∼ 15° to the normal to the surface and is temperature-dependent.

In the case of surface waves in nematics we will assume that the forces which determine the orientation of the molecules at the surface are strong and even when the surface is distorted by the wave, the director makes a fixed angle with the normal to the surface. In this case it has been shown by Langevin and Bouchiat (1972) that the dispersion relation for surface waves on nematics is very similar to that for surface waves on normal liquids. The effective viscosity coefficient entering this relation depends on the angle between the wave vector $\mathbf{q}$ of the surface wave and $\mathbf{n}_{||}$, the projection of the director on the surface. The orientation of the director is generally determined by the applied magnetic field H assumed to be parallel to the surface. Owing to the similarity between surface waves on normal liquids and nematics, we first briefly discuss surface waves on normal liquids (Landau and Lifshitz, 1959, Chap. 7).

A. Surface waves on normal liquids

The equation of motion of the liquid (assumed incompressible) is given by the Navier–Stokes equation

$$\rho(\partial v_i/\partial t) + \nabla_j T_{ij} = 0 \qquad (11.1)$$

where the stress tensor is

$$T_{ij} = P\delta_{ij} - \eta(\partial v_i/\partial x_j + \partial v_j/\partial x_i), \qquad (11.2)$$

where P is the pressure and η is the shear viscosity coefficient. We neglect the effects of gravity which are only important at very long wavelengths. The liquid occupies the half-space $z < 0$ with the undisturbed surface the plane $z = 0$. We require a solution of Eq. (11.1) which vanishes as $z \to -\infty$ and satisfies the boundary condition that the surface stresses vanish at the free surface

$$T_{ij}b_j - P_0 b_i = \sigma[(R_1)^{-1} + (R_2)^{-1}]b_i, \qquad (11.3)$$

where $\mathbf{b}$ is a unit vector normal to the surface, P_0 is the external pressure, σ is the surface tension coefficient, and R_1 and R_2 are the principal radii of curvature of the surface. For small vertical displacements $\zeta(x, y)$ of the surface

$$(R_1)^{-1} + (R_2)^{-1} = -(\partial^2/\partial x^2 + \partial^2/\partial y^2)\zeta(x, y). \qquad (11.4)$$

The solution of Eq. (11.1) takes the form

$$\begin{aligned} \zeta(x, y) &= \zeta \exp(iqx - i\omega t), \\ v_x &= v_x(z) \exp(iqx - i\omega t), \\ v_z &= v_z(z) \exp(iqx - i\omega t), \\ P &= P_0 + P_1(z) \exp(iqx - i\omega t), \end{aligned} \qquad (11.5)$$

assuming that the surface wave propagates in the x direction. With this geometry no surface wave involving v_y is possible. By substituting Eq. (11.5) in (11.1) and using the condition that the liquid is incompressible

$$iqv_x + v_z' = 0 \qquad (11.6)$$

we obtain

$$\begin{aligned} (-i\omega\rho + \eta q^2)v_x - \eta v_x'' + iqP_1 &= 0 \\ (-i\omega\rho + \eta q^2)v_z - \eta v_z'' + P_1' &= 0, \end{aligned} \qquad (11.7)$$

where a prime indicates differentiation with respect to z. The solution of these equations may be taken in the form

$$\begin{aligned} v_x(z) &= A_x \exp(mz), \\ v_z(z) &= A_z \exp(mz), \\ P_1(z) &= P_1 \exp(mz). \end{aligned} \qquad (11.8)$$

Substituting Eq. (11.8) in (11.6) and (11.7) we obtain

$$\begin{aligned} iqA_x + mA_z &= 0 \\ (-i\omega\rho + \eta(q^2 - m^2))A_x + iqP_1 &= 0 \\ (-i\omega\rho + \eta(q^2 - m^2))A_z + mP_1 &= 0. \end{aligned} \qquad (11.9)$$

The allowed values of m are determined by setting the determinant of the coefficients of Eq. (11.9) equal to zero. This gives

$$(-i\omega\rho + \eta(q^2 - m^2))(q^2 - m^2) = 0 \qquad (11.10)$$

which has the two solutions

$$m_1 = q, \qquad m_2 = (q^2 - i\omega\rho/\eta)^{1/2}. \qquad (11.11)$$

The solution with $\mathrm{Re}\, m > 0$ is always to be taken, in order to satisfy the boundary condition at $z = -\infty$. The fluid velocity and pressure in the bulk of the liquid are

$$\begin{aligned} v_x(z) &= A_1 \exp(qz) + A_2 \exp(m_2 z), \\ v_z(z) &= -i[A_1 \exp(qz) + (q/m_2)A_2 \exp(m_2 z)], \\ P_1(z) &= (\omega\rho/q)A_1 \exp(qz). \end{aligned} \qquad (11.12)$$

The coefficients A_1 and A_2 are to be chosen to satisfy the boundary condition (11.3). Substituting Eq. (11.12) in (11.3) we obtain

$$\begin{aligned} (\omega\rho + 2i\eta q^2)A_1 + 2i\eta q^2 A_2 &= \sigma q^3 \zeta \\ 2qm_2 A_1 + (q^2 + m_2^2)A_2 &= 0. \end{aligned} \qquad (11.13)$$

There is a further consistency condition $v_z(z = 0) = \partial\zeta/\partial t$ which can be written

$$\omega\zeta = A_1 + (q/m_2)A_2. \qquad (11.14)$$

These equations lead to the dispersion relation

$$D_0(\omega) = 0$$

where

$$D_0(\omega) = \sigma q^3/\rho - (\omega + 2i\eta q^2/\rho)^2 - 4\eta^2 m_2 q^3/\rho^2. \qquad (11.15)$$

The solution of Eq. (11.15) depends on the magnitude of the dimensionless quantity $\sigma\rho/\eta^2 q$.

(i) $q < \sigma\rho/\eta^2$. For long wavelengths and small viscosity, the solutions of Eq. (11.15) are approximately

$$\omega = \pm(\sigma/\rho)^{1/2} q^{3/2} - (2i\eta q^2/\rho) \qquad (11.16)$$

and correspond to propagating waves.

(ii) $q > \sigma\rho/\eta^2$. For short wavelengths and large viscosity, there are two solutions of Eq. (11.15), ω_s and ω_F, corresponding to slowly and rapidly damped waves:

$$\begin{aligned} \omega_S &\simeq -i(\sigma q/\eta) \\ \omega_F &\simeq -i(\eta q^2/\rho)c, \end{aligned} \qquad (11.17)$$

where $c = 0.91262\ldots$is a solution of $[1-(c/2)]^2 = (1-c)^{1/2}$. The rapidly damped wave is analogous to a shear wave in the bulk liquid.

The spectral intensity of the mean square fluctuations of the surface have been given by Bouchiat and Meunier (1971):

$$P(\omega) = (k_B T q/\pi\omega\rho)\,\mathrm{Im} D_0^{-1}(\omega). \qquad (11.18)$$

The spectral intensity of the scattered light is proportional to $P(\omega)$.

B. Surface waves on nematics

The discussion of surface waves on nematics follows the same general lines as in normal liquids. An additional feature is provided by the coupling between orientational fluctuations and the fluid velocity. As above, the nematic occupies the half-space $z < 0$, and the unperturbed free surface of the nematic is the plane $z = 0$. The equations of motion of the fluid (assumed incompressible) are (see Sec. VI.A)

$$\rho(\partial v_i/\partial t) + (\partial/\partial x_j)(t_{ij} + T_{ij}) = 0 \qquad (11.19)$$

$$f_i + f_i' + (\partial/\partial x_j)\Pi_{ij} = 0, \qquad (11.20)$$

where nonlinear terms have been neglected and the stress tensor t_{ij} is given by Eq. (6.11). Equation (11.20) is the director equation, Π_{ij} and f_i arise from the elastic restoring forces and applied field, and f_i' is given by Eq. (6.14). The boundary conditions at the free surface are the same as for Eq. (11.3):

$$t_{ij} b_j - P_0 b_i = \sigma[(R_1)^{-1} + (R_2)^{-1}] b_i. \qquad (11.21)$$

The surface tension σ is necessarily the same in all directions, i.e., the orientation of the director does not affect the surface stress. The simplest situation is where the director in the unperturbed state $\mathbf{n}_0$ lies in the free surface and parallel to an applied field H (as in the case of PAA). We consider the two special cases below: (a) $\mathbf{q} \perp \mathbf{n}_0$, (b) $\mathbf{q} \parallel \mathbf{n}_0$, where q is the wave vector of the surface wave. The case where the director makes an angle with the surface (e.g., MBBA) is considered in (c).

(a) $\mathbf{q} \perp \mathbf{n}_0$. The surface wave propagates perpendicular to $\mathbf{n}_0$ which lies in the surface. From symmetry there is no coupling between the director and the fluid velocity. The dispersion relation and spectral intensity of the surface waves are given by Eqs. (11.15) and (11.18), respectively, with the viscosity coefficient η replaced by $\frac{1}{2}\alpha_4$.

(b) $\mathbf{q} \parallel \mathbf{n}_0$. The surface wave propagates parallel to the unperturbed director which lies in the surface. The solution of Eqs. (11.19) and (11.20) can be taken in the form (11.5) together with

$$n_z = n_z(z) \exp(iqx - i\omega t), \qquad (11.22)$$

where n_z is the small displacement of the director in the z direction. From Eq. (6.11) the components of the stress tensor required are

$$\begin{aligned} T_{xx} + t_{xx} &= P - (\alpha_1 + \alpha_4 + \alpha_5 + \alpha_6) d_{xx}, \\ T_{zz} + t_{zz} &= P - \alpha_4 d_{zz} \\ T_{xz} + t_{xz} &= -\alpha_3 N_z - (\alpha_4 + \alpha_6) d_{zx}, \\ T_{zx} + t_{zx} &= -\alpha_2 N_z - (\alpha_4 + \alpha_5) d_{xz}. \end{aligned} \qquad (11.23)$$

Substituting Eq. (11.23) in (11.19), we obtain the equations for the fluid velocity

$$\begin{aligned} &(-i\omega\rho + q^2(\alpha_1 + \alpha_4 + \alpha_5 + \alpha_6)) v_x - \tfrac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6) v_x'' \\ &\quad -\tfrac{1}{2} q(\alpha_4 + \alpha_6 - \alpha_3) v_z' + iqP_1 + i\omega\alpha_3 \eta_z' = 0 \qquad (11.24) \\ &[-i\omega\rho + \tfrac{1}{2} q^2(\alpha_4 + \alpha_5 - \alpha_2) v_z - \alpha_4 v_z'' \\ &\quad -(i/2) q(\alpha_4 + \alpha_5 + \alpha_2) v_x' + P_1' - \omega q \alpha_2 n_z = 0. \end{aligned}$$

The equation for the director (11.20) is

$$\begin{aligned} &(-i\omega\gamma_1 + k_{33} q^2 - k_{11}(\partial^2/\partial z^2) + \chi_a H^2) n_z \\ &\quad -(i/2) q(\gamma_1 - \gamma_2) v_z + \tfrac{1}{2} v_x'(\gamma_1 + \gamma_2) = 0. \end{aligned} \qquad (11.25)$$

This equation can be simplified as the elastic terms and magnetic field terms are small. For $k = 10^{-6}$ dyn, $\chi_a = 10^{-7}$, $H = 3000$ G, and $q \simeq 300$ cm^{-1}, we have $kq^2 \simeq 10^{-1}$ cgs and $\chi_a H^2 \simeq 1$ cgs. These are to be compared with $\omega\gamma_1$ where $\gamma_1 \simeq 0.1$ poise and ω is the frequency shift which may be several MHz. With neglect of these terms Eq. (11.25) becomes

$$-i\omega\gamma_1 n_z - (i/2) q(\gamma_1 - \gamma_2) v_z + \tfrac{1}{2}(\gamma_1 + \gamma_2) v_x' = 0. \qquad (11.26)$$

This approximation has the following consequence. The boundary condition $t_{xz} = 0$ gives

$$\alpha_3 N_z + (\alpha_4 + \alpha_6) d_{zx} = 0, \qquad z = 0. \qquad (11.27)$$

From Eq. (11.26) evaluated at $z = 0$, we then find

$$(d_{zx})_{z=0} = 0, \qquad (N_z)_{z=0} = 0. \qquad (11.28)$$

The first boundary condition is the same as in a normal fluid. The second requires that the molecules at the surface always remain parallel to the surface.

Equations (11.24) are simplified by using (11.26) to eliminate n_z and the condition $\nabla\cdot\mathbf{v} = 0$:

$$[-i\omega\rho + q^2(\eta_3' + 3\eta_1' - 2\eta_2')]v_x - \eta_1' v_x'' + iqP_1 = 0$$
$$(-i\omega\rho + q^2\eta_1')v_z - (2\eta_2' - \eta_1')v_z'' + P_1' = 0. \qquad (11.29)$$

Apart from the different viscosity coefficients, these equations are of exactly the same form as Eq. (11.7) for a normal fluid. The viscosity coefficients entering Eq. (11.29) are

$$2\eta_1' = \alpha_4 + \alpha_6 - \alpha_3(\gamma_2/\gamma_1), \qquad 2\eta_2' = \alpha_4$$
$$\eta_3' + 4\eta_1' = \alpha_1 + 2\alpha_4 + \alpha_5 + \alpha_6. \qquad (11.30)$$

This is the notation of Langevin and Bouchiat (1972) and differs from Miesowicz (Table I). The solution of Eq. (11.29) is taken in the form (11.8) and it is found that the solutions for m are

$$2\eta_1' m_{\substack{1\\2}}^2 = (\eta_3' + 2\eta_1')q^2 - i\omega\rho \pm[q^4(\eta_3'^2 + 4\eta_1'\eta_3') - 2i\omega\rho\eta_3' q^2 - \omega^2\rho^2]^{1/2}. \qquad (11.31)$$

The dispersion relation for the surface modes is

$$D_n(\omega) = 0 \qquad (11.32)$$

with

$$D_n(\omega) = \sigma q^2(m_2^2 - m_1^2) - \rho\omega^2[(m_2^2 + q^2)m_1^{-1} - (m_1^2 + q^1)m_2^{-1}] - i\omega\eta_1'(m_1^2 + q^2)(m_2^2 + q^2)[(m_1)^{-1} - (m_2)^{-1}]. \qquad (11.33)$$

The solutions of Eq. (11.32) again depend on the quantity $\sigma\rho/\eta^2 q$ where η is a typical viscosity coefficient. For typical values of the parameters, $\sigma\rho/\eta^2 \sim 10^4\ \text{cm}^{-1}$.

(i) $q < \sigma\rho/\eta^2$. The solutions of Eq. (11.32) correspond to propagating waves with

$$\omega = \pm(\sigma/\rho)^{1/2}q^{3/2} - (2iq^2/\rho)(\eta_1' + \tfrac{1}{8}\eta_3'). \qquad (11.34)$$

(ii) $q > \sigma\rho/\eta^2$. As in the case of a normal liquid, we obtain a slowly damped and rapidly damped wave. For the slowly damped wave, the solutions of Eq. (11.31) are approximately

$$m_{\substack{1\\2}} = q[1 + \eta_3'/2\eta_1' \pm (\eta_3'/\eta_1' + \eta_3'^2/4\eta_1'^2)^{1/2}]^{1/2}. \qquad (11.35)$$

From Eq. (11.33), neglecting the second term, for the slowly damped wave

$$\omega_S = -\frac{i\sigma q^2}{\eta_1'}\frac{(m_1 + m_2)}{m_1 m_2(1 + m_1^2)(1 + m_2^2)}. \qquad (11.36)$$

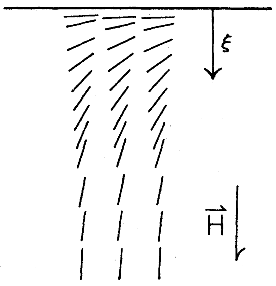

FIG. 21. The free surface in a perpendicular field. The director lies parallel to the free surface but reorients to be parallel to the field in a distance ξ.

The solution for the rapidly damped wave is of the form

$$\omega_F = -(i\eta_1' q^2/\rho)c, \qquad (11.37)$$

where c is a constant.

It should be noted that the dispersion relation has the particular solution $m_1 = m_2$. It has been shown by Langevin and Bouchiat (1972) that for the special value of the frequency satisfying this relation, no special feature appears in the light scattering spectrum.

The spectral intensity of the scattered light is given by

$$P_n(\omega) = (k_B T/\pi\omega)\,\text{Im}[(m_2^2 - m_1^2)/D_n(\omega)]. \qquad (11.38)$$

(c) We briefly consider situations where the director makes an angle with the free surface. Langevin and Bouchiat (1972) have considered the case where the director lies parallel to the free surface and a field H is applied perpendicular to the surface (see Fig. 21). When $q\xi \ll 1$, where ξ is the magnetic coherence length, the spectrum of surface waves reduces to Eq. (11.38), i.e., case (b), $\mathbf{q} \parallel \mathbf{n}_0$. If $q\xi \leq 0.1$, the spectrum of surface waves may be shown to be equivalent to that of a nematic with $\mathbf{q} \parallel \mathbf{n}_0$ and covered with a film of thickness ξ and a viscosity coefficient depending on η_1', η_2', and η_3' of Eq. (11.30).

In the case where the director $\mathbf{n}_0$ makes an angle with the surface and $q\xi < 0.1$ the spectrum of surface waves in a vertical field or a horizontal field $\mathbf{H} \parallel \mathbf{q}$ is that of case (b) and in a horizontal field $\mathbf{H} \perp \mathbf{q}$ is that of case (a) above.

In summary the spectrum of surface waves in nematics gives information on the surface tension σ and α_4 when $\mathbf{H} \perp \mathbf{q}$ and on σ and $\eta_1' + \frac{1}{8}\eta_3'$ when $\mathbf{H} \parallel \mathbf{q}$ in the interesting case of small viscosities.

The light scattered from a free surface of two liquid crystals, PAA and MBBA, has been observed by Langevin (1972). In PAA where the director lies in the surface the viscosity is small and the spectrum can be analyzed in terms of Eq. (11.34). No anisotropy in the spectrum was observed for $\mathbf{H} \perp \mathbf{q}$ and $\mathbf{H} \parallel \mathbf{q}$. The surface tension and viscosity coefficients deduced from the measurements at 122°C were $\sigma = 38 \pm 4$ dyn/cm and $\eta_2' = \eta_1' + \eta_3'/8 = 0.036 \pm 0.004$ P. From Table I $\eta_2' = \eta_3$, and this value is in good agreement with that of Miesowicz (Table II).

In MBBA the director makes an angle of 75° with the surface and the viscosity is much greater than PAA. This makes the analysis of the spectrum more difficult and we refer the reader to the paper of Langevin (1972) for details.

XII. SOUND PROPAGATION

There have been a number of recent experimental studies on the velocity and absorption of sound in the liquid crystal MBBA (Martinoty and Candau, 1970; Lord and Labes, 1970; Mullen *et al.*, 1972; Wetsel *et al.*, 1972; Natale and Commins, 1972; Eden *et al.*, 1973), and in PAA (Kemp and Letcher, 1971). Earlier work on the ultrasonic properties of liquid crystals has been reviewed by Edmonds and Orr (1966). The velocity of sound s is of the same order ($\sim 10^5$ cm/sec) as found in ordinary liquids. The experiments of Mullen *et al.* (1972) on MBBA oriented in a magnetic field show that in the frequency range 2–10 MHz there is a small anisotropy in the sound velocity. They found $s_{||} - s_{\perp} \sim 10^{-3}s$ where $s_{||}$ and $s_{\perp}$ are the sound velocities for propagation parallel and perpendicular to the director. The absorption of sound is very anisotropic and strongly temperature-dependent (Lord and Labes, 1970; Natale and Commins, 1972). Eden *et al.* (1973) have studied the velocity and absorption of sound in MBBA over a wide range of temperatures and frequencies. For $T \ll T_c$ in the nematic phase the dispersion in the velocity and absorption can be well described by a single relaxation process. In the vicinity of the transition the properties of MBBA are characteristic of a multiply relaxing fluid. The sound velocity shows a pronounced minimum and the absorption a maximum for $T \sim T_c$.

There have been a number of theoretical studies of the dispersion in the velocity and absorption of sound in liquid crystals. Hoyer and Nolle (1956) have interpreted the pretransitional effects in the sound velocity and absorption in terms of the Frenkel concept of heterophase fluctuations. Edmonds and Orr (1966) have discussed the sound dispersion and absorption by use of an analogy with the behavior of normal liquids in the vicinity of a critical point. A more quantitative discussion has recently been given by Imura and Okano (1973b). The temperature dependence of the sound velocity has been discussed by Kapustin and Mart'yanova (1971) using the Maier–Saupe theory. The hydrodynamic equations for liquid crystals have recently been generalized by Jähnig (1973a) to include a frequency dependence of the elastic and dissipative parameters arising from slowly relaxing internal processes. The equations have been used to discuss the dispersion in the velocity and absorption of sound.

A. Sound velocity

The experimental observation of the anisotropy in the sound velocity in MBBA indicates that at the frequencies used (2–10 MHz) the liquid crystal has some of the properties of an anisotropic solid, in that the compressibility is different parallel and perpendicular to the director. According to our present ideas about the structure of liquid crystals they should behave as liquids at sufficiently low frequencies, and the compressibility should be isotropic. The observed anisotropy is probably the result of a slow relaxation process in the liquid crystal. The observations of Mullen *et al.* (1972) indicate a relaxation time of approximately 10^{-8} sec. Jähnig (1973b) has suggested that this relaxation process is associated with the flexibility of the hydrocarbon chains. We note that the relaxation time for an orientational fluctuation of wave vector q is of order kq^2/η (see Sec. VIII, C), where k is an elastic constant and n is a viscosity coefficient. Using $k = 10^{-6}$ dyn, $\eta = 0.1$ P and $s = 10^5$ cm/sec, we see that for all experimentally attainable wave vectors $sq > kq^2/\eta$. This indicates that the director does not relax appreciably during a period of oscillation of the sound wave.

The experimental results on the sound velocity anisotropy can be interpreted in terms of the elastic properties of a simple model. At these frequencies a liquid crystal in some respects behaves like a solid, and the elastic free energy density contains terms like

$$F_{\mathrm{el}} = \tfrac{1}{2}C_{11}(u_{xx} + u_{yy})^2 + C_{13}u_{zz}(u_{xx} + u_{yy}) + \tfrac{1}{2}C_{33}u_{zz}^2 \tag{12.1}$$

when the C_{ij} are elastic constants and the u_{ij} are elastic strains. The director has been chosen to be along the z axis. This elastic energy density is similar to that for a uniaxial solid except all terms relating to shears have been set equal to zero. The additional relation $C_{13}^2 = C_{11}C_{33}$ eliminates propagating shear wave modes. The ratio of the compressibilities parallel and perpendicular to the director is C_{11}/C_{33} and the sound velocity is given by

$$s^2 = \rho^{-1}[C_{11} + (C_{33} - C_{11}) \cos^2\theta], \tag{12.2}$$

where θ is the angle between $\mathbf{q}$ and the director. This angular dependence is consistent with the observations of Mullen *et al.* (1972) and the sound speed anisotropy

$$\Delta = \frac{s_{||} - s_{\perp}}{s_{||} + 2s_{\perp}} = \frac{3[(C_{33})^{1/2} - (C_{11})^{1/2}]}{(C_{33})^{1/2} + 2(C_{11})^{1/2}} \tag{12.3}$$

is of order 10^{-3}. A single relaxation time approximation for the frequency dependence of the anisotropy gives

$$C_{33}(\omega) - C_{11}(\omega) = \text{const}\, \omega^2\tau_s^2(1 + \omega^2\tau_s^2)^{-1}. \tag{12.4}$$

The observed frequency dependence of the velocity anisotropy was closer to linear than that given by Eq. (12.4). The relaxation time τ_s was estimated to be $\sim 10^{-8}$ sec.

In cholesterics a small anisotropy in the sound velocity, independent of frequency, has been calculated by Lubensky (1972b). The velocity was found to be slightly higher along the pitch axis and the anisotropy $\Delta = k_{22}t_0^2/2\rho s^2$. For $k_{22} = 10^{-6}$ dyn, $t_0 = 10^5$ cm^{-1}, and $s = 10^5$ cm sec^{-1}, we have $\Delta = 10^{-6}$. This effect is probably too small to be measured and would be masked by relaxation effects. The possible existence of a slow structural relaxation process in cholesterics has been pointed out by Papoular (1970). He estimated that the time τ_{sp} for the pitch to relax to its equilibrium value is $\tau_{sp}^{-1} \simeq k_{22}t_0^2/\eta$, where η is a viscosity coefficient. Using the above values and $\eta = 0.1$ P, $\tau_{sp} \sim 10^{-5}$ sec. This relaxation process could couple with the sound wave through the pressure dependence of t_0 and would lead to a dispersion in the sound velocity in the range $\omega\tau_{sp} \sim 1$ of the same form as Eq. (12.4). The sound attenuation would show a dispersion proportional to $\omega\tau_{sp}(1 + \omega^2\tau_{sp}^2)^{-1}$.

The sound velocity shows a pronounced minimum as T_c is approached. This can be understood qualitatively as arising from the increase in the specific heat as the transition is approached (Kapustin and Mart'yanova, 1971). We write the free energy density as the sum of two parts

$$F = F_i + F_0(T - T_c^{**}), \qquad (12.5)$$

where F_i is the free energy density of the isotropic phase and F_0 is the contribution of the ordering and is assumed to depend on $T - T_c^{**}$ where T_c^{**} is the superheating critical temperature. Then, neglecting for simplicity the difference between the adiabatic and isothermal sound velocities, we have approximately

$$\begin{aligned} s^2 &= \rho(\partial^2 F_i/\partial\rho^2) + \rho(\partial^2 F/\partial T^2)(\partial T_c^{**}/\partial\rho)^2 \\ &= s_i^2 - \rho C(\partial T_c^{**}/\partial\rho)^2/T, \end{aligned} \qquad (12.6)$$

where s_i is the sound velocity in the isotropic phase, and C is the specific heat. The increase in C leads to a decrease in the sound velocity as T_c is approached, in qualitative agreement with the observations of Mullen *et al.* (1972) and Eden *et al.* (1973).

B. Absorption of sound

The sound absorption can be related to the viscosity coefficients discussed in Sec. VI. The simplest discussion is based on the entropy production function R [Eq. (6.13)]. As discussed in the previous section we may assume that the director relaxes so slowly relative to this period of oscillation of the sound wave that the terms involving $\dot{\mathbf{n}}$ can be neglected. For longitudinal sound propagating in the z direction (not necessarily parallel to the director) from the equation of continuity

$$\rho_0 d_{zz} = -\partial\rho/\partial t = \rho_1\omega\sin(\omega t - qz), \qquad (12.7)$$

where ρ_1 is the amplitude of the density fluctuation. All other components of d_{ij} vanish. The rate of entropy production (loss of energy from the wave) is

$$TR = -d_{zz}t_{zz} = (\rho_1^2/\rho_0^2)\omega^2\sin^2(\omega t - qz)\mu(\theta), \qquad (12.8)$$

where

$$\mu(\theta) = \mu_1 + \mu_7 + (\mu_2 + \mu_3 + \mu_8 + \mu_9)n_z^2 + \mu_4 n_z^4 \qquad (12.9)$$

and the μ_i are the viscosity coefficients defined in Eq. (6.50). The sound attenuation constant α is the fractional loss in amplitude per unit length. This is $\frac{1}{2}$ the ratio of the average energy loss TR to the energy transport $E = \frac{1}{2}(\rho_1^2/\rho_0^2)s^3$. Thus

$$\alpha(\theta) = \tfrac{1}{2}(\omega^2/\rho_0 s^3)\mu(\theta). \qquad (12.10)$$

The anisotropy of the sound attenuation has been measured in MBBA by Lord and Labes (1970), Wetsel *et al.* (1972), and Natale and Commins (1972), and in PAA and *p*-azoxyphenetole (PAP) by Kemp and Letcher (1971). From the angular dependence the latter authors were able to obtain values for some viscosity coefficients in PAA and PAP. In MBBA the anisotropy in the absorption varied approximately linearly with the frequency in the range 2–6 MHz while in PAA the absorption was frequency-independent in the range 5–18 MHz.

C. Dispersion

We consider in this section the effect of a relatively slow internal relaxation process (with time scale comparable to the ultrasound period) on the velocity and absorption of sound. The hydrodynamics of liquid crystals has been generalized by Jähnig (1973) to include a frequency dependence of the elastic and dissipative parameters. The treatment of Jähnig is based on the general theory of Rytov (1958, 1970). A simple discussion is contained in Landau and Lifshitz (1959, Chap. 8).

In the presence of a slow internal relaxation process for a parameter (for example, the order parameter S), the assumption that local thermodynamic equilibrium is established in a time short compared to the period of the sound wave is not justified. In the simplest case it is assumed that the internal parameter is governed by an equation

$$\partial S/\partial t = -\tau^{-1}(S - S_0). \qquad (12.11)$$

We have chosen the order parameter as an example of an internal parameter, and τ is the relaxation time for S to relax to its equilibrium value S_0. Assuming $S' = S - S_0$ has the time dependence $\exp(-i\omega t)$, we have

$$(1 - i\omega\tau)S' = (\partial S_0/\partial\rho)\rho', \qquad (12.12)$$

where ρ' is the density fluctuation produced by the sound wave. The pressure fluctuation may be shown to be (Landau and Lifshitz, 1959)

$$P' = s_0^2 + (s_0^2 - s_\infty^2)[\rho_0\tau/(1 - i\omega\tau)]\nabla\cdot\mathbf{v}, \qquad (12.13)$$

where

$$s_0^2 = (\partial P/\partial\rho)_{eq}, \qquad s_\infty^2 = (\partial P/\partial\rho)_S. \qquad (12.14)$$

The sound velocities s_0 and s_∞ apply in the two cases (a) $\omega\tau < 1$, (b) $\omega\tau > 1$. In (a) the order parameter relaxes to its local equilibrium value in a time short compared with the period of the sound wave, while in (b) the frequency of the sound is so high that the order parameter does not relax. From Eq. (12.13) we see that there is an additional contribution to the bulk viscosity of

$$\zeta = \rho\tau(s_\infty^2 - s_0^2)/(1 - i\omega\tau) \qquad (12.15)$$

which depends on the frequency. Neglecting all other dissipative processes, the dispersion relation for a sound wave of frequency ω and wave vector q is

$$\omega^2/q^2 = s_0^2 + (s_0^2 - s_\infty^2)[i\omega\tau/(1 - i\omega\tau)]. \qquad (12.16)$$

solving for q we obtain

$$\begin{aligned} q &= (\omega/s_0) + (i\omega^2\tau/2s_0^3)(s_\infty^2 - s_0^2), \qquad \omega\tau < 1 \\ q &= (\omega/s_\infty) + i[(s_\infty^2 - s_0^2)/2\tau s_\infty^3], \qquad \omega\tau > 1. \end{aligned} \qquad (12.17)$$

When $\omega\tau < 1$, the attenuation is proportional to the square of the frequency, and the sound velocity is s_0. In the opposite case of high frequencies, $\omega\tau > 1$, the sound velocity is s_∞, and the attenuation is independent of frequency. The attenuation has a maximum at the frequency given by $\omega\tau = (s_\infty/s_0)^{1/2}$.

The dispersion in the sound velocity and absorption have been studied in MBBA by Eden *et al.* (1973). For $T \ll T_c$ the dispersion is well described by a single relaxation time $\tau \sim 10^{-8}$ sec. The relaxation time and the strength $s_\infty^2 - s_0^2$ increase substantially as T_c is approached. In the vicinity of T_c the acoustic properties are complex and characteristic of a multiply relaxing fluid.

XIII. APPLICATIONS OF MOLECULAR FIELD THEORY

The molecular field description of the nematic–isotropic or cholesteric–isotropic transition was developed in Sec. II. We now consider some applications of this theory to phenomena in liquid crystals at temperatures close to the transition temperature T_c. A number of pretransitional effects connected with fluctuations in the order parameter $S_{\alpha\beta}$ can be observed just above T_c. These pretransitional or short-range order effects have been discussed by de Gennes (1969a, 1971a).

A. Magnetic birefringence

Above T_c the order parameter is small and in the presence of a uniform field the free energy density [Eq. (2.1)] is

$$g - g_i = \tfrac{1}{2}A S_{\alpha\beta}S_{\alpha\beta} - \tfrac{1}{2}\chi_a H_\alpha H_\beta S_{\alpha\beta} \tag{13.1}$$

where summation over repeated indices is implied.

We have omitted the cubic and quartic terms in Eq. (2.1) because they are small. The equilibrium value of the order parameter is determined by minimizing Eq. (13.1) with respect to $S_{\alpha\beta}$ subject to the condition that $S_{\alpha\beta}$ have vanishing trace. This condition is relaxed by means of a Lagrange multiplier γ; thus

$$A S_{\alpha\beta} - \chi_a H_\alpha H_\beta + \gamma\delta_{\alpha\beta} = 0. \tag{13.2}$$

The condition $S_{\alpha\alpha} = 0$ gives $\gamma = \frac{1}{3}\chi_a H^2$ and then

$$S_{\alpha\beta} = (\chi_a/A)(H_\alpha H_\beta - \tfrac{1}{3}H^2\delta_{\alpha\beta}). \tag{13.3}$$

It has been shown by de Gennes (1971a) that any tensor property with the same symmetry as $S_{\alpha\beta}$ will be proportional to $S_{\alpha\beta}$ if $S_{\alpha\beta}$ is small. Thus the dielectric anisotropy can be written

$$\delta\epsilon_{\alpha\beta} = (M\chi_a/A)(H_\alpha H_\beta - \tfrac{1}{3}H^2\delta_{\alpha\beta}), \tag{13.4}$$

where M is a constant of proportionality. We denote by $n_{||}$ and $n_\perp$ the refractive indices for a light wave polarized parallel and perpendicular to the magnetic field. From Eq. (13.4)

$$\begin{aligned} n_{||}^2 - n_\perp^2 &= M\chi_a H^2/A \\ &= \alpha(T)H^2. \end{aligned} \tag{13.5}$$

Since M and χ_a are not expected to behave anomalously at T^*, this predicts that $\alpha(T) \sim (T - T^*)^{-1}$. Thus α^{-1} should extrapolate to zero at T^* (but the interval beyond T_c cannot be observed), and vary linearly with temperature above T_c [in principle, $\alpha(T)$ could have a slightly stronger nonanalytic singularity at T^*, as occurs with conventional critical phenomena. Since the critical region is hidden from us, it is probably fruitless to introduce this sophistication.] Near T_c, α may be much larger than in other organic liquids, approximately according to the enhancement

$$\alpha(T_c)/\alpha(2T_c) = T_c/(T_c - T^*). \tag{13.6}$$

Measurements of the magnetic birefringence in MBBA have been made by Stinson and Litster (1970) who find that the linear law $\alpha^{-1}(T) \sim T - T^*$ is well obeyed. T^* is within a few degrees of T_c giving an enhancement of about 100 from Eq. (13.6). This should be contrasted with the prediction of the Maier–Saupe theory which gives [see Eq. (2.21)]

$$T_c/(T_c - T^*) = 0.22A_0/(0.22A_0 - 0.20A_0) = 10. \tag{13.7}$$

B. Elastic constants and coherence lengths in nematics

We now consider a nematic liquid crystal in which the order parameter is slowly varying in space. The free energy will contain terms which depend on the gradient of the order parameter. These terms must be scalars and consistent with the symmetry of a nematic. If we confine ourselves to terms of $O(S^2)$, the most general form for the inhomogeneous part of the free energy density is

$$g_{sp} = \tfrac{1}{2}L_1(\nabla_\alpha S_{\beta\gamma})(\nabla_\alpha S_{\beta\gamma}) + \tfrac{1}{2}L_2(\nabla_\alpha S_{\alpha\gamma})(\nabla_\beta S_{\beta\gamma}). \tag{13.8}$$

We will refer to the constants L_1 and L_2 as elastic constants. In the Oseen–Frank curvature elasticity theory (see Sec. III), we found three independent elastic constants for nematics in contrast to just two here. Evidently Eq. (13.8) is only qualitatively correct in the nematic phase; in general it is necessary to retain higher terms in the expansion in S. The elastic constants L_1 and L_2 will depend on T and P, but to a good approximation may be considered to be constants.

In order to obtain the relations between the constants L_1 and L_2 and the Oseen–Frank elastic constants we substitute Eq. (1.6) for a uniaxial liquid crystal in Eq. (13.8):

$$\begin{aligned} g_{sp} = {} & \tfrac{1}{3}(L_1 + \tfrac{1}{6}L_2)(\nabla S)^2 + \tfrac{1}{6}L_2(\mathbf{n}\cdot\nabla S)^2 \\ & + S^2[L_1 n_{\beta,\alpha}n_{\beta,\alpha} + \tfrac{1}{2}L_2(\nabla\cdot\mathbf{n})^2 + \tfrac{1}{2}L_2(\mathbf{n}\cdot\nabla\mathbf{n})^2] \\ & + \tfrac{1}{6}L_2[2(\nabla\cdot\mathbf{n})\mathbf{n} - \mathbf{n}\cdot\nabla\mathbf{n}]\cdot(\nabla S^2). \end{aligned} \tag{13.9}$$

In the case where S is constant this can be reduced to the form found by Oseen and Frank by neglecting terms which only contribute to surface energies and writing

$$n_{\beta,\alpha}n_{\beta,\alpha} = (\nabla\cdot\mathbf{n})^2 + (\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + (\mathbf{n}\cdot\nabla\mathbf{n})^2. \tag{13.10}$$

Then

$$g_{sp} = S^2[(L_1 + \tfrac{1}{2}L_2)(\nabla\cdot\mathbf{n})^2 + L_1(\mathbf{n}\cdot\nabla \times \mathbf{n})^2 + (L_1 + \tfrac{1}{2}L_2)(\mathbf{n}\cdot\nabla\mathbf{n})^2]. \qquad (13.11)$$

Comparison with Eq. (3.14) gives

$$k_{11} = k_{33} = 2S^2(L_1 + \tfrac{1}{2}L_2)$$
$$k_{22} = 2S^2L_1. \qquad (13.12)$$

Thus to order S^2, $k_{11} = k_{33}$ and all three elastic constants vary with temperature like S^2 (Saupe, 1960a). When the magnitude of the order parameter S varies spatially, from Eq. (13.9), there are cross terms between splay and bend and ∇S.

The elastic constants of liquid crystals have been calculated by means of extensions of the Maier–Saupe and Onsager theories (Sec. II) by Nehring and Saupe (1971), Priest (1972, 1973), and Straley (1973a).

Stability of the equilibrium nematic configuration requires that for any deformation the energy Eq. (13.8) must be positive. The necessary conditions can be shown to be

$$L_1 > 0, \qquad L_1 + \tfrac{2}{3}L_2 > 0. \qquad (13.13)$$

It is possible for L_2 to be either positive or negative. It has been shown by de Gennes (1971a) that the orientation of the molecules at a nematic–isotropic liquid interface can depend on the sign of L_2. If $L_2 > 0$ the surface energy is less when the molecules lie parallel to the interface, while if $L_2 < 0$, the surface energy is less in the perpendicular configuration.

It was shown in Sec. VIII,B that the intensity of light scattering by orientational fluctuations in nematics is proportional to $\epsilon_a^2 k_B T/kq^2$, where ϵ_a is the dielectric anisotropy and k is an elastic constant. In the nematic phase $\epsilon_a^2 \sim S^2$ and from Eq. (13.12) $k \sim S^2$ so that the light scattering intensity is only slowly varying with temperature (from the factor k_BT). This is in accord with the observations of Chatelain (1948) on PAA and of Haller and Litster (1970) on MBBA.

Corresponding to the two elastic constants in Eq. (13.8), we can define two coherence lengths

$$\xi_1^2 = L_1/|A|, \qquad \xi_2^2 = |L_2|/|A|. \qquad (13.14)$$

According to the mean field theory both have the form $\xi_0 |(T/T^*) - 1|^{-1/2}$ where ξ_0 is a microscopic length determined by the range of intermolecular forces $\xi_0 \sim 20$ Å. At T_c, using $T_c - T^* \sim 1°\mathrm{K}$, the coherence length is enhanced by a factor of 10–20. The particular combination of ξ_1 and ξ_2 which enters a given problem depends on the type of deformation involved. For qualitative discussion we will assume $\xi_1 \sim \xi_2 \sim \xi$.

C. Elastic constants in cholesterics

The order parameter in cholesterics is also defined by Eqs. (1.1) or (1.3). In optically active materials the magnetic susceptibility tensor is symmetric. The expansion of the free energy in powers of $S_{\alpha\beta}$ is given by Eq. (2.1) (as in the nematic case). New features appear when we consider the terms involving gradients of $S_{\alpha\beta}$. Symmetry allows an additional term besides those given in Eq. (13.8) and for cholesterics

$$g_{sp}^{(c)} = \tfrac{1}{2}L_1(\nabla_\alpha S_{\beta\gamma})(\nabla_\alpha S_{\beta\gamma}) + \tfrac{1}{2}L_2(\nabla_\alpha S_{\alpha\gamma})(\nabla_\beta S_{\beta\gamma}) - 2t_0L_1\epsilon_{\alpha\beta\gamma}S_{\alpha\mu}\nabla_\gamma S_{\beta\mu}, \qquad (13.15)$$

where $\epsilon_{\alpha\beta\gamma}$ is the totally antisymmetric tensor of order three. The last term in $g_{sp}^{(c)}$ is a pseudoscalar which changes sign under inversion: such terms can appear in the free energy of cholesterics but not in nematics. The pitch of the cholesteric is $2\pi/t_0$. When Eq. (1.6) is substituted in (13.15) the last term becomes $+t_0L_1S^2\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n}$, in agreement with the corresponding term in the elastic energy Eq. (3.14).

The equilibrium form of the order parameter in a cholesteric is given by

$$S_{\alpha\beta} = S(n_\alpha n_\beta - \tfrac{1}{3}\delta_{\alpha\beta}) \qquad (13.16)$$

with $n_x = \cos t_0z$, $n_y = \sin t_0z$, and $n_z = 0$. The magnitude of the order parameter S is determined as in the nematic case by minimizing the free energy

$$g^{(c)} = g + g_{sp}^{(c)} \qquad (13.17)$$

where g is given by Eq. (2.1). Substituting Eq. (13.16) in (13.17), we find (when $H = 0$)

$$g^{(c)} - g_i = \tfrac{1}{3}(A - 3L_1t_0^2)S^2 - \tfrac{2}{27}BS^3 + \tfrac{1}{9}CS^4. \qquad (13.18)$$

This is of exactly the same form as in the nematic case, Eq. (2.4), and thus all the results of Section II.A may be taken over for the cholesteric case.

D. Light scattering in nematics above T_c

Light scattering in liquid crystals arises from orientational fluctuations (see Sec. VIII) or equivalently order parameter fluctuations. There is a large increase in these fluctuations as T_c is approached from above. The light scattering intensity with wave vector transfer q is proportional to the spatial Fourier transform of the correlation function of the fluctuations in the dielectric constant:

$$I(q) = \int_V d\mathbf{r}\,\exp(i\mathbf{q}\cdot\mathbf{r})\,\langle\delta\epsilon(r)\,\delta\epsilon(0)\rangle, \qquad (13.19)$$

where $\delta\epsilon = \mathbf{p}_0\cdot\delta\boldsymbol{\varepsilon}\cdot\mathbf{p}_1$, $\mathbf{p}_0$, and $\mathbf{p}_1$ are unit vectors along the directions of polarization of the incident and scattered light, and $\delta\boldsymbol{\varepsilon}$ is the fluctuation in the dielectric tensor. In the isotropic phase $\delta\boldsymbol{\varepsilon}$ is proportional to the order parameter [Eq. (13.4)]

$$\delta\epsilon_{\alpha\beta} = MS_{\alpha\beta} \qquad (13.20)$$

and we can write Eq. (13.19) in terms of the order parameter fluctuations

$$I(q) = M^2 \int d\mathbf{r} \exp(i\mathbf{q}\cdot\mathbf{r}) \langle S_{\alpha\beta}(\mathbf{r}) S_{\gamma\delta}(0) \rangle p_{0\alpha} p_{0\gamma} p_{1\beta} p_{1\delta}. \tag{13.21}$$

The particular component of the order parameter is determined by the polarization of the incident and scattered light.

The mean square fluctuations in the order parameter can be calculated from the free energy density equations (2.1) and (13.8). Introducing the Fourier transform

$$S_{\alpha\beta}(\mathbf{r}) = \frac{1}{(V)^{1/2}} \sum_{q} \exp(i\mathbf{q}\cdot\mathbf{r}) S_{\alpha\beta}(\mathbf{q}),$$
$$S_{\alpha\beta}(-\mathbf{q}) = S_{\alpha\beta}{}^*(\mathbf{q}) \tag{13.22}$$

into Eqs. (2.1) and (13.8) and integrating over the volume V, we find for the fluctuation part of the free energy (omitting cubic and quartic terms)

$$\Delta G = \tfrac{1}{2} \sum_{\mathbf{q}} [(A + L_1 q^2) \mid S_{\alpha\beta}(\mathbf{q}) \mid^2 + L_2 q_\alpha q_\beta S_{\alpha\gamma}(\mathbf{q}) S_{\beta\gamma}{}^*(\mathbf{q})]. \tag{13.23}$$

Without loss of generality we choose $\mathbf{q}$ along the z axis of a Cartesian coordinate system. Making use of the "traceless tensor" condition $S_{\gamma\gamma} = 0$ to eliminate S_{zz}, we find

$$\begin{aligned}\Delta G = \sum_{\mathbf{q}} [&\tfrac{3}{4}(A + L_1 q^2 + \tfrac{2}{3} L_2 q^2) \mid S^+ \mid^2 \\ &+ \tfrac{1}{4}(A + L_1 q^2) \mid S^- \mid^2 \\ &+ (A + L_1 q^2 + \tfrac{1}{2} L_2 q^2)(\mid S_{xz} \mid^2 + \mid S_{yz} \mid^2) \\ &+ (A + L_1 q^2) \mid S_{xy} \mid^2]\end{aligned} \tag{13.24}$$

where we have omitted the argument q and

$$S^{\pm} = S_{xx} \pm S_{yy}. \tag{13.25}$$

The equipartition theorem then gives

$$\langle \mid S^+(q) \mid^2 \rangle = \frac{2k_B T}{3A(1 + \xi_1{}^2 q^2 + \tfrac{2}{3}\xi_2{}^2 q^2)},$$
$$\langle \mid S^-(q) \mid^2 \rangle = 4\langle \mid S_{xy}(q) \mid^2 \rangle = \frac{2k_B T}{A(1 + \xi_1{}^2 q^2)},$$
$$\langle \mid S_{xz}(q) \mid^2 \rangle = \langle \mid S_{yz}(q) \mid^2 \rangle = \frac{\tfrac{1}{2} k_B T}{A(1 + \xi_1{}^2 q^2 + \tfrac{1}{2}\xi_2{}^2 q^2)}. \tag{13.26}$$

The denominators of each of these expressions has the form $A(1 + \xi^2 q^2)$ where ξ^2 is some combination of the coherence lengths (13.14). In a typical light scattering experiment, $q \sim 10^5$ cm^{-1} and since $\xi \sim 10^2$ Å, we have $\xi q \sim 10^{-1}$ and the angular dependence of the scattering is small. The intensity of the light scattering from fluctuations is thus proportional to $(T - T^*)^{-1}$, which becomes large close to T_c with an extrapolated divergence at T^*. This temperature dependence has been verified in MBBA by Stinson and Litster (1970). The small angular dependence of the scattered light in MBBA in the isotropic phase, arising from the factors $\xi^2 q^2$ in Eq. (13.26), has been observed by Stinson and Litster (1973). They were able to determine $\xi_1 = (6.8 \pm 1.0)[(T/T^*) - 1]^{-1/2}$ Å in agreement with the mean field prediction for the temperature dependence. Earlier results by Chu *et al.* (1972) gave a different temperature dependence for ξ_1 (impurities may have been a complicating factor).

E. Light scattering in cholesterics above T_c

The calculation of the light scattering intensity in cholesterics arising from order parameter fluctuations proceeds exactly as in the nematic case in the previous section. The only difference is that the contribution to the free energy density due to spatial variations is given by Eq. (13.15). The mean square thermal averages of the fluctuations are

$$\langle \mid S^- \mid^2 \rangle = 4\langle \mid S_{xy} \mid^2 \rangle = \frac{2k_B T(1 + \xi_1{}^2 q^2)}{A[(1 + \xi_1{}^2 q^2)^2 - 4\xi_1{}^4 t_0{}^2 q^2]},$$
$$\langle \mid S_{xz} \mid^2 \rangle = \langle \mid S_{yz} \mid^2 \rangle = \frac{\tfrac{1}{2} k_B T(1 + \xi_1{}^2 q^2 + \tfrac{1}{2}\xi_2{}^2 q^2)}{A[(1 + \xi_1{}^2 q^2 + \tfrac{1}{2}\xi_2{}^2 q^2)^2 - \xi_1{}^4 t_0{}^2 q^2]}. \tag{13.27}$$

The fluctuations in S^+ are the same as in the nematic phase. If we examine $\langle \mid S_{xy} \mid^2 \rangle$, we see that (for given ξ_1) the maximum scattered intensity is at an angle determined by $q = 0$ if $\xi_1 t_0$ is less than $\frac{1}{2}$ as in the nematic case. If $\xi_1 t_0$ is greater than $\frac{1}{2}$ a maximum appears at a finite angle determined by $\xi_1{}^2 q^2 = 2\xi_1 t_0 - 1$. We then have a broad scattering peak reminiscent of the Bragg peak in the ordered phase. De Gennes (1971a) has pointed out that, as the isotropic–cholesteric transition is of first order, $\xi_1(T_c) t_0 < 1$. If $\xi_1 t_0$ attained the value 1, the fluctuations in S_{xy} would diverge for $q = t_0$. The temperature $T^{(c)*}$ determined by $\xi_1(T^{(c)*}) t_0 = 1$ is thus the temperature below which the isotropic phase is unstable against the formation of a spiral structure. The first-order transition occurs at a temperature T_c greater than $T^{(c)*}$, and thus $\xi_1(T_c) t_0$ is less than unity. Probably in most cases $\xi_1(T_c) t_0 < \frac{1}{2}$ and the tendency to build up a spiral structure in the isotropic phase is small.

Rayleigh light scattering in the isotropic phase of cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate (CEEEC) has been observed by Yang (1972). Both the temperature dependence and wave vector dependence of the intensity were found to be in good agreement with the mean field predictions [Eq. (13.27)]. Bragg type scattering due to cholestericlike ordering in the isotropic phase was observed close to T_c.

F. Dynamics of fluctuations above T_c

The dynamics of fluctuations in nematics and cholesterics has been considered by de Gennes (1969a, 1971a). In Sec. VIII it was found that there is an important coupling between orientational and shear wave motions in nematics below T_c. We anticipate that these features will also be present above T_c. The equations of motion for $\mathbf{v}$, the fluid velocity, and $S_{\alpha\beta}$, the order parameter, are taken by de Gennes in the form

$$\rho(\partial v_\alpha/\partial t) + \nabla_\alpha P + \nabla_\beta T_{\alpha\beta} = 0 \tag{13.28}$$

$$(\partial/\partial t) S_{\alpha\beta} + \Phi_{\alpha\beta} = 0. \tag{13.29}$$

Equation (13.28) expresses the conservation of momentum and $T_{\alpha\beta}$ is the stress tensor. We regard the liquid as incompressible and the pressure P is a Lagrange multiplier to be determined so that $\nabla\cdot\mathbf{v} = 0$. Equation (13.29) describes the relaxation of the order parameter; this equation replaces the director equation considered in Sec. VI. We regard $\mathbf{v}$ and $S_{\alpha\beta}$ as small quantities and have omitted all terms quadratic or of higher order in these variables. We will also omit temperature fluctuations, as they do not couple strongly to the orientational or shear wave modes. Thus we need not consider the equation of motion of the entropy.

The stress tensor, $T_{\alpha\beta}$, and $\Phi_{\alpha\beta}$ must be determined. The entropy production R may be shown to be

$$RT = -T_{\alpha\beta} d_{\alpha\beta} - \Phi_{\alpha\beta}\phi_{\alpha\beta} \tag{13.30}$$

where

$$d_{\alpha\beta} = \tfrac{1}{2}(\partial v_\alpha/\partial x_\beta + \partial v_\beta/\partial x_\alpha), \qquad \phi_{\alpha\beta} = -\partial g/\partial S_{\alpha\beta}, \tag{13.31}$$

where g is the free energy density. We now expand $T_{\alpha\beta}$ and $\Phi_{\alpha\beta}$ in terms of $d_{\alpha\beta}$ and $\phi_{\alpha\beta}$. These phenomenological relations must satisfy the Onsager reciprocity and the entropy production must be positive definite. Phenomenological relations satisfying these requirements are

$$\begin{aligned} T_{\alpha\beta} &= -\eta' d_{\alpha\beta} - \nu\phi_{\alpha\beta} \\ \Phi_{\alpha\beta} &= \nu d_{\alpha\beta} - \zeta\phi_{\alpha\beta}. \end{aligned} \tag{13.32}$$

The entropy production is positive provided

$$\eta' > 0, \qquad \zeta > 0. \tag{13.33}$$

The hydrodynamic equations are

$$\rho(\partial v_\alpha/\partial t) + \nabla_\alpha P - \nabla_\beta(\eta' d_{\alpha\beta} + \nu\phi_{\alpha\beta}) = 0 \tag{13.34}$$

$$(\partial/\partial t) S_{\alpha\beta} - \zeta\phi_{\alpha\beta} + \nu d_{\alpha\beta} = 0. \tag{13.35}$$

At long wavelengths we may neglect the derivative terms in the free energy and then $\phi_{\alpha\beta} = -A S_{\alpha\beta}$. Thus the order parameter relaxes at a rate ζA to its equilibrium value. The parameter ν describes the torque exerted on the order parameter tensor by a velocity gradient. η' is a shear viscosity coefficient. The shear viscosity measured in a capillary flow experiment is

$$\eta_0 = \eta' + (\nu^2/\zeta). \tag{13.36}$$

The "traceless" condition, $S_{\alpha\alpha} = 0$, is satisfied by Eq. (13.35) as the fluid is incompressible. We now consider some applications of these equations.

G. Flow birefringence

We suppose that the liquid is flowing steadily in the x direction, and there is a velocity gradient in the y direction so that the fluid velocity takes the form $v_x(y)$. We will not consider the boundary conditions on the fluid as these will not have an appreciable effect on the orienting effect of the shear flow in the bulk of the fluid. From Eq. (13.35), using $\phi_{\alpha\beta} = -A S_{\alpha\beta}$, we find that the only nonzero component of $S_{\alpha\beta}$ is

$$S_{xy} = -(\nu/2\zeta A)(\partial v_x/\partial y). \tag{13.37}$$

We can reduce the order parameter to diagonal form by choosing a new set of axes x', y' which are rotated counter clockwise by an angle of $\pi/4$ with respect to the x, y axes. In this new coordinate

$$S_{x'x'} = S_{xy}, \qquad S_{y'y'} = -S_{xy} \tag{13.38}$$

and other components are zero. From Eqs. (13.20) and (13.37) we obtain the difference in the two principal dielectric susceptibilities

$$\begin{aligned} \delta\epsilon_{x'x'} = \delta\epsilon_{y'y'} &= 2MS_{xy} \\ &= -(M\nu/\zeta A)(\partial v_x/\partial y). \end{aligned} \tag{13.39}$$

Thus the anisotropy in the principal refractive indices n_x' and n_y' is

$$n_{x'}^2 - n_{y'}^2 = -\beta(T)(\partial v_x/\partial y), \tag{13.40}$$

where $\beta(T) = M\nu/\zeta A$. The most important temperature dependence arises from the factor A, and β^{-1} should vary approximately like $T - T^*$ close to T_c. The transport coefficient ν/ζ has the dimensions of a viscosity coefficient and its temperature dependence might be expected to be similar to that of the shear viscosity in the isotropic liquid. In PAA the shear viscosity varies as $\exp(W/kT)$, where W can be regarded as an activation energy for diffusion (Porter, Bassall, and Johnson, 1966). Recent measurements of the temperature dependence of flow birefringence in MBBA by Martinoty *et al.* (1971) are in good agreement with Eq. (13.40). The temperature dependence of ν/ζ was obtained by comparing the magnetic birefringence equation (13.5) (Stinson and Litster, 1970) and the flow birefringence equation (13.39) and found to be exponential with $W = 4.7$ kcal/mole. When the temperature dependence of ν/ζ is taken into account the coefficient A was found to be accurately linear in T with $T_c - T^* \sim 1$°K.

H. Inelastic light scattering

The spectral distribution of the light scattered by order parameter fluctuations is determined by the Fourier transform in space and time of the correlation functions of the order parameter:

$$I_{\alpha\beta}(\mathbf{q},\omega) = \int d\mathbf{r} \int_{-\infty}^{\infty} dt \times \exp(i\mathbf{q}\cdot\mathbf{r} - i\omega t)\langle S_{\alpha\beta}(\mathbf{r},t) S_{\alpha\beta}(0,0)\rangle \tag{13.41}$$

(no summation over repeated indices). The particular component $I_{\alpha\beta}$ which is relevant depends on the polarization of the incident and scattered light as in Eq. (13.21).

For very long wavelengths we may neglect the coupling between the order parameter and the shear flow in Eq. (13.35) and the order parameter obeys the simple equation

$$(\partial/\partial t)\, S_{\alpha\beta} + \zeta A\, S_{\alpha\beta} = 0. \tag{13.42}$$

The relaxation rate of the order parameter, $\Gamma = \zeta A$, becomes small close to T_c as $T - T^*$. If the gradient terms in the free energy [Eq. (13.8)] are included, Γ is replaced approximately by $\Gamma_q = \zeta A(1 + \xi^2 q^2)$ where ξ^2 is a combination of the coherence lengths [Eq. (13.14)]. The correlation function (13.40) is given by the Lorentzian form

$$I_{\alpha\beta}(\mathbf{q}, \omega) = [2\Gamma/(\Gamma^2 + \omega^2)]\langle \mid S_{\alpha\beta}(\mathbf{q}) \mid^2 \rangle. \tag{13.43}$$

At shorter wavelengths it is necessary to take account of the coupling between the orientational and shear wave modes in Eqs. (13.34) and (13.35). Without loss of generality we consider a plane wave with wave vector q propagating in the z direction. From Eqs. (13.34) and (13.35) we then find that the variables v_x and S_{xz} are coupled and v_y and S_{yz} are coupled. From symmetry these pairs give identical modes. The other components of the order parameter, S_{xx}, S_{yy}, and S_{xy} are not coupled to the hydrodynamic flow and relax as in Eq. (13.41) with the rate Γ.

The Fourier transform in space and Laplace transform in time of Eqs. (13.34) and (13.35) for the variables v_x and S_{xz} are

$$\begin{aligned} (s\rho + \tfrac{1}{2}\eta' q^2) v_x(q, s) + iq\nu A\, S_{xz}(q, s) &= \rho v_x(q, t = 0) \\ (s + \zeta A)\, S_{xz}(q, s) + \tfrac{1}{2} i\nu q v_x(q, s) &= S_{xz}(q, t = 0). \end{aligned} \tag{13.44}$$

The Laplace transform of the correlation function (13.41) is then

$$I_{xz}(q, s) = [(\rho s + \tfrac{1}{2}\eta' q^2)/D(s)]\langle \mid S_{xz}(q) \mid^2 \rangle, \tag{13.45}$$

where

$$D(s) = (s\rho + \tfrac{1}{2}\eta' q^2)(s + \zeta A) + \tfrac{1}{2}\nu^2 q^2 A. \tag{13.46}$$

Finally the correlation function (13.41) is

$$\begin{aligned} I_{xz}(q, \omega) &= 2R_e I_{xz}(q, s = i\omega) \\ &= \frac{2\Gamma(4\rho^2\omega^2 + \eta_0\eta' q^4)}{(2\rho\omega^2 - \Gamma\eta_0 q^2)^2 + \omega^2(2\rho\Gamma + \eta' q^2)^2} \\ &\quad \times \langle \mid S_{xz}(q) \mid^2 \rangle, \end{aligned} \tag{13.47}$$

where η_0 is given by Eq. (13.36). The spectral distribution is more complicated than a single Lorentzian. In the limit $\eta_0 q^2 \ll 2\rho\Gamma$ we recover Eq. (13.43). In the opposite limit $\eta' q^2 \gg 2\rho\Gamma$ we also find a single Lorentzian with an increased width $\Gamma' = \Gamma(\eta_0/\eta')$.

The linewidth $\Gamma = \zeta A$ of the Rayleigh scattering in the isotropic phase of MBBA has been measured by Stinson and Litster (1970) and found to be several MHz. The viscosity coefficient ζ^{-1} was assumed to have an exponential temperature dependence, $\exp(W/kT)$, with $W \sim 7.1$ kcal/mole. The temperature dependence of the coefficient A was then found to be accurately linear with $T_c - T^* \sim 1$°K in agreement with the mean field prediction. The linewidth of the Rayleigh scattering in the isotropic phase of a cholesteric (CEEEC) has been measured by Yang (1972) and found to be of order 1 kHz (much smaller than in MBBA). The temperature dependence was found to be similar with some departure from linearity close to T_c.

I. Shear waves

The hydrodynamic equations (13.34) and (13.35) also have a shear wave mode solution. We again consider a plane wave with wave vector q along the z axis and frequency ω. After eliminating the variable S_{xz} by means of Eq. (13.35) the equation obeyed by the fluid velocity is

$$(-i\omega\rho + \tfrac{1}{2}\eta(\omega) q^2) v_x = 0, \tag{13.48}$$

where the frequency-dependent viscosity coefficient is given by

$$\eta(\omega) = \eta' + [\nu^2 A/(\Gamma - i\omega)]. \tag{13.49}$$

Thus at low frequencies, $\omega < \Gamma$, the effective viscosity is $\eta' + (\nu^2 A/\Gamma)$, while at high frequencies it is η'. The shear wave impedance [see Eq. (9.20)] is

$$Z = \tfrac{1}{2}(1 - i)(\rho\omega\eta(\omega))^{1/2}. \tag{13.50}$$

The real part of the impedance, $R = \mathrm{Re}Z$, may be shown to be (Martinoty *et al.*, 1971)

$$R = \tfrac{1}{2}(\rho\omega)^{1/2}[\eta_2 + (\eta_1^2 + \eta_2^2)^{1/2}]^{1/2}, \tag{13.51}$$

where η_1 and η_2 are the real and imaginary parts of $\eta(\omega)$, respectively:

$$\eta_1 = \eta' + [\nu^2\Gamma A/(\omega^2 + \Gamma^2)], \qquad \eta_2 = [\omega\nu^2 A/(\omega^2 + \Gamma^2)]. \tag{13.52}$$

It has been pointed out by de Gennes (1971a) that the concept of an effective viscosity coefficient only applies when the penetration depth of the shear waves, $\delta = \mid \eta/\rho\omega \mid^{1/2}$, is much larger than the coherence length $\xi(T)$. When $\omega \sim \Gamma$, we have

$$\xi^2/\delta^2 \sim L_1\rho\zeta/\eta. \tag{13.53}$$

This parameter is of the same order as the parameter $\mu = k\rho/\eta^2 \sim 10^{-4}$ introduced in Sec. VIII. Thus $\xi/\delta \sim 10^{-2}$ and the above considerations are realistic. The shear impedance in MBBA above T_c has been measured by Martinoty *et al.* (1971). The results are well described by the de Gennes theory.

J. Viscosity coefficients

We briefly consider the relation between the viscosity coefficients α_i introduced in Sec. VI and η_0 [Eq. (13.36)] (Papoular, 1969b). Suppose that the liquid is flowing steadily in the x direction and a linear velocity gradient exists along the y axis. The effective viscosity in the nematic phase [Eq. (7.12)] is

$$2\eta = \alpha_4 + (\alpha_3 + \alpha_6)n_x^2 + (\alpha_5 - \alpha_2)n_y^2 + 2\alpha_1 n_x^2 n_y^2, \tag{13.54}$$

where n_x and n_y are the components of the director along x and y, respectively. In the isotropic phase we average over all orientations of the director: $\langle n_x^2\rangle_{\mathrm{av}} = \langle n_y^2\rangle_{\mathrm{av}} = \frac{1}{3}$, $\langle n_x^2 n_y^2\rangle_{\mathrm{av}} = \frac{1}{15}$, and

$$2\bar{\eta} = 2\eta_0 = \alpha_4 + \tfrac{2}{15}\alpha_1 + \tfrac{1}{3}(\alpha_3 + \alpha_6 + \alpha_5 - \alpha_2). \tag{13.55}$$

It has been argued by Papoular (1969b) that $\bar{\eta} > \eta_1$ (see Table I) and the viscosity coefficients should increase abruptly at T_c.

Below T_c the $\langle n_i^2\rangle_{\mathrm{av}}$ were expressed by Papoular in terms of the order parameter S. The qualitative features of the temperature dependence of the viscosity coefficients, observed by Porter, Barrall, and Johnson (1966), can be explained in this way in terms of the temperature dependence of S.

XIV. NUCLEAR MAGNETIC RESONANCE

Nuclear magnetic resonance (NMR) spectroscopy in liquid crystals differs from that in normal liquids in one important respect: in normal liquids the direct dipole–dipole interaction between nuclear spins averages to zero as a result of the rapid molecular tumbling. In liquid crystals the molecules are partially oriented and the direct dipole–dipole interaction between spins on the same molecule is a major factor determining the form of the NMR spectrum. Typically direct dipole interactions between protons in the same molecule may give rise to shifts up to 5000 Hz. Owing to the rapid translational diffusion of the molecules in the liquid crystal phase the dipole–dipole interaction between spins on different molecules averages to zero.

NMR studies have found a number of applications in the field of liquid crystals:

(1) The dipolar splitting of resonance lines yields a measure of the order parameter (if the nuclear separation is known) (Saupe, 1964). When applicable this technique is the most accurate available. The procedure may be complicated in that molecules which show liquid crystallinity are typically large and contain a large number of proton spins. As a consequence, there exists a large multiplicity of spin states and the NMR spectrum under low resolution is a single broad line with some superimposed structure, or under high resolution is a complex spectrum of lines.

(2) The alignment of impurities dissolved in a liquid crystal can be measured by NMR (Saupe and Englert, 1963) or the closely related ESR technique (Carrington and Luckhurst, 1964). These spin probes tend to be aligned by their interaction with the host molecules. The highly resolved NMR spectrum of a simple solute molecule can frequently be observed on top of the broad unresolved spectrum from the liquid crystal solvent. A great deal of precise information can be obtained about the ordered solute molecule, including relative bond lengths and bond angles and the signs and magnitudes of spin–spin coupling constants and anisotropic chemical shifts. Reviews of these applications have been given by Buckingham and McLauchlan (1967); Luckhurst (1968); Snyder and Meiboom (1969); and Diehl and Khetrapal (1969), and they will not be discussed in this section.

(3) Spin relaxation processes arise from fluctuations in the medium, among which the orientational fluctuations are an important component. These latter fluctuations lead to a characteristic frequency dependence ($T_1 \sim \omega^{1/2}$) for the spin–lattice relaxation time (Pincus, 1969a). A study of these relaxation times can give information about the spectrum of fluctuations.

A. The Hamiltonian

The Hamiltonian for a system of nuclear spins in a molecule in the presence of an external field H along the z direction is

$$\mathcal{H} = -\sum_i g_i\beta_n H I_{iz} - \sum_{i>j} (g_i g_j \beta_n^2/r_{ij}^3) \times (3(\boldsymbol{\nu}_{ij}\cdot\mathbf{I}_i)(\boldsymbol{\nu}_{ij}\cdot\mathbf{I}_j) - \mathbf{I}_i\cdot\mathbf{I}_j), \tag{14.1}$$

where g_i is the nuclear gyromagnetic ratio of spin i, β_n is the nuclear magneton, r_{ij} is the separation of nuclei i and j, and $\boldsymbol{\nu}_{ij}$ is a unit vector along $\mathbf{r}_{ij}$. The first term in Eq. (14.1) is the Zeeman energy of the spins in the applied field and the second term is the dipole–dipole interaction between the nuclei. Under most circumstances $H \simeq 10^4$ G, whereas the field due to one nucleus at the position of another is of order $\beta_n/r^3 \sim 1$ G. Thus the Zeeman energy dominates the Hamiltonian. The applied field generally determines the direction of the preferred axis in the nematic (surface effects may also be important).

The small chemical shifts and indirect spin-spin coupling constants have been omitted in Eq. (14.1). For protons in diamagnetic materials the chemical shifts range up to 5.10^{-2} G for $H = 10^4$ G, and the indirect spin–spin couplings range up to about 2.10^{-3} G. Nuclear quadrupole interactions have also been neglected.

For the purposes of illustration we will consider a simple model in which the molecules are taken to be rigid rods with two identical nuclear spins located on the axis separated by a distance a. The Zeeman energy is

$$\mathcal{H}_z = -g\beta_n H(I_{1z} + I_{2z}). \tag{14.2}$$

The dipole–dipole interaction is conveniently written

$$\mathcal{H}_d = -(g^2\beta_n^2/a^3)\{(3\nu_z^2 - 1)[I_{1z}I_{2z} - \tfrac{1}{4}(I_1^+I_2^- + I_1^-I_2^+)] + \tfrac{3}{4}[\nu_+^2 I_1^- I_2^- + \text{c.c.}] + \tfrac{3}{2}\nu_z[\nu_-(I_{1z}I_2^+ + I_1^+I_{2z}) + \text{c.c.}]\}, \tag{14.3}$$

where $\nu_\pm = \nu_x \pm i\nu_y$, $I^\pm = I_x \pm iI_y$, and $\boldsymbol{\nu}$ is a unit vector along the molecular axis. The components of $\boldsymbol{\nu}$ and $\mathbf{I}$ are referred to a space fixed set of axes x, y, z with the applied field along z. The three terms in the square brackets in Eq. (14.3) have different effects. The first term gives rise to a first-order shift of the energy levels of the spin system for oriented molecules. This term effectively alters the magnetic field acting on a spin. It also gives a contribution to the spin–spin relaxation time T_2. In normal liquids $3\nu_z^2 - 1$ averages to zero owing to the rapid molecular tumbling and the energy level shift is zero. The second and third terms can give rise to higher-order shifts in the nuclear spin energy levels, but more importantly contribute to the spin–lattice and spin–spin relaxation times. These effects have been discussed in normal liquids by Abragam (1961).

B. Dipolar shifts of energy levels in nematics

In the simple model introduced above the important dipolar shift in the NMR spectrum arises from the first term in Eq. (14.3)

$$\mathcal{H}_d^{(1)} = -(g^2\beta_n^2/a^3)(3\nu_z^2 - 1)[I_{1z}I_{2z} - \tfrac{1}{4}(I_1^+I_2^- + I_1^-I_2^+)]. \qquad (14.4)$$

Assuming both spins have $I = \frac{1}{2}$ this interaction splits the NMR spectrum by

$$\hbar\Delta\omega = \tfrac{3}{2}(g^2\beta_n^2/a^3)\langle 3\nu_z^2 - 1\rangle, \qquad (14.5)$$

where the angular brackets indicate an average over the motion of a molecule and over all molecules. Two limiting cases arise depending on the time τ of typical fluctuations of the molecular axis.

(a) $\Delta\omega\tau \gg 1$. In this case the molecules are essentially stationary during the interaction time $\Delta\omega^{-1}$. The average of Eq. (14.5) over all molecules then leads to a spectrum depending on the instantaneous distribution of orientations of the molecules in the specimen (i.e., a "powder" type spectrum).

(b) $\Delta\omega\tau \ll 1$. In this case the molecules reorient rapidly and the splitting depends only on the average molecular orientation.

In liquid crystals the latter case is generally realized in NMR. The situation may be reversed in ESR where $\Delta\omega$ is much larger (Pincus, 1969b). The orientational fluctuations in liquid crystals give a τ of order 10^{-9} secs (see Sec. XIV.D). In NMR $\Delta\omega \sim 10^5$ sec^{-1} and $\Delta\omega\tau \sim 10^{-4}$. We are thus justified in averaging Eq. (14.5) over the motion of a molecule. We assume that the time average is equivalent to a space average over the orientations of many molecules (as in the definition of the order parameter in Sec. I.A). The average in Eq. (14.5) can then be expressed in terms of the order parameter S

$$\Delta\omega = (3g^2\beta_n^2/\hbar a^3)S. \qquad (14.6)$$

[Note that we have assumed that the director and applied field are in the same direction. If the angle between the director and the field is α, then S in Eq. (14.6) is replaced by $\frac{1}{2}S(3\cos^2\alpha - 1)$]. If the internuclear distance a is known, the measurement of the dipolar splitting of the NMR line gives directly the value of the order parameter. The order parameter in PAA measured by McColl (1972) and McColl and Shih (1972) and reduced to constant volume is shown in Fig. 22.

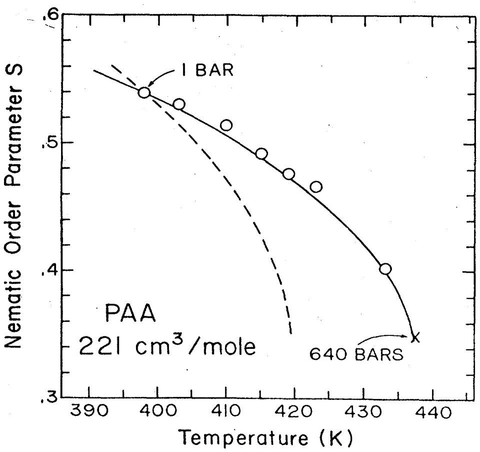

FIG. 22. The nematic order parameter in PAA versus temperature at the constant molar volume 221 cm³/mole. Circles, experimental data of McColl and Shih (1972); cross, experimental transition value of S. The dashed curve is a theoretical model including steric and energetic effects (see McColl and Shih).

For molecules of a general shape the dipolar splitting is determined by the Hamiltonian

$$\mathcal{H}_d^{(1)} = -\sum_{i>j}(g_ig_j\beta_n^2/r_{ij}^3)\langle 3\cos^2\theta_{ij} - 1\rangle[I_{iz}I_{jz} - \tfrac{1}{4}(I_i^+I_j^- + I_i^-I_j^+)], \qquad (14.7)$$

where θ_{ij} is the angle between $\boldsymbol{\nu}_{ij}$ and the field. The average $\frac{1}{2}\langle 3\cos^2\theta_{ij} - 1\rangle$ can be expressed in terms of the order parameter (1.2) and factors depending on the molecular geometry. Introducing a coordinate system x', y', z' fixed in the molecule and assuming the directions of $\mathbf{H}$ and $\mathbf{n}$ coincide, we have

$$\tfrac{1}{2}\langle 3\cos^2\theta_{ij} - 1\rangle = \langle P_2(\mathbf{n}\cdot\boldsymbol{\nu}_{ij})\rangle = \tfrac{4}{5}\pi\sum_{m=-2}^{2} Y_2^{m*}(\boldsymbol{\nu}_{ij})\langle Y_2^m(\mathbf{n})\rangle, \qquad (14.8)$$

where the Y are normalized spherical harmonies $[Y_l^{m*} = (-)^m Y_l^{-m}]$ (Messiah, 1964) and the unit vectors are to be expressed in the molecule fixed axes. The $Y_2^m(\boldsymbol{\nu}_{ij})$ are factors depending on the molecular geometry and the $\langle Y_2^m(\mathbf{n})\rangle$ are related to the order parameter (1.2) by

$$\langle Y_2^0(\mathbf{n})\rangle = 3(5/16\pi)^{1/2}S_{z'z'},$$
$$\langle Y_2^1(\mathbf{n})\rangle = -(15/8\pi)^{1/2}(S_{x'z'} + iS_{y'z'}),$$
$$\langle Y_2^2(\mathbf{n})\rangle = (15/32\pi)^{1/2}(S_{x'x'} - S_{y'y'} + 2iS_{x'y'}). \qquad (14.9)$$

In general the dipolar Hamiltonian (14.7) will depend on the five parameters $S_{\alpha'\beta'}$. If the principal axes in the molecule of this tensor are known, then only two parameters remain:

$$S_{z'z'} = \tfrac{2}{3}S, \qquad S_{y'y'} - S_{x'x'} = \tfrac{2}{3}D, \tag{14.10}$$

where S is the usual order parameter and D is a measure of the difference of the alignment of the two transverse axes of the molecule along the director. In this case Eq. (14.8) simplifies to

$$\tfrac{1}{2}\langle 3\cos^2\theta_{ij} - 1\rangle = \tfrac{1}{2}S(3\cos^2\theta_{ij}' - 1) - \tfrac{1}{2}D\sin^2\theta_{ij}' \times \cos 2\phi_{ij}', \tag{14.11}$$

where θ_{ij}' and ϕ_{ij}' are the spherical polar angles of the vector $\boldsymbol{\nu}_{ij}$ in the molecular coordinate system. The anisotropy in the magnetic susceptibility of a nematic also involves the parameters S and D [see Eq. (15.2)] (assuming the principal axes of the molecular susceptibility and $S_{\alpha'\beta'}$ coincide). These parameters have been determined by Alben, McColl, and Shih (1972) in PAA from the NMR and susceptibility measurements. Assuming a principal axis system in which the z' axis is the long axis (axis of smallest moment of inertia) and the x' axis is perpendicular to the benzene rings, it was found $S \simeq 0.52$, $D \simeq 0.07$ at 120°C. The fact that D is positive indicates that the x' axis has less tendency than the y' axis to lie along the director.

Above T_c, in the presence of the field H, the order parameter has a small nonzero value given by Eq. (13.3). Thus in the isotropic phase a small dipolar splitting of the NMR lines exists. Using the values $\chi_a = 10^{-6}$, $H = 10^4$ G, $A' = 10^5$ cgs, and $T - T^* = 1$°K, we find $S = 10^{-3}$. The dipolar splitting in the isotropic phase is thus of order 10^{-3} G which is at the limits of observation and would require a very homogeneous field to be resolved.

The NMR spectra of impurity molecules dissolved in a nematic host were first observed by Saupe and Englert (1963). Equations (14.8)–(14.11) also apply to the case of impurity molecules with the change that S is replaced by its value for the impurity molecules. The ESR spectra of impurity free radicals aligned by their interaction with a nematic host have been observed by several workers [for reviews see Luckhurst (1968), Diehl and Khetrapal (1969), and Pincus (1969b)]. If the free radicals have anisotropic g tensors or anisotropic hyperfine interactions with neighboring nuclear spins, the impurity order parameter may be obtained in a similar way to that discussed above for the dipolar interactions of nuclear spins. In this case one must be careful about the condition $\Delta\omega\tau \ll 1$ where $\Delta\omega$ is the relevant anisotropic shift or splitting. Typical hyperfine splittings are of order 10 gauss which gives $\Delta\omega \simeq 10^8$ sec^{-1}. Thus for $\tau = 10^{-9}$ sec one is close to the limit $\Delta\omega\tau \sim 1$. An extra broadening of the ESR lines is expected in this case (Abragam, 1961, Chap. VIII).

Many molecules which show liquid crystallinity are large and contain a large number of magnetic nuclei. The NMR spectrum under low resolution is a single broad line, and the method of moments has been used to analyze the spectrum (Lippmann and Weber, 1957; Bravo *et al.*, 1969). The second moment, $\langle\Delta\omega_i^2\rangle$, of the NMR spectrum for nuclear species i resulting from dipole–dipole interactions is (Abragam, 1961 Chap. IV)

$$\begin{aligned}\langle\Delta\omega_i^2\rangle = {}& \tfrac{3}{4}(g_i^4\beta_n^4/\hbar^2N_i)I_i(I_i+1) \\ & \times \sum_{i'\neq i} r_{ii'}^{-6}\langle(1-3\cos^2\theta_{ii'})^2\rangle \\ & + \tfrac{1}{3}(g_i^2\beta_n^4/\hbar^2N_i)\sum_{i,k} g_k^2I_k(I_k+1) \\ & \times r_{ik}^{-6}\langle 1-3\cos^2\theta_{ik})^2\rangle.\end{aligned} \tag{14.12}$$

The first sum is over all the N_i spins in the molecule of the same species as the observed spin and the second sums are over all the spins i and the unlike spins k with spin I_k in the molecule. In each case r_{ij} is the distance separating the two spins, θ_{ij} is the angle between $\boldsymbol{\nu}_{ij}$ and the applied field, and the angular brackets indicate an average over many molecules.

C. Dipolar shifts of energy levels in cholesterics

In this section we consider briefly the dipolar splitting in the NMR spectra of cholesterics for the simple model of a linear molecule containing two identical spins (Pincus, 1969b). The cholesteric is more complicated than the nematic because the molecules have a twisted arrangement and they do not all have their axes parallel to H. We assume that the cholesteric is a single crystal, and we consider the two cases where H is parallel and perpendicular to the twist axis.

1. *H parallel to twist axis*

Assuming that the cholesteric structure is not distorted by the magnetic field, the preferred direction of all the molecules is perpendicular to H. Then from Eq. (14.5) the NMR splitting is

$$\Delta\omega = \tfrac{3}{2}(g^2\beta_n^2/\hbar a^3)S \tag{14.13}$$

which is $-\tfrac{1}{2}$ the value obtained in the nematic state. Again measurement of $\Delta\omega$ provides a direct way of obtaining S.

2. *H perpendicular to twist axis*

This geometry is more complicated because (a) molecules in different cholesteric planes are not equivalent with respect to the field; and (b) the field distorts the cholesteric structure. We first consider the case where the applied field is sufficiently weak that the distortion of the cholesteric structure can be neglected. According to Sec. IV.C, this requires $H \ll H_c$. We use the geometry of that section in which the twist axis is the z axis and H is along the y axis. For a particular group of molecules whose preferred direction makes an angle ϕ with the x axis, the splitting, according to Eq. (14.5), is

$$\Delta\omega(\phi) = \tfrac{3}{2}(g^2\beta_n^2/\hbar a^3)S(3\sin^2\phi - 1) \tag{14.14}$$

and varies between $2\omega_m$ and $-\omega_m$ where $\omega_m = \tfrac{3}{2}(g^2\beta_n^2/\hbar a^3)S$. The NMR spectrum of these molecules consists of two lines at frequencies $\omega_0 \pm \tfrac{1}{2}\Delta\omega(\phi)$. The power absorbed per unit volume at a frequency shift ω' from ω_0 is proportional to the number of molecules per unit volume, $N(\omega')$, with frequency shift ω'. Taking into account the two possible transitions,

$$N(\omega') = \tfrac{1}{4}\int_0^{2\pi} N(\phi)[\delta(\omega' - \tfrac{1}{2}\Delta\omega(\phi)) + \delta(\omega' + \tfrac{1}{2}\Delta\omega(\phi))]\,d\phi, \tag{14.15}$$

where $N(\phi)$ is the number of molecules per unit volume with orientation ϕ:

$$N(\phi) = (N/p)(\partial z/\partial\phi), \tag{14.16}$$

where N is the number density and p is the pitch of the cholesteric. In the case of a uniform twist $\phi = t_0 z$, $p = 2\pi/t_0$, and $N_0(\phi) = N/2\pi$. Then Eq. (14.15) gives

$$\begin{aligned} N_0(\omega') &= (N/4\pi)f(|\omega'|), \qquad \omega_m/2 < |\omega'| < \omega_m, \\ &= (N/4\pi)[f(|\omega'|) + f(-|\omega'|)], \\ &\qquad\qquad 0 < |\omega'| < \omega_m/2, \end{aligned} \tag{14.17}$$

where

$$f(|\omega'|) = [(\omega_m - |\omega'|)(\tfrac{1}{2}\omega_m + |\omega'|)]^{-1/2}.$$

The function $N_0(\omega')$ is plotted in Fig. 23 (and referred to there as $H \simeq 0$).

When the cholesteric structure is distorted by the applied field, the distribution of the molecular axes, $N(\phi)$, can be obtained from the results of Sec. IV.C. It is given by

$$N(\phi) = (N/p)[\kappa\xi_2/(1 - \kappa^2 \sin^2\phi)^{1/2}], \tag{14.18}$$

where $\xi_2 = (k_{22}/\chi_a H^2)^{1/2}$, p is the pitch, and κ is a parameter determined by H and the zero field pitch (see Sec. IV.C). From Eq. (14.12) we then obtain

$$\begin{aligned} N(\omega') &= (N\kappa\xi_2/2p)g(|\omega'|)f(|\omega'|), \qquad \tfrac{1}{2}\omega_m < |\omega'| < \omega_m \\ &= (N\kappa\xi_2/2p)[g(|\omega'|)f(|\omega'|) \\ &\quad + g(-|\omega'|)f(-|\omega'|)], \qquad |\omega'| < \tfrac{1}{2}\omega_m \end{aligned} \tag{14.19}$$

where

$$g(|\omega'|) = [1 - \tfrac{2}{3}(\kappa^2/\omega_m)(|\omega'| + \tfrac{1}{2}\omega_m)]^{-1/2}.$$

The function $N(\omega')$ is plotted in Fig. 23 for $H = \frac{3}{4}H_c$ and $H = 0.92H_c$.

Thus in the cholesteric case we obtain a continuous spectrum of width $2\omega_m$. The order parameter in the cholesteric can be determined from a measurement of ω_m. When $H \to H_c$ the cholesteric assumes a nematic structure with the preferred direction for all the molecules parallel to the field. In this limit it can be shown that $N(\omega') \to (N/4)[\delta(\omega' - \omega_m) + \delta(\omega' + \omega_m)]$ and the spectrum consists of two sharp lines separated by $2\omega_m$ as in the nematic case considered in the previous section.

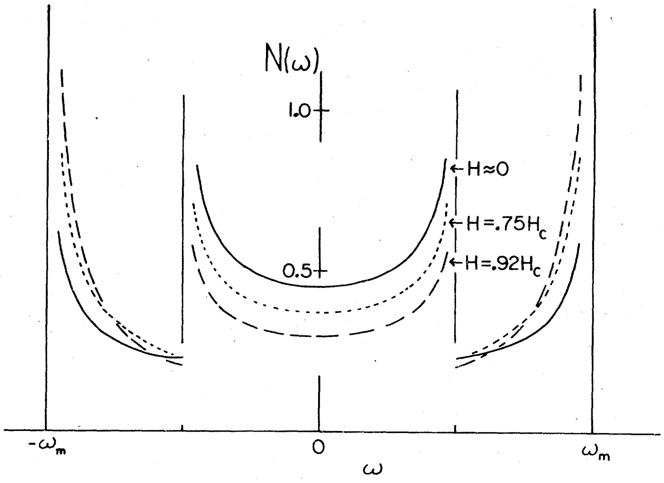

FIG. 23. NMR absorption spectrum of a cholesteric with the magnetic field perpendicular to the pitch axis for different values of the magnetic field.

It was pointed out by Pincus (1969b) that these results are modified if the molecules diffuse rapidly along the twist axis. The broadening of the spectrum will be reduced. As an illustration, suppose the molecules diffuse along the pitch axis and that the molecular axis adiabatically follows the local order as the molecule diffuses. Then, if the molecule diffuses a distance greater than $p/2$ during a time ω_m^{-1}, i.e., $4D/p^2 > \omega_m$, where D is the diffusion constant, the broadening of the spectrum disappears. In this case it is appropriate to average Eq. (14.14) over all values of ϕ and the NMR spectrum consists of two lines. For an undistorted cholesteric structure $\langle\sin^2\phi\rangle = \frac{1}{2}$ and the splitting is

$$\Delta\omega = \tfrac{3}{4}(g^2\beta_n{}^2/\hbar a^3)\,S. \tag{14.20}$$

In the more general case when H is not much less than H_c and the cholesteric structure is distorted, we have from Eq. (14.18)

$$\begin{aligned} \langle\sin^2\phi\rangle &= \int_0^{\pi/2} N(\phi)\sin^2\phi\, d\phi \Big/ \int_0^{\pi/2} N(\phi)\, d\phi \\ &= (1/\kappa^2)[1 - (E/K)] \end{aligned} \tag{14.21}$$

when K and E are the complete elliptic integrals of modulus κ of the first and second kind. The splitting of the NMR lines is

$$\Delta\omega = \tfrac{3}{2}(g^2\beta_n{}^2/\hbar a^3)\,S[(3/\kappa^2)(1 - E/K) - 1]. \tag{14.22}$$

As $H \to H_c$, $\kappa \to 1$, and we approach the nematic state and the effects of translational diffusion become unimportant.

D. Nuclear relaxation in nematics

The orientational fluctuations in a nematic are an important mechanism for spin relaxation and lead to a characteristic frequency dependence of the spin-lattice and spin–spin relaxation times (Pincus, 1969a). We again consider the simple model of rodlike molecules with two nuclear spins located on the axis. The molecules are aligned by the applied field. If we assume that the fluctuations in orientation of the molecules are small, ν_z is nearly constant in Eq. (14.3) and to a first approximation the term leading to relaxation of the spins is

$$\mathbf{H}_d^{(2)} = -\tfrac{3}{2}(g^2\beta_n^2/a^3)\ \nu_z[\nu_-(I_{1z}I_2^+ + I_1^+I_{2z}) + \text{c.c.}]. \tag{14.23}$$

The spin–lattice relaxation time derived from this interaction is given by Abragam (1961, Chap. VIII):

$$T_1^{-1} = \tfrac{3}{2}(g^4\beta_n^4/a^6)I(I+1)J(\omega_0), \tag{14.24}$$

where $J(\omega_0)$ is the value of the Fourier transform, at the nuclear Larmor frequency, of the correlation function of the orientational fluctuations

$$J(\omega_0) = \int_{-\infty}^{\infty} dt G(t) \exp(-i\omega_0 t), \tag{14.25}$$

where

$$G(t) = \langle \nu_z(t)\nu_-(t)\nu_z(0)\nu_+(0)\rangle. \tag{14.26}$$

The transverse relaxation time is $T_2 = \frac{2}{5}T_1$ (Abragam, 1961, Chap. VIII). To a first approximation we regard ν_z in Eq. (14.26) as independent of the time, and we replace $G(t)$ by

$$\begin{aligned} G(t) &\simeq \langle \nu_z^2\rangle\langle \nu_-(t)\nu_+(0)\rangle \\ &= \tfrac{1}{3}(2S+1)\langle \nu_-(t)\nu_+(0)\rangle. \end{aligned} \tag{14.27}$$

In the last line we have expressed $\langle \nu_z^2\rangle$ in terms of the order parameter S. The factor $\frac{1}{3}(2S+1)$ describes the average molecular alignment and is 1 for complete alignment and $\frac{1}{3}$ for random orientations. Different approximations to this correlation function have been made by Pincus (1969a), who found it was proportional to S, and Lubensky (1970), who found it was proportional to S^2. Equation (14.27) is exact for small fluctuations where ν_z is constant to a first approximation and (apart from a numerical constant) is also correct in the isotropic state. The orientational fluctuations in nematics have been discussed in Sec. VIII, and the correlation function (14.27) has been determined. Using Eqs. (8.13) and (8.48) (assuming $k_{11} = k_{22} = k_{33} = k$)

$$J(\omega) = \frac{1}{3}(2S+1)\frac{2}{(2\pi)^3}\int d\mathbf{q}\, \frac{k_BT}{kq^2 + \chi_aH^2}\,\frac{\Gamma_S^2}{\omega^2 + \Gamma_S^2}, \tag{14.28}$$

where Γ_S is given by Eq. (8.34). In the case where all the Frank elastic constants are equal, we have approximately

$$\Gamma_S = (kq^2 + \chi_aH^2)/\eta, \tag{14.29}$$

where η is a typical viscosity coefficient. The terms in χ_aH^2 in Eqs. (14.28) and (14.29) may be neglected, as they are very small compared with kq^2 over practically the entire range of the integral in Eq. (14.28). The corrections due to these terms have been considered by Blinc *et al.* (1969). From Eq. (14.28) we then find

$$J(\omega_0) = [(2S+1)k_BT/3\pi k](\eta/2k\omega_0)^{1/2}. \tag{14.30}$$

The spin–lattice relaxation time can now be written

$$T_1^{-1} = \omega_D^2 t_c, \tag{14.31}$$

where $\omega_D = g^2\beta_n^2/\hbar a^3$ is the dipolar frequency and the correlation time

$$t_c = [(2S+1)k_BT/2\pi k]I(I+1)(\eta/2k\omega_0)^{1/2}. \tag{14.32}$$

One of the most striking features of this result is the frequency dependence $t_c \sim \omega_0^{-1/2}$. For $T = 300°\text{K}$, $k = 10^{-6}$ dyn, $\eta = 0.1$ P, and $\omega_0 = 10^7\ \text{sec}^{-1}$, we find $t_c = 10^{-9}$ sec. This was the estimate used in Sec. XIV.B for the correlation time for orientational fluctuations. For a dipolar frequency $\omega_D \simeq 10^5\ \text{sec}^{-1}$, we find $T_1 \simeq 1$ sec, which is comparable with the spin–lattice relaxation time in ordinary liquids arising from the rotational and translational diffusion of the molecules.

Other contributions to the relaxation in a nematic arise from the modulation of intermolecular dipole–dipole interaction. This fluctuates because of the relative orientational fluctuations of the molecules, and also because of the relative translational diffusion of the molecules. An analogous calculation leads to

$$T_{1\ \text{inter}}^{-1} = (3g^4/2)(\beta_n^4/r_0^6)I(I+1)J_{\text{inter}}(\omega), \tag{14.33}$$

where r_0 is the average separation of the molecules,

$$J_{\text{inter}}(\omega) = [(2S+1)k_BT/3\pi k]\{2\omega_0[(k/\eta) + D]\}^{-1/2}, \tag{14.34}$$

and D is the translational diffusion constant. It has been assumed that the translational motion and orientational fluctuations are independent. Using Stokes law $D \simeq k_BT/6\pi\eta a$, where a is the molecular dimension; thus D and k/η are of the same order of magnitude and $T_{1\ \text{inter}}^{-1}$ is comparable with Eq. (14.31).

The striking frequency dependence of Eqs. (14.30) and (14.34) arises from the fact that the amplitude of the orientational fluctuations diverges as $q \to 0$. Contributions from other fluctuations will not behave in this way, allowing us to separate the contributions of the orientational fluctuations. The frequency dependence $T_1 \sim \omega_0^{1/2}$ in nematics has been verified by Weger and Cabane (1969), Blinc *et al.* (1969), and Doane and Visintainer (1969).

XV. DETERMINATION OF THE ORDER PARAMETER

There are several methods by which the order parameters in a nematic can be determined experimentally. The NMR method, discussed in the previous chapter, is generally the most accurate when applicable. In this section we discuss some other methods for the determination of the order parameter in nematics.

A. Magnetic susceptibility

The relation between the order parameter and the magnetic susceptibility is given by Eqs. (1.4) and (1.5). If the molecules are axially symmetric, the anisotropy in the susceptibility is

$$\begin{aligned}\chi_a &= \chi_{||} - \chi_{\perp} \\ &= N\chi_a^{(0)}S,\end{aligned} \qquad (15.1)$$

where N is the number density and $\chi_a^{(0)}$ is the anisotropy in the susceptibility of an isolated molecule (the effects of molecular interactions have been neglected). Thus from a measurement of χ_a, S can be obtained provided N and $\chi_a^{(0)}$ are known. The latter quantity can be obtained from measurements on single crystals, the assumption being made that the molecules are completely aligned in the crystal. This method for the determination of S was used by Zwetkoff (1942) and Saupe and Maier (1961).

If the molecules are not axially symmetric, the two order parameters (14.10) are required, and the anisotropy in the susceptibility is

$$\chi_a = (N/2)[S(2\chi_3^{(0)} - \chi_1^{(0)} - \chi_2^{(0)}) + D(\chi_2^{(0)} - \chi_1^{(0)})], \qquad (15.2)$$

where $\chi_i^{(0)}$ are the principal molecular susceptibilities. The order parameters $S = 0.52$ and $D = 0.07$ have been obtained by Alben, McCall, and Shih (1972) in PAA at 120°C (see Sec. XIV.B).

B. Refractive index

Let $\alpha_{\alpha\beta}^{(0)}$ be the polarizability tensor of an isolated molecule and define an average polarizability by an equation analogous to (1.3)

$$\alpha_{\alpha\beta} = \alpha^{(0)}\delta_{\alpha\beta} + \alpha_a^{(0)}S_{\alpha\beta}, \qquad (15.3)$$

where $\alpha^{(0)}$ is the average and $\alpha_a^{(0)}$ the anisotropy in the polarizability of a molecule (assumed uniaxial). We may not, however, identify $(1+4\pi n\alpha)^{1/2}$ with the refractive index; there are important local field corrections (α is the component of $\alpha_{\alpha\beta}$ determined by the polarization of the light wave). Zwetkoff (1942) and Chatelain (1955) used the Lorentz–Lorentz internal field, which is strictly only valid in materials of cubic symmetry, to relate the polarizability to the refractive index. Saupe and Maier (1961) have argued that a nematic is more like a uniaxial crystal and used the internal field determined by Neugebauer (1950) for a uniaxial crystal to relate the measured refractive indices to the polarizability. In this model the refractive indices for the extraordinary and ordinary waves are given by

$$\begin{aligned}(n_e^2-1)/(n_e^2+2) &= (4\pi/3)[n/(A_1+\alpha_{||}^{-1})] \\ (n_0^2-1)/(n_0^2+2) &= (4\pi/3)[n/(A_2+\alpha_{\perp}^{-1})],\end{aligned} \qquad (15.4)$$

where A_1 and A_2 are parameters dependent on the crystal structure ($A_1 + 2A_2 = 0$) and $\alpha_{||}$ and $\alpha_{\perp}$ are the principal components of the polarizability tensor (15.3)

$$\begin{aligned}\alpha_{||} &= \alpha^{(0)} + \tfrac{2}{3}\alpha_a^{(0)}S \\ \alpha_{\perp} &= \alpha^{(0)} - \tfrac{1}{3}\alpha_a^{(0)}S.\end{aligned} \qquad (15.5)$$

Again measurements of the refractive indices in the nematic and crystal (assumed perfectly aligned) are required to determine $\alpha_{||} - \alpha_{\perp}$ and $\alpha_a^{(0)}$, respectively. The parameter A_1 was determined experimentally by setting the average polarizability of a molecule in the nematic and isotropic phases equal. Methods of measurement of the refractive indices of nematics have recently been discussed by Haller, Huggins, and Freiser (1972).

C. Dichroism

This method for determining the order parameter requires the existence of a convenient absorption band, either electronic or vibrational, in the molecule which in the simplest case is linearly polarized. Suppose the transition moment has an oscillator strength f and is linearly polarized making an angle α with the long axis of the molecules. Then it is not difficult to show that the oscillator strengths parallel and perpendicular to the director are

$$\begin{aligned}f_{||} &= \tfrac{1}{3}f + \tfrac{2}{3}f(1-\tfrac{3}{2}\sin^2\alpha)S \\ f_{\perp} &= \tfrac{1}{3}f - \tfrac{1}{3}f(1-\tfrac{3}{2}\sin^2\alpha)S.\end{aligned} \qquad (15.6)$$

Solving these equations for S gives

$$S = (f_{||} - f_{\perp})/f(1-\tfrac{3}{2}\sin^2\alpha). \qquad (15.7)$$

The experimentally determined values of $f_{||}$ and $f_{\perp}$ cannot be used directly in this equation as there are corrections due to local field effects and the anisotropy in the refractive indices. Using the Neugebauer (1950) form for the internal field, Saupe and Maier (1961) have shown that the actual oscillator strengths are related to the experimentally measured oscillator strengths by

$$\begin{aligned}f_{||} &= \frac{3n_e'}{n_e'^2+2-2a(n_e'^2-1)}f_{||}^{(\mathrm{exp})} \\ f_{\perp} &= \frac{3n_0'}{n_0'^2+2+a(n_0'^2-1)}f_{\perp}^{(\mathrm{exp})},\end{aligned} \qquad (15.8)$$

where $a = 3A_1/4\pi n$ and n_e' and n_o' are the refractive indices excluding the contribution from the particular absorption band of interest.

D. X-ray scattering

It is also possible to obtain information on the orientational ordering in nematics from the intensity and angular distribution of x-ray scattering (de Gennes, 1972c). At short wavelengths, $qa > 1$, where $\mathbf{q}$ is the wave vector transfer in the scattering and $a \sim 1$–2 Å is a bond length in a molecule, the scattering intensity is proportional to

$$I(\mathbf{q}) = \sum_{i,j} \alpha_i \alpha_j^* \langle \exp(i\mathbf{q}\cdot\mathbf{R}_{ij}) \rangle. \tag{15.9}$$

The sum extends only over those atoms in a single molecule, α_i is the atomic form factor of atom i, and $\mathbf{R}_{ij}$ is the distance separating the atoms i and j. Terms in Eq. (15.9) which atoms i and j are on different molecules have been omitted because the fluctuations in the phase factor $\mathbf{q}\cdot\mathbf{R}_{ij}$ for these terms make their contribution to the scattered intensity small. For two neighboring atoms on the same molecule, the distance R_{ij} is nearly constant and the contribution to the intensity only decreases as $(qR_{ij})^{-1}$.

In order to carry out the averaging in Eq. (15.9) the exponential is expanded in spherical harmonics (Messiah, 1964, Chap. 9). Taking into account the axial symmetry of the nematic

$$I(\mathbf{q}) = \sum_{l=0}^{\infty} I_l(q)\, P_l(\cos\theta_q), \tag{15.10}$$

where θ_q is the angle between $\mathbf{q}$ and the director,

$$I_l(q) = (2l+1) i^l \sum_{i,j} \alpha_i \alpha_j^* j_l(qR_{ij}) \langle P_l(\mathbf{n}\cdot\boldsymbol{\nu}_{ij}) \rangle, \tag{15.11}$$

j_l is the spherical Bessel function, and $\boldsymbol{\nu}_{ij}$ is a unit vector along $\mathbf{R}_{ij}$. This result can be simplified by introducing a set of axes x', y', z' fixed in the molecule and referring both vectors to this set of axes. Then

$$\langle P_l(\mathbf{n}\cdot\boldsymbol{\nu}_{ij}) \rangle = (4\pi/2l+1) \sum_{m=-l}^{l} Y_l^{m*}(\boldsymbol{\nu}_{ij}) \langle Y_l^m(\mathbf{n}) \rangle, \tag{15.12}$$

where the Y_l^m are the normalized spherical harmonics and the unit vectors are to be expressed in the molecule fixed axes. The case $l = 2$ has been considered in Sec. XIV.B. Substituting Eq. (15.12) in (15.11)

$$I_l(\mathbf{q}) = \sum_{m=-l}^{l} C_{lm}(q) \langle Y_l^m(\mathbf{n}) \rangle, \tag{15.13}$$

where the $C_{lm}(q)$ depend on the molecular geometry:

$$C_{lm}(q) = 4\pi i^l \sum_{i,j} \alpha_i \alpha_j^* j_l(qR_{ij}) Y_l^{m*}(\boldsymbol{\nu}_{ij}). \tag{15.14}$$

The relations between the $\langle Y_2^m(\mathbf{n}) \rangle$ and the order parameters are given in Eq. (14.9). In general there are five unknown quantities $S_{\alpha'\beta'}$ [if the principal axes of this tensor are known, only the two parameters S and D, Eq. (14.10), remain]. For axially symmetric molecules only the term $m = 0$ in Eq. (15.13) remains (this would appear to be a good approximation in many cases as $D \ll S$).

The factor $I_l(q)$ in Eq. (15.10) can be determined from an analysis of the angular distribution of the scattered intensity. The interest in this method lies in the possibility of obtaining information about the higher harmonics, e.g., $l = 4$ in the orientational distribution of the molecules. The NMR method and other methods discussed in this chapter only give information about the $l = 2$ harmonics. Measurements on the degree of order in nematics by x-ray scattering have been made by Delord (1969).

XVI. SMECTIC LIQUID CRYSTALS

The smectic phases of a liquid crystal are layered structures. In the A and C phases there is no long-range positional order in the arrangement of the molecules within the layers and thus each layer resembles a two-dimensional liquid. Adjacent layers may slip easily over one another. In the A phase the long axes of the molecules are perpendicular to the layers, while in the C phase they make a finite angle to the normal to the layer. Less is known about the low-temperature B phase. It is associated with a more regular mosaic structure (Sackmann and Demus, 1966; Taylor, Fergason, and Arora, 1970). A single domain B phase gives an x-ray diagram with peaks at certain points of a three-dimensional reciprocal lattice suggesting a hexagonal order in each layer (Levelut and Lambert, 1971). It has been suggested by de Gennes and Sarma (1972) and Martin *et al.* (1972) that the B phase differs from a crystal in that the layers slip easily on each other, i.e., their shear modulus is zero. Within each layer there is a crystalline arrangement which can support shears. This model is supported by the recent observations by Liao *et al.* (1973) of propagating longitudinal and transverse sound wave modes in a smectic B.

A. Focal conic texture

In the absence of any constraints, the layers in a smectic A would be flat. The molecules tend to lie parallel to one another as their side-to-side attractions are relatively strong. In general, however, a smectic placed between microscope slides or cooled from the isotropic liquid does not assume the simple form (with flat layers), but becomes bent in order to conform to the boundary conditions. The arrangement is something like the strata in a geological formation, but the smectic arrangement is simpler because the layers, while preserving their thickness exactly, can slide easily over one another and adjust to the surface conditions. It has been shown from a study of the optical properties of the smectic texture that the surfaces of the layers form a series of Dupin cyclides (which we describe below). An extensive discussion has been given by Bragg (1934) and more recently by Bouligand (1972), so that a brief description will suffice here.

The Dupin cyclides are generated as follows. Consider an ellipse: the locus of the vertices of the circular cones passing through the ellipse is a set of four hyperbolas, of which we choose one arbitrarily. This hyperbola passes through one focus of the ellipse and lies in the plane perpendicular to the ellipse which contains the major axis. Conversely, the ellipse is a locus of the vertices of circular cones passing through the hyperbola. It is possible to draw surfaces which are perpendicular to all straight lines which pass through both conics. These surfaces are Dupin cyclides, and they have the special property that any two surfaces are equidistant everywhere. This makes it possible for a layered smectic structure to assume this form. In the smectic

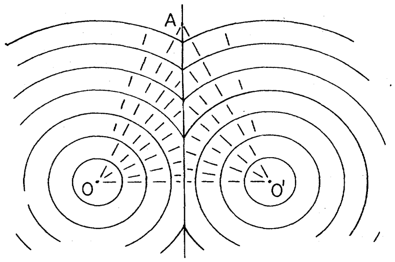

FIG. 24. A special case of the Dupin cyclides. The starting ellipse was chosen to be a circle, and the corresponding hyperbolas degenerated into straight lines. Every line (e.g., OA) passing through the circle and axis is normal to the layers. In general a cone-shaped region e.g., OAO') is filled with the smectic.

A case the optic axis at any point coincides with the straight line passing through the two conics.

This arrangement is best illustrated by considering the simple case where the ellipse becomes a circle and the hyperbola becomes the straight line perpendicular to the plane of the circle and passing through the center. The cyclides are now toruses which are intersected at right angles by every straight line that passes through both the circle and its axis. This is shown in Fig. 24. The more general case is obtained by letting the circle become an ellipse and the cones in Fig. 24 be pushed over to one side. The toruses become distorted, but the characteristic properties of the cyclides are maintained—every straight line passing through the ellipse and hyperbola is normal to the layers, and the surfaces are equidistant. The packing of the cones to fill up all of space, and the optical properties of the resulting texture, is discussed in detail by Bragg (1934). It has also been shown by Geurst (1971) that this focal conic texture of a smectic liquid crystal follows from the appropriate Oseen–Frank elastic free energy (see below).

B. Elastic theory of smectics A

The simplest treatment of the elastic theory of smectics A is due to Oseen (1933). He neglected all changes in internal parameters such as the density, the distance l between layers, and the deviation of the preferred direction $\mathbf{n}$ from the normal to the planes, since these distortions would be expected to require relatively large energies. Thus Oseen considered only undulations of the layers in which l is kept constant and the director remains normal to the planes. The local state of a smectic A may then be described in terms of the director $\mathbf{n}(\mathbf{r})$ which is a unit vector along the preferred direction of the molecules and normal to the planes containing the molecules. The condition that the distance between the planes remain constant can be written

$$l^{-1}\int_A^B \mathbf{n}\cdot d\mathbf{l} = \text{constant}, \tag{16.1}$$

where A and B are any two points fixed in the medium. This integral measures the number of layers which is crossed in going from A to B and must be independent of the path along which the integral is taken. Thus we must have $\operatorname{curl}\mathbf{n} = 0$, and the only allowed distortion is a splay. The elastic theory of the smectic A structure based on the director only will be identical with that derived for nematics in Sec. III because the two structures have the same symmetry properties. Using the condition $\operatorname{curl}\mathbf{n} = 0$, the elastic energy [Eq. (3.14)] reduces to

$$F = \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2 - \tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2. \tag{16.2}$$

A smectic A behaves like a nematic in which k_{22} and k_{33} have large values so that twists and bends do not occur. The only allowed deformation is a splay, and the smectic A can deform into the focal conic texture described in the previous section (Geurst, 1971).

A small deformation of $\mathbf{n}$ is related to the deformation of the planes containing the molecules in the following way. In the planar equilibrium state assume that the optic axis $\mathbf{n}$ is along the z axis, and let $u_z(x, y)$ be the displacement of a plane in the z direction. This is independent of z in order that the planes remain equidistant. Then the deformation of $\mathbf{n}$ is given by

$$\delta n_x = -\partial u_z/\partial x, \qquad \delta n_y = -\partial u_z/\partial y. \tag{16.3}$$

The possibilities for fluctuations are greatly restricted by the condition $\operatorname{curl}\mathbf{n} = 0$. For small deformations $\delta\mathbf{n}(\mathbf{q})$ of $\mathbf{n}$ with wave vector $\mathbf{q}$, this condition requires that $\delta\mathbf{n}(\mathbf{q})$ vanish except when $q_z = 0$, i.e., only fluctuations parallel to the planes are allowed.

It is thus necessary to generalize the Oseen description to allow for deformations of internal parameters (de Gennes, 1969b). We let $u_z(\mathbf{r})$ be the small displacement of the planes in the z direction, $\delta\mathbf{n}(\mathbf{r})$ the small change in the director, and $\Delta\rho(\mathbf{r})$ the small change in the density. Retaining only quadratic terms in the small displacements, the elastic energy takes the form

$$\begin{aligned} F = {} & \tfrac{1}{2}\mu[(\delta n_x + \partial u_z/\partial x)^2 + (\delta n_y + \partial u_z/\partial y)^2] \\ & + \tfrac{1}{2}A(\Delta\rho)^2 + \tfrac{1}{2}B(\partial u_z/\partial z)^2 + C\Delta\rho(\partial u_z/\partial z) \\ & + \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2 - \tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2. \end{aligned} \tag{16.4}$$

In this expression μ is the elastic force constant for rotating the molecules relative to the normal to the layers, A and B are the compressibilities of the smectic parallel and perpendicular to the layers, and C is a cross term between these two types of compression. We will generally make the simplifying assumption that μ is large, which imposes the constraint (16.3). Then Eq. (16.4) becomes

$$\begin{aligned} F = {} & \tfrac{1}{2}A(\Delta\rho)^2 + \tfrac{1}{2}B(\partial u_z/\partial z)^2 + C\Delta\rho(\partial u_z/\partial z) \\ & + \tfrac{1}{2}k_{11}(\partial^2 u_z/\partial x^2 + \partial^2 u_z/\partial y^2)^2 \\ & + \tfrac{1}{2}\chi_a H^2[(\partial u_z/\partial x)^2 + (\partial u_z/\partial y)^2], \end{aligned} \tag{16.5}$$

where we have assumed that the field H is along the z direction and have omitted a constant term, $-\tfrac{1}{2}\chi_a H^2$. This is the form for the elastic free energy density of a smectic considered by Landau and Lifshitz (1958, Chap. 13) and de Gennes (1969b). Stability requires that $AB - C^2 > 0$. Using $\Delta\rho = -\rho(u_{xx} + u_{yy} + u_{zz})$ where u_x, etc. is the displacement in the x direction and $u_{xx} = \partial u_x/\partial x$, it can be written in the alternate form

$$F = \tfrac{1}{2}A\rho^2(u_{xx} + u_{yy})^2 + \tfrac{1}{2}(B + A\rho^2 - 2C\rho)u_{zz}^2 + (A\rho^2 - C\rho)u_{zz}(u_{xx} + u_{yy}) + \tfrac{1}{2}k_{11}(\partial^2 u_z/\partial x^2 + \partial^2 u_z/\partial y^2)^2 + \tfrac{1}{2}\chi_a H^2[(\partial u_z/\partial x)^2 + (\partial u_z/\partial y)^2]. \tag{16.6}$$

It is of interest to compare this with the elastic energy density of a uniaxial crystalline solid:

$$F = \tfrac{1}{2}C_{11}(u_{xx}^2 + u_{yy}^2) + C_{12}u_{xx}u_{yy} + C_{13}u_{zz}(u_{xx} + u_{yy}) + \tfrac{1}{2}C_{33}u_{zz}^2 + \tfrac{1}{2}C_{55}(u_{xz}^2 + u_{yz}^2) + (C_{11} - C_{12})u_{xy}^2. \tag{16.7}$$

Thus a smectic will not support shears ($C_{55} = 0$, $C_{11} = C_{12}$). The elastic constants in Eq. (16.6) are related to the usual elastic moduli C_{ij} by

$$A\rho^2 = C_{11}, \quad A\rho^2 - C\rho = C_{13}, \quad B + A\rho^2 - 2C\rho = C_{33}. \tag{16.8}$$

The elastic free energy [Eq. (16.5)] can be used to discuss elastic deformations of a smectic A. We briefly consider the case of a smectic in which the density is held constant, i.e., $\Delta\rho = 0$. Minimizing the free energy with respect to variations in u_z leads to the linear equation

$$[B(\partial^2/\partial z^2) - k_{11}(\partial^2/\partial x^2 + \partial^2/\partial y^2)^2 + \chi_a H^2(\partial^2/\partial x^2 + \partial^2/\partial y^2)]u_z(x, y, z) = 0. \tag{16.9}$$

This equation, with given boundary conditions, determines the elastic deformation of the layers. A rough estimate for the ratio of the elastic constants is $(k_{11}/B)^{1/2} \sim l$ where l is the smectic layer spacing, $l \sim 20$–30 Å. For a deformation with wave vector $q_\perp$ in the xy plane the variation in the z direction has a characteristic length of order $(B/k_{11})^{1/2}q_\perp^{-2} \sim (lq_\perp^2)^{-1} \gg q_\perp^{-1}$ when $q_\perp l \ll 1$. Thus if a smectic plane is deformed, e.g., on the surface, the deformation will extend almost unchanged over many planes.

C. Depolarized light scattering

This form for the static deformations of a smectic plays an important role in the depolarized light scattering by smectics recently observed by Clark and Pershan (1973) and Ribotta *et al.* (1973). The smectic lies parallel to the xy plane with optic axis along z (see Fig. 25). It is supposed that static deformations exist in the smectic which lead to depolarized light scattering: if the light enters the smectic as an ordinary ray, part of the light is scattered as an extraordinary ray and vice versa. The deformations lead to a very small variation in the refractive index in the z direction and the light scattering is restricted by the condition $k_{oz} = k_{ez}$ as shown in Fig. 25. The wave vectors k_o and k_e of the ordinary and extraordinary waves are given by

$$k_o = (\omega/c)n_o, \qquad k_e = (\omega/c)\frac{n_o n_e}{(n_o^2 \sin^2\theta_e + n_e^2 \cos^2\theta_e)^{1/2}}, \tag{16.10}$$

where n_o and n_e are the principal refractive indices. The condition $k_{oz} = k_{ez}$ then gives the following relation between the angles θ_o and θ_e:

$$\cos\theta_o = \frac{n_e \cos\theta_e}{(n_o^2 \sin^2\theta_e + n_e^2 \cos^2\theta_e)^{1/2}}. \tag{16.11}$$

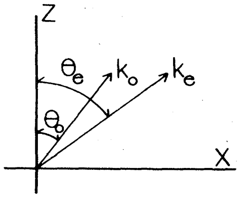

FIG. 25. Geometry to describe depolarized light scattering by static deformations in smectics. The wave vectors of ordinary ($\mathbf{k}_0$) and extraordinary ($\mathbf{k}_e$) waves are shown.

In the experiment either $\mathbf{k}_o$ or $\mathbf{k}_e$ may be the wave vector of the incident light, and according to Eq. (16.11) the scattered light will lie on a circle around the z axis. In Fig. 25 the case $n_e > n_o$ and $\theta_o < \theta_e$ has been sketched.

If the incident beam lies in the xz plane then the depolarized scattering is determined by the $\delta\epsilon_{yz}$ component of the dielectric constant. By symmetry $\delta\epsilon_{yz} \sim \epsilon_a(\partial u_z/\partial y)$ and the scattered intensity is proportional to $\epsilon_a^2 q_y^2 \langle | u_z(\mathbf{q}) |^2 \rangle$, where $\mathbf{q} = \mathbf{k}_e - \mathbf{k}_o$. Thus the scattered intensity is zero in the xz plane ($q_y = 0$). The scattered intensity would also be expected to be small for large values of q_y as the amplitude of the deformations will be small at shorter wavelengths. Experimentally a crescent of scattered light is observed with zero intensity in the xz plane in qualitative agreement with the above considerations.

D. Fredericksz transition in smectic A

The possibility of a Fredericksz transition in a smectic A in a magnetic field has been considered by Rapini (1972). One possible geometry which he considered is shown in Fig. 26. The smectic is confined between parallel glass slides with the boundary condition that the molecules at the surfaces remain parallel to the surfaces. The layers are thus normal to the surface at the glass. The magnetic field H is applied perpendicular to the glass. The results of Rapini indicate that a transition does occur at a critical field H_c of the same order as that found in the nematic case (Sec. IV,B). However, for $H > H_c$ the distortion increases very slowly with increasing field and will be difficult to detect.

This transition can be discussed by generalizing the elastic theory of smectics A of the previous section. We neglect all internal parameters and take the elastic energy in the form

$$F = \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2 - \tfrac{1}{2}\chi_a(\mathbf{n}\cdot\mathbf{H})^2 + \tfrac{1}{2}E((\mathbf{n} - \mathbf{n}_o)\cdot\mathbf{n}_o)^2, \tag{16.12}$$

where $\mathbf{n}_o$ is a unit vector along the y direction. The last term in Eq. (16.12) is thus quartic in the small deformation δn_x and will determine the rate of increase of the deformation with field above H_c. Dimensional arguments lead to the rough estimate $k_{11}/E \sim l^2$, where l is the layer separation in the smectic. From Fig. 26 we may take the director in

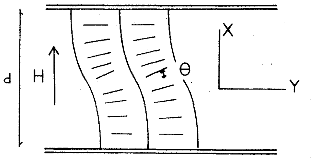

FIG. 26. Fredericksz transition in a smectic A.

the form

$$n_x = \sin\theta(x) \qquad n_y = \cos\theta(x). \tag{16.13}$$

Substitution of Eq. (16.13) into (16.12) and minimization of the elastic energy with respect to θ leads to the equation

$$k_{11}\cos\theta(d/dx)[\cos\theta(d\theta/dx)] + (E+\chi_a H^2)\sin\theta\cos\theta - E\sin\theta = 0. \tag{16.14}$$

If this equation is linearized in θ, it is found that a nontrivial solution satisfying the boundary conditions is first possible when the field reaches the critical value

$$H_c = (\pi/d)(k_{11}/\chi_a)^{1/2} \tag{16.15}$$

which is the same as in the nematic case. From Eq. (16.14) we obtain the first integral

$$k_{11}\cos^2\theta(d\theta/dx)^2 = (E+\chi_a H^2)(\cos^2\theta - \cos^2\theta_m) - 2E(\cos\theta - \cos\theta_m), \tag{16.16}$$

where θ_m is the maximum distortion at $x = 0$. From this equation we obtain the inequality

$$(\chi_a H^2 + E)(\cos\theta + \cos\theta_m) - 2E > 0 \tag{16.17}$$

which leads to

$$\cos\theta_m > [1 + (\chi_a H^2/E)]^{-1} \qquad \text{or} \qquad \theta_m^2 < 2\chi H^2/E. \tag{16.18}$$

Thus we expect $\theta_m^2 < 2(l/\xi)^2$, where ξ is the magnetic coherence length. At the transition $\xi \sim d$ and thus θ_m is very small. This result is a consequence of the fact that it costs a large energy to rotate the molecules relative to the normal to the layers. The transition has been called a "ghost" by Rapini and is probably not observable.

E. Fluctuations in smectic A

In order to study fluctuations in a smectic A we introduce the Fourier transforms of the fluctuations in density and layer displacement

$$\Delta\rho(\mathbf{r}) = V^{-1/2}\sum_q \exp(i\mathbf{q}\cdot\mathbf{r})\rho_{\mathrm{q}} \qquad \rho_{\mathrm{q}} = \rho_{-\mathrm{q}}^*$$
$$u_z(\mathbf{r}) = V^{-1/2}\sum_q \exp(i\mathbf{q}\cdot\mathbf{r})u_{z\mathrm{q}} \qquad u_{z\mathrm{q}} = u_{z-\mathrm{q}}^*. \tag{16.19}$$

Substituting in Eq. (16.5) and integrating the elastic energy density over the volume V of the smectic, we find the elastic free energy

$$F_{\mathrm{el}} = \tfrac{1}{2}\sum_q [A\,|\,\rho_{\mathrm{q}}\,|^2 + (Bq_z^2 + k_{11}q_\perp^4 + \chi_a H^2 q_\perp^2)\,|\,u_{z\mathrm{q}}\,|^2 + iCq_z u_{z\mathrm{q}}\rho_{-\mathrm{q}}]. \tag{16.20}$$

Using the equipartition theorem, we find the mean square fluctuations

$$\langle|\,\rho_{\mathrm{q}}\,|^2\rangle = \frac{k_BT}{A}\left(\frac{Bq_z^2 + k_{11}q_\perp^4 + \chi_a H^2 q_\perp^2}{\bar{B}q_z^2 + k_{11}q_\perp^4 + \chi_a H^2 q_\perp^2}\right)$$
$$\langle|\,u_{z\mathrm{q}}\,|^2\rangle = \frac{k_BT}{\bar{B}q_z^2 + k_{11}q_\perp^4 + \chi_a H^2 q_\perp^2}$$
$$\langle u_{z\mathrm{q}}\rho_{-\mathrm{q}}\rangle = \frac{iCq_z}{A}\,\frac{k_BT}{\bar{B}q_z^2 + k_{11}q_\perp^4 + \chi_a H^2 q_\perp^2}, \tag{16.21}$$

where $\bar{B} = B - (C^2/A)$.

The mean square fluctuation of a layer is

$$\langle u_z^2\rangle = \frac{1}{(2\pi)^3}\int_{q<q_m} d\mathbf{q}\,\langle\,|\,u_{z\mathrm{q}}\,|^2\rangle. \tag{16.22}$$

We have introduced a cutoff q_m at short wavelengths where the expressions (16.21) break down. Substituting Eq. (16.21) in (16.22) and carrying out the integration, we find

$$\langle u_z^2\rangle \simeq [k_BT/4\pi(k_{11}\bar{B})^{1/2}]\ln 2q_m\xi, \tag{16.23}$$

where ξ is the magnetic coherence length. The mean square fluctuations of a layer thus diverge in an infinite sample when $H \to 0$.

The instability of a layered structure, periodic in one direction, has been discussed by Landau and Lifshitz (1958, Chap. 13), de Gennes (1969b), and also in Sec. X in the case of the cholesteric structure. The smectic structure is readily stabilized by a magnetic field or by boundaries. Using the numerical values $\bar{B} = 10^{11}$ ergs/cm^3, $k_{11} = 10^{-6}$ dyn, $\chi_a = 10^{-6}$, $H = 1$ G, and $q_m = 10^7$ cm^{-1}, we find $(\langle u^2\rangle)^{1/2} = 1$ Å which is small. These fluctuations can have the effect of blurring the distinction between the "ordered" (smectic) and disordered (nematic) phases. In finite regions or in the presence of a field H it is possible for order to exist. The transformation from nematic to smectic phases need not be marked by a phase transition since there is no symmetry being broken.

F. X-ray scattering

The effects of fluctuations of the layers on the scattering of x rays has been considered by Caille (1972). Denote the position of the nth layer in a single domain smectic by $z_n = nl + u_{nz}(\boldsymbol{\varrho})$, where u_{nz} is the displacement of the layer and $\boldsymbol{\varrho} = x, y$. The intensity of x-ray scattering with wave vector transfer $\mathbf{q}$ is proportional to

$$I(\mathbf{q}) = |f|^2\sum_n \int d\boldsymbol{\varrho}\,\exp(iq_z nl)\,\exp(i\mathbf{q}_\perp\cdot\boldsymbol{\varrho})G_n(\boldsymbol{\varrho}), \tag{16.24}$$

where f is the molecular scattering factor (assumed isotropic) and

$$G_n(\boldsymbol{\varrho}) = \langle \exp[iq_z(u_n(\boldsymbol{\varrho}) - u_0(0))] \rangle \tag{16.25}$$

gives the effects of fluctuations. Using a continuum approximation [as in Eq. (16.5)], $G_n(\boldsymbol{\varrho}) = G(\mathbf{r})$, where

$$\begin{aligned} G(\mathbf{r}) = \exp\{ &-[q_z^2/(2\pi)^3] \int d\mathbf{q}' \\ &\times [1 - \exp(-i\mathbf{q}'\cdot\mathbf{r})] \langle | u_{z\mathbf{q}}' |^2 \rangle \}. \end{aligned} \tag{16.26}$$

The mean square fluctuations (with $H = 0$) are given in Eq. (16.21), and (16.26) can be evaluated to give

$$\begin{aligned} G(\mathbf{r}) &= \exp(-M)(l^2/4\pi^2\alpha z)^X \qquad \rho^2 \ll \alpha z \\ &= \exp(-2M)(l/2\pi\rho)^{2X} \qquad \rho^2 \gg \alpha z \end{aligned} \tag{16.27}$$

where

$$M = k_B T\gamma\pi/2\bar{B}\alpha l^2, \quad X = k_B T\pi/2\bar{B}\alpha l^2, \quad \alpha^2 = k_{11}/\bar{B}, \tag{16.28}$$

and γ is Euler's constant. The integral in Eq. (16.26) has been cut off at $q' = 2\pi/l$. M is the Debye–Waller factor in which we have set $q_z = 2\pi/l$ corresponding to the first Bragg reflection. The dependence of the x-ray intensity on q is obtained by substituting Eq. (16.27) in (16.24). For the two principal directions

$$\begin{aligned} I(q) &\sim | q_z - (2\pi/l) |^{-1+X}, \qquad q_\perp = 0 \\ &\sim q_\perp^{-1+2X}, \qquad q_z = 2\pi/l. \end{aligned} \tag{16.29}$$

In a smectic $X \sim 1$ and the dependence of the intensity on wave vector is anisotropic and very different from that in a crystalline solid (where $X = 0$). The anisotropy arises because the fluctuations of the smectic layers are more strongly correlated in a direction perpendicular to the layers than parallel. The anisotropy in the intensity has been observed by Diele *et al.* (1972a). Close to the smectic–nematic transition $\bar{B} \to 0$ and M and X both become large. In this case the harmonic approximation used here is not valid.

G. Light scattering in smectic A

The scattering of light is determined by the fluctuations in the dielectric constant. By symmetry we can relate these fluctuations to the fluctuations in the orientation, density, and layer spacing u by

$$\begin{aligned} \delta\epsilon_{xx} &= a_\perp \Delta\rho + b_\perp(\partial u/\partial z), \\ \delta\epsilon_{zz} &= a_{\|}\Delta\rho + b_{\|}(\partial u/\partial z), \\ \delta\epsilon_{xz} &= -\epsilon_a(\partial u/\partial x), \\ \delta\epsilon_{yz} &= -\epsilon_a(\partial u/\partial y), \end{aligned} \tag{16.30}$$

where $\epsilon_a = \epsilon_{\|} - \epsilon_\perp$ is the anisotropy in the dielectric constant and a and b are certain coefficients. An interesting case is that of depolarized light scattering which is determined by $\delta\epsilon_{xz}$ or $\delta\epsilon_{yz}$. From Eq. (16.21) we have

$$\langle | \delta\epsilon_{xz}(q) |^2 \rangle = \frac{\epsilon_a^2 k_B T q_x^2}{\bar{B} q_z^2 + k_{11} q_x^4 + \chi_a H^2 q_x^2}. \tag{16.31}$$

This becomes large $q_z = 0$ and then

$$\langle | \delta\epsilon_{xz}(q) |^2 \rangle = \epsilon_a^2 k_B T/(k_{11} q_x^2 + \chi_a H^2) \tag{16.32}$$

which is of the same form as found in a nematic. The large scattering occurs from the thermal undulations of the layers. The condition $q_z = 0$ could be achieved by scattering from the surface waves on a smectic or by very precise alignment of a single crystal. This latter condition is difficult to achieve. From Eq. (16.31) we require the angle ϕ between q and the layers to be $\phi = q_z/q \simeq (k_{11}/\bar{B})^{1/2} q \simeq ql = 10^{-2} - 10^{-3}$. Brillouin scattering from the density fluctuations in a smectic A has been observed by Liao *et al.* (1973) and will be discussed further below.

H. Dynamics of fluctuations in smectic A

The character of the modes of a smectic A depends on the direction of propagation. We assume that the smectic layers lie parallel to the xy plane. For a general direction of propagation $q_x, q_z \neq 0$ it was shown by de Gennes (1969b) that there are two propagating sound wave modes and one overdamped transverse viscous mode. The propagating modes are a mixture of longitudinal and transverse modes. In the case $q_z = 0$ (propagation along the layers) there is one propagating longitudinal mode, one overdamped shear mode, and a very slowly damped undulation mode. In the case $q_x = 0$ (propagation perpendicular to the layers) there is one propagating longitudinal mode and two viscously damped shear modes. The smectic A is thus intermediate between a solid (three propagating modes) and an isotropic liquid (one propagating mode and two overdamped shear wave modes).

The equation of motion of the smectic A is

$$\rho(\partial v_i/\partial t) + (\partial/\partial x_j) T_{ij} = 0, \tag{16.33}$$

where v_i is the velocity and T_{ij} is the stress tensor. The reactive part of the stress tensor, $T_{ij}^{(r)}$, is determined from the elastic energy [Eq. (16.6)]. Using $\Delta\rho = -\rho(u_{xx} + u_{yy} + u_{zz})$ where $u_{xx} = \partial u_x/\partial x$, etc. and u_x, u_y, and u_z are the displacements in the x, y, and z directions, we find

$$\begin{aligned} T_{xx}^{(r)} &= -A\rho^2(u_{xx} + u_{zz}) + C\rho u_{zz}, \\ T_{zz}^{(r)} &= -A\rho^2(u_{xx} + u_{zz}) + C\rho(u_{xx} + 2u_{zz}) - Bu_{zz}, \\ T_{zx}^{(r)} &= [k_{11}(\partial^3/\partial x^3) - \chi_a H^2(\partial/\partial x)] u_z. \end{aligned} \tag{16.34}$$

We assume, without loss of generality, that the disturbance is propagating in the xz plane and denote the wave vector by $\mathbf{q} \equiv q_x, q_z$. Thus terms in u_{yy} are zero.

The viscous part of the stress tensor $T_{ij}^{(v)}$ is taken to be symmetric. The most general form consistent with the uniaxial symmetry of a smectic A is

$$T_{ij}^{(\text{visc})} = -(\eta_1 d_{kk} + \eta_2 d_{kl} n_k n_l)\delta_{ij} - (\eta_3 d_{kk} + \eta_4 d_{kl} n_k n_l) n_i n_j - \eta_5 d_{ij}. \qquad (16.35)$$

Substituting Eqs. (16.34) and (16.35) in (16.33), and assuming that the disturbance varies with time like exp $(-i\omega t)$, we obtain the three equations

$$[\rho\omega + (i/2) q^2 \eta_5] v_y = 0, \qquad (16.36)$$

$$u_x[\rho\omega^2 - A\rho^2 q_x^2 + i\omega(q_x^2(\eta_1 + \eta_5) + \tfrac{1}{2} q_z^2 \eta_5)] - u_z[A\rho^2 - C\rho - i\omega(\eta_1 + \eta_2 + \tfrac{1}{2}\eta_5)] q_x q_z = 0, \qquad (16.37)$$

$$u_z[\rho\omega^2 - \rho q_z^2(A\rho - 2C) - Bq_z^2 - q_x^2(k_{11} q_x^2 + \chi_a H^2) + i\omega(q_z^2 \eta_T + \tfrac{1}{2} q_x^2 \eta_5)] - u_x[A\rho^2 - C\rho - i\omega(\eta_1 + \eta_3 + \tfrac{1}{2}\eta_5)] q_x q_z = 0, \qquad (16.38)$$

where $\eta_T = \eta_1 + \eta_2 + \eta_3 + \eta_4 + \eta_5$. Equation (16.36) leads to an overdamped transverse mode familiar in isotropic liquids. We first consider Eqs. (16.37) and (16.38) in two special cases:

(i) $q_z = 0$. Equation (16.37) leads to a propagating longitudinal sound wave mode with dispersion relation

$$\omega^2 = \rho A q_x^2 - i\omega q_x^2[(\eta_1 + \eta_5)/\rho]. \qquad (16.39)$$

Equation (16.38) leads to two overdamped modes with approximate dispersion relations

$$\omega_S = -2i(k_{11} q_x^2 + \chi_a H^2)/\eta_5, \qquad \omega_F = -(i/2\rho)\eta_5 q_x^2. \qquad (16.40)$$

These modes are very similar to the slow and fast relaxing modes of nematics (see Sec. VIII). The slow mode in this case is an undulation of the layers.

(ii) $q_x = 0$. Equation (16.37) leads to a viscously damped transverse mode of exactly the same form as Eq. (16.36), as must be the case from symmetry. The longitudinal sound wave mode is described by Eq. (16.38) and has dispersion relation

$$\omega^2 + i\omega q_z^2 \eta_T/\rho - q_z^2[A\rho + (B/\rho) - 2C] = 0. \qquad (16.41)$$

(iii) q_x, $q_z \neq 0$. In the case of a general direction of propagation, Eqs. (16.37) and (16.38) lead to two propagating sound wave modes. To determine the velocities of these modes, we neglect the viscosity coefficients and the small terms in k_{11} and H^2. The dispersion relation for these modes is

$$\omega^4 - \omega^2\{A\rho q_x^2 + [A\rho + (B/\rho) - 2C] q_z^2\} + (BA - C^2) q_x^2 q_z^2 = 0. \qquad (16.42)$$

The two sound velocities thus satisfy the relations

$$s_1^2 + s_3^2 = A\rho + [(B/\rho) - 2C]\cos^2\theta$$
$$s_1^2 s_3^2 = (AB - C^2)\sin^2\theta\cos^2\theta, \qquad (16.43)$$

where θ is the angle between the direction of propagation and the normal to the smectic planes.

Liao, Clark, and Pershan (1973) have observed the Brillouin scattering from monodomain samples of β-methyl butyl *p*((*p*-methoxy benzylidine) amino) cinnamate in the smectic A and B phases. Their results confirm that there are two propagating sound waves in the smectic A structure, and they have measured the three elastic constants A, B, and C. The orientational dependence of the velocities also agrees well with that predicted by Eqs. (16.43). In the smectic B phase Liao *et al.* observed three propagating modes, which is consistent with the assumed crystalline ordering within the layers of this phase.

I. Molecular field description of the smectic A Phase

The Maier–Saupe molecular field description of the nematic phase (Sec. II) has been extended by McMillan (1971) and Kobayashi (1971) to describe the smectic A phase. An additional order parameter is introduced to describe the positional ordering of the molecules in the layered structure. As in the Maier–Saupe theory, McMillan assumes that the ordering arises from the angular-dependent attractive interaction between molecules. The specific form for the potential used was

$$V(\mathbf{r}_{\mathrm{AB}}, \boldsymbol{\nu}_{\mathrm{A}}\cdot\boldsymbol{\nu}_{\mathrm{B}}) = -\frac{C}{2\pi^{3/2} r_0^3}(3\cos^2\theta_{\mathrm{AB}} - 1) \times \exp(-r_{\mathrm{AB}}^2/r_0^2), \qquad (16.44)$$

where C is a constant, r_{AB} is the distance between the centers of mass of the molecules A and B, θ_{AB} is the angle between their molecular axes $\boldsymbol{\nu}_{\mathrm{A}}$ and $\boldsymbol{\nu}_{\mathrm{B}}$, and r_0 determines the range of the force.

In the molecular field description the potential (16.44) is replaced by an effective potential for a single molecule

$$V(\mathbf{r}_{\mathrm{A}}, \boldsymbol{\nu}_{\mathrm{A}}) = N_T \int d\mathbf{r}_{\mathrm{B}}\, d\boldsymbol{\nu}_{\mathrm{B}} P(\mathbf{r}_{\mathrm{B}}, \boldsymbol{\nu}_{\mathrm{B}}) V(\mathbf{r}_{\mathrm{AB}}, \boldsymbol{\nu}_{\mathrm{A}}\cdot\boldsymbol{\nu}_{\mathrm{B}}), \qquad (16.45)$$

where $P(\mathbf{r}, \boldsymbol{\nu})$ is the probability of finding a molecule at $\mathbf{r}$ with orientation $\boldsymbol{\nu}$ and N_T is the number of molecules. We will assume that the smectic A phase is uniaxial and that the positional ordering takes place in planes normal to the z axis. In this case the probability P only depends on the coordinate z and the angle θ that the molecule makes with the z axis; it can be expanded in a Fourier series:

$$P(\mathbf{r},\boldsymbol{\nu}) = (1/2\pi V)[P^{(0)}(\theta) + P^{(1)}(\theta)\cos(2\pi z/l) + \cdots], \qquad (16.46)$$

where V is the volume. The effective one-molecule potential can also be written in this form

$$\begin{aligned} V(\mathbf{r},\boldsymbol{\nu}) &= V(z,\theta) \\ &= V_0(\theta) + V_1(\theta)\cos(2\pi z/l) + \cdots, \end{aligned}$$

where

$$\begin{aligned} V_0(\theta_{\mathrm{A}}) &= (N/2\pi)\int d\mathbf{r}_{\mathrm{B}}\, d\boldsymbol{\nu}_{\mathrm{B}} P^{(0)}(\theta_{\mathrm{B}}) V(r_{\mathrm{AB}}, \boldsymbol{\nu}_{\mathrm{A}}\cdot\boldsymbol{\nu}_{\mathrm{B}}), \\ V_1(\theta_{\mathrm{A}}) &= (N/2\pi)\int d\mathbf{r}_{\mathrm{B}}\, d\boldsymbol{\nu}_{\mathrm{B}} P^{(1)}(\theta_{\mathrm{B}}) V(r_{\mathrm{AB}}, \boldsymbol{\nu}_{\mathrm{A}}\cdot\boldsymbol{\nu}_{\mathrm{B}}) \\ &\quad \times \cos(2\pi/l)(z_{\mathrm{A}} - z_{\mathrm{B}}), \end{aligned} \tag{16.47}$$

and N is the number density. With the potential assumed by McMillan, Eq. (16.44), we find

$$\begin{aligned} V_0(\theta) &= -A_0 S(1 - \tfrac{3}{2}\sin^2\theta), \\ V_1(\theta) &= -A_0\alpha\sigma(1 - \tfrac{3}{2}\sin^2\theta), \end{aligned} \tag{16.48}$$

where $A_0 = NC$, $\alpha = 2\exp[-(\pi r_0/l)^2]$, and the order parameters are defined by

$$\begin{aligned} S &= \int_0^\pi \sin\theta d\theta P^{(0)}(\theta)(1 - \tfrac{3}{2}\sin^2\theta) \\ \sigma &= \tfrac{1}{2}\int_0^\pi \sin\theta d\theta P^{(1)}(\theta)(1 - \tfrac{3}{2}\sin^2\theta). \end{aligned} \tag{16.49}$$

The order parameter S describes the orientational ordering and is the same as that of Maier and Saupe. The order parameter σ is related to the ordering of the molecules into layers and is a measure of the amplitude of the density wave along z.

The theory is made self-consistent by choosing the distribution function to be

$$P(\mathbf{r},\boldsymbol{\nu}) = (L/2\pi VI)\exp(-V(z,\theta)/kT), \tag{16.50}$$

where L is the length of the specimen in the z direction and the normalization constant is

$$I = \int_0^L dz \int_0^\pi \sin\theta d\theta \exp[-V(z,\theta)/kT]. \tag{16.51}$$

Comparing Eq. (16.46) and Eq. (16.50), we have

$$\begin{aligned} P^{(0)}(\theta) &= I^{-1}\int_0^L dz \exp[-V(z,\theta)/kT] \\ P^{(1)}(\theta) &= 2I^{-1}\int_0^L dz \cos(2\pi z/l)\exp[-V(z,\theta)/kT]. \end{aligned} \tag{16.52}$$

When these results are substituted in Eqs. (16.49), we obtain the two self-consistency requirements

$$\begin{aligned} S &= I^{-1}\int_0^L dz\int_0^\pi \sin\theta d\theta \exp[-V(z,\theta)/kT](1 - \tfrac{3}{2}\sin^2\theta] \\ \sigma &= I^{-1}\int_0^L dz\int_0^\pi \sin\theta d\theta \exp[-V(z,\theta)/kT] \\ &\quad \times \cos(2\pi z/l)(1 - \tfrac{3}{2}\sin^2\theta). \end{aligned} \tag{16.53}$$

There are three possible solutions to these equations.

(a) $S = \sigma = 0$ isotropic liquid phase.

(b) $S \neq 0$, $\sigma = 0$ nematic phase.

(c) $S \neq 0$, $\sigma \neq 0$ smectic phase.

The most stable phase is that which minimizes the free energy per particle

$$F = -(A_0/2)(S^2 + \alpha\sigma^2) - kT\ln I. \tag{16.54}$$

The two equations (16.53) have been solved numerically by McMillan to obtain the order parameters, transition temperatures, entropy, and specific heat. Two parameters, A_0 and α, enter the theory. The nematic–isotropic transition temperature T_c is determined by A_0. The other parameter $\alpha = 2\exp[-(\pi r_0/l)^2]$ varies between 0 and 2 and determines the smectic–nematic transition temperature T_{SN}. T_{SN} is an increasing function of α and coincides with T_c for $\alpha = 0.98$. The smectic–nematic transition is of second order for $\alpha < 0.7$ and of first order for $0.7 < \alpha < 0.98$. The orientational order parameter is continuous at a second-order smectic–nematic transition and changes discontinuously at a first-order transition. Possible second-order nematic–smectic phase transitions have been reported by Doane *et al.* (1972) in the homologous series 4-*n*-alkoxybenzylidene-4′-phenylazoaniline and by Cabane and Clark (1973) in 4-nitrile-benzilidine-*p*-*N* octyloxy-aniline.

McMillan has argued that the layer spacing l is determined by the length of the molecule while the range of the force r_0 is determined by the interaction of the central core of the molecules. On this assumption α increases with increasing length of the molecules in a homologous series of compounds in which the central core of the molecule is the same and the length is determined by the attached alkyl chains. This is in qualitative agreement with the phase diagrams of homologous series studied by Arnold (1968).

Recent x-ray measurements by McMillan (1972) on cholesteryl myristate indicate that the order parameter varies more rapidly with temperature in the smectic phase and exhibits a smaller jump at T_{SN} than predicted by the above model. The reason for the large jump in the order parameters at T_{SN} in the model is the strong correlation between the orientational and positional order parameters. McMillan (1972) has modified the above model by including an attractive *s*-wave potential, which relaxes this correlation, and obtained better agreement with experiment.

J. Landau theory of nematic–smectic A transition

The Landau theory of the nematic–smectic A transition has been considered by de Gennes (1972a) and McMillan (1972). A useful analogy between smectics A and superconductors has been pointed out by de Gennes (1972a). The order parameter in a smectic A determines the amplitude of the density wave. Retaining only the lowest Fourier component, we can write the density as

$$\rho(\mathbf{r}) = \rho_0 + \tfrac{1}{2}[\exp(2\pi iz/l)\chi(\mathbf{r}) + \text{c.c.}], \tag{16.55}$$

where ρ_0 is the average density and the order parameter $\chi(\mathbf{r})$ is a complex quantity slowly varying in $\mathbf{r}$. The phase of χ determines the position of the layers. Near the nematic–smectic transition we assume that χ is small and expand the free energy density in powers of χ:

$$g = g_n + A(T)\,|\chi|^2 + \tfrac{1}{2}B\,|\chi|^4 + \tfrac{1}{2}m_l^{-1}\,|\partial\chi/\partial z|^2 + \tfrac{1}{2}m_t^{-1}\{\,|[\partial/\partial x - (2\pi i/l)\,\delta n_x]\chi\,|^2 + |[\partial/\partial y - (2\pi i/l)\,\delta n_y]\chi\,|^2\}, \qquad (16.56)$$

where g_n is the free energy density of the nematic state. It has been assumed that the smectic layers are parallel to the xy plane and the fluctuations in the director, $\delta n_{x,y}$, are included in order that the free energy be invariant under small rotations of the layers. The condition that χ is small is satisfied in the nematic state and in the smectic state if the transition is of second order. We assume that the coefficient $A(T) = A'(T - T_{\mathrm{SN}}^*)$, where T_{SN}^* is close to the nematic–smectic transition temperature (for a second-order transition $T_{\mathrm{SN}}^* = T_{\mathrm{SN}}$) and B, m_l, m_t are constants.

The free energy [Eg. (16.56)] is of exactly the same form as the Landau–Ginzburg free energy density for a superconductor (de Gennes, 1966) if we identify $\delta\mathbf{n}$ with the vector potential. This analogy can be carried further: the condition that the layer separation in the smectic is constant is

$$l^{-1}\oint \mathbf{n}\cdot d\mathbf{l} = 0 \qquad (16.57)$$

where the integral is taken around a closed circuit in the smectic. This condition is equivalent to the flux quantization in a superconductor.

In the presence of elastic distortions the free energy density [Eq. (16.56)] must be supplemented by the elastic free energy density

$$g_{\mathrm{el}} = \tfrac{1}{2}k_{11}(\nabla\cdot\mathbf{n})^2 + \tfrac{1}{2}k_{22}(\mathbf{n}\cdot\mathrm{curl}\,\mathbf{n})^2 + \tfrac{1}{2}k_{33}(\mathbf{n}\times\mathrm{curl}\,\mathbf{n})^2. \qquad (16.58)$$

It is useful to define a quantity $\mathbf{h} = (2\pi/l)$ curl $\mathbf{n}$, analogous to a magnetic field, and then the last two terms of Eq. (16.58) are equivalent to the magnetic field energy density in a superconductor.

Two important types of lengths enter into Eqs. (16.56) and (16.58):

(a) coherence lengths $\xi = [2mA(T)]^{-1/2}$, where m may be either m_l or m_t. These lengths determine the distance over which a local perturbation affects $|\chi|$. For example, the core of a dislocation in the smectic phase is of dimension ξ.

(b) penetration depths $\lambda = (l/2\pi)(mkB/A)^{1/2}$. A small twist or bend deformation applied to the surface of a smectic penetrates a distance λ into the bulk smectic (k is the appropriate elastic constant; k_{22} for twist and k_{33} for bend).

The order parameter and director are determined by minimizing the free energies (16.56) and (16.58). The resulting equations have been extensively studied in the theory of superconductivity (de Gennes, 1966), and this analogy leads immediately to the following results in the case of a second-order transition.

(1) A splay deformation does not couple to the order parameter $|\chi|$ if the phase of χ is chosen appropriately. Thus a splay deformation, i.e., undulation of layers or focal conic structure, will not affect T_{SN}.

(2) As in a superconductor the ratio $\kappa = \lambda/\xi$ plays an important role. When $\mathbf{h} = (2\pi/l)$ curl $\mathbf{n}$ is nonzero (i.e., in the presence of twist or bend), two types of behavior can occur depending on the value of κ.

(a) If $\kappa < 1/\sqrt{2}$ the smectic behaves like a type I superconductor and the nematic–smectic transition is first order for finite $\mathbf{h}$. The transition temperature $T_{\mathrm{SN}}(h)$ is determined by equating the free energies of the deformed nematic state and the smectic state:

$$(k/2)(\mathrm{curl}\,\mathbf{n})^2 \simeq A^2[T_{\mathrm{SN}}(h)]/2B \qquad (16.59)$$

with $k = k_{22}$, k_{33} for twist and bend, respectively. In the smectic state the twist or bend is excluded. This is the analog of the Meissner effect in superconductors.

(b) If $\kappa > 1/\sqrt{2}$ the smectic behaves like a type II superconductor and shows a mixed state. In the smectic mixed state the deformation h is relaxed by the formation of a regular array of dislocations. Thus if a deformed nematic state is cooled, a second-order transition to a smectic mixed state occurs at a temperature $T_{\mathrm{SN}}^{(m)}$ given approximately by

$$|h|\pi\xi^2 = \pi$$

or

$$A'(T_{\mathrm{SN}} - T_{\mathrm{SN}}^{(m)}) = (1/2m)\,|h|, \qquad (16.60)$$

where $m = m_t$ for twist and $m = (m_l m_t)^{1/2}$ for bend deformations. If the deformation described by h takes place over a distance d, then $h \sim 2\pi/dl$. Using the estimate $2mA'T_{\mathrm{SN}} \approx \xi_0^{-2} \approx l^{-2}$ the decrease in the transition temperature is

$$(T_{\mathrm{SN}} - T_{\mathrm{SN}}^{(m)})/T_{\mathrm{SN}} \approx l/d \qquad (16.61)$$

which may be measurable.

(3) The twist and bend elastic constants k_{22} and k_{33} are analogous to the susceptibility in the superconducting case. In the nematic phase, at temperatures just above T_{SN}, fluctuations will lead to an increase in these elastic constants. This is the analog of fluctuation diamagnetism in superconductors (Schmid, 1969). The order parameter vanishes on the average in the nematic state, but close to T_{SN} fluctuations lead to the formation of smectic droplets of size ξ. These droplets do not accept twist or bend deformations, and thus give rise to an increase in the elastic constants k_{22} and k_{33}. The order of magnitude of the effect is simply estimated as follows: the free energy density associated with a deformation δn of extent ξ is $(1/2m)(2\pi/l)^2\delta n^2\,|\chi|^2$. This leads to a contribution to an elastic constant of $\delta k \sim (1/2m)(2\pi/l)^2\xi^2\,|\chi|^2$. The free energy required to produce a fluctuation in $|\chi|^2$ of volume ξ^3 is $A(T)\,|\chi|^2\xi^3 \sim k_BT$, which gives $|\chi|^2 \sim 2mk_BT/\xi$. Thus we obtain the estimate $\delta k \sim (2\pi/l)^2 k_BT\xi$. The exact

results (de Gennes, 1972a) are

$$\delta k_{22} = (\pi k_B T/6m_t l^2)[m_l/A(T)]^{1/2}$$

$$\delta k_{33} = (\pi k_B T/6l^2)[m_l A(T)]^{-1/2}. \qquad (16.62)$$

In each case the fluctuation contribution is predicted to increase as $(T - T_{\mathrm{SN}})^{-\nu}$. The molecular field description gives $\nu = \frac{1}{2}$, while an analogy with critical phenomena suggests $\nu \simeq \frac{2}{3}$.

A large increase in the bend elastic constant near the smectic A transition has been observed in *p*-butoxybenzylidene-*p*′-*β*-methylbutylaniline (BBMBA) (Cheung and Meyer, 1973) and in *p*-cyanobenzylidene-*p*′-octyloxyaniline (CBOOA) (Cheung, Meyer, and Gruler, 1973; Cladis, 1973) using the Fredericksz transition technique. In BBMBA the nematic–smectic A transition is weakly first order and the exponent $\nu \simeq \frac{1}{2}$. In CBOOA recent volumetric studies (Torza and Cladis, 1974) show that the transition is also (very weakly) first order. The temperature dependence of the bend elastic constant in the purer samples (Cladis, 1973) gave an exponent $\nu \simeq \frac{1}{2}$. The splay elastic constant in these materials showed no anomaly as expected theoretically. The twist elastic constant in CBOOA has been measured by Rayleigh scattering by Delaye, Ribotta, and Durand (1973). The fluctuation contribution was found to diverge with an exponent $\nu \simeq \frac{2}{3}$.

(4) The liquid structure factor $S(q)$ has been measured by x-ray scattering in several liquid crystals by McMillan (1972, 1973). Strong pretransitional scattering was observed in the nematic phase just above T_{SN} and interpreted using the Landau theory. From Eqs. (16.55) and (16.56) the contribution to $S(\mathbf{q})$ from fluctuations in χ is (neglecting director fluctuations)

$$S(\mathbf{q}) = \frac{k_B T}{A(T)\{1 + \xi_l^2[|q_z| - (2\pi/l)]^2 + \xi_t^2 q^2\}}, \qquad (16.63)$$

where ξ_l and ξ_t are the two coherence lengths. The scattered intensity as a function of q is a Lorentzian centered at the position of the first Bragg peak. McMillan (1973) has obtained values for A, ξ_l, and ξ_t from the x-ray data on *p*-*n*-octyloxybenzylidene-*p*′-toluidine and confirmed the wave vector dependence in Eq. (16.63). The observed temperature dependence of these parameters in this liquid crystal agreed with the molecular field predictions.

K. Elastic theory of smectics C

In the smectic C structure the preferred direction of alignment of the molecules is tilted away from the normal to the layers. A smectic C can then be biaxial (Taylor, Fergason, and Arora, 1970) whereas a smectic A is uniaxial. The elastic theory of smectics C has been considered by the Orsay group (1971b) and by Rapini (1972). This theory is the analog of the Oseen description of smectics A, and all changes in internal parameters (density, interlayer distance, and tilt angle) are neglected. The Orsay group used the Lagrangian description for the elastic strains in which a vector $\mathbf{\Omega}(x, y, z)$ describing the local rotation is introduced.

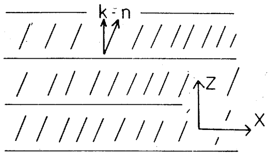

FIG. 27. Assumed structure of a smectic C liquid crystal.

In order to be consistent with the elastic theory for nematics (Sec. III), we use an alternative Eulerian description based on the director. This is compared below with the Orsay theory in Sec. XVI,K2.

1. Eulerian description

The unperturbed smectic C structure is taken to be a planar layered structure with the z axis perpendicular to the layers. We introduce two unit vectors $\boldsymbol{\kappa}$ and $\mathbf{n}$; $\boldsymbol{\kappa}$ is normal to the layers and $\mathbf{n}$ is along the preferred direction of the molecules as shown in Fig. 27. In the unperturbed state $\boldsymbol{\kappa} = \boldsymbol{\kappa}_0$ is along the z axis, and $\mathbf{n} = \mathbf{n}_0$ lies in the xz plane making an angle θ_0 with $\boldsymbol{\kappa}_0$. A small elastic distortion is described by the components κ_x, κ_y of $\boldsymbol{\kappa}$ and $\delta n_x = n_x - n_{0x}$, n_y and $\delta n_z = n_z - n_{0z}$ of $\mathbf{n}$. In the Oseen description the constraints are

$$\text{(a)}\ \mathbf{n}^2 = 1;\ \text{i.e., } \mathbf{n}_0\cdot\delta\mathbf{n} = \delta n_x \sin\theta_0 + \delta n_z \cos\theta_0 = 0. \qquad (16.64)$$

(b) $\mathbf{n}\cdot\boldsymbol{\kappa} = \cos\theta_0$; i.e., the tilt angle is constant. Together with Eq. (16.64) this gives

$$\delta n_x = \kappa_x \cos\theta_0$$

$$\delta n_z = -\kappa_x \sin\theta_0. \qquad (16.65)$$

(c) curl $\boldsymbol{\kappa} = 0$; i.e., the distance between layers is constant. In terms of the components κ_x and κ_y, this condition is

$$\partial\kappa_x/\partial z = \partial\kappa_y/\partial z = 0$$

$$\partial\kappa_x/\partial y = \partial\kappa_y/\partial x. \qquad (16.66)$$

We can thus define six independent curvature strain components

$$a_1 = \partial n_y/\partial y \qquad a_2 = \partial n_y/\partial z \qquad a_3 = \partial n_y/\partial x$$

$$a_4 = \partial\kappa_x/\partial x \qquad a_5 = \partial\kappa_y/\partial y$$

$$a_6 = \tfrac{1}{2}(\partial\kappa_x/\partial y + \partial\kappa_y/\partial x). \qquad (16.67)$$

We now proceed, as in the nematic case, to expand the free energy density up to terms quadratic in the curvature strains:

$$g = \sum_{i=1}^{6} \alpha_i a_i + \tfrac{1}{2} \sum_{i,j=1}^{6} \alpha_{ij} a_i a_j, \qquad (16.68)$$

where the α are the curvature elastic moduli. The symmetry properties of the smectic C structure places restrictions on these elastic moduli which may be determined as in the nematic case. For nonpolar, optically inactive molecules all the linear terms vanish and the most general expression for the elastic energy density contains nine elastic constants:

$$\begin{aligned} g = {} & \tfrac{1}{2}\alpha_{11}(n_{yy})^2 + \tfrac{1}{2}\alpha_{22}(n_{yz})^2 + \tfrac{1}{2}\alpha_{33}(n_{yx})^2 + \alpha_{23}n_{yz}n_{yx} \\ & + \tfrac{1}{2}\alpha_{44}\kappa_{xx}{}^2 + \tfrac{1}{2}\alpha_{55}\kappa_{yy}{}^2 + \alpha_{45}\kappa_{xx}\kappa_{yy} + \alpha_{14}n_{yy}\kappa_{xx} \\ & + \alpha_{15}n_{yy}\kappa_{yy}, \end{aligned} \tag{16.69}$$

where $n_{yx} = \partial n_y/\partial x$ etc. Certain terms which only contribute to surface energies have been neglected. The first four terms in Eq. (16.69) refer to rotations of the director without any distortion of the layers. The elastic moduli α_{44}, α_{55}, and α_{45} refer to undulations of the layers, and the last two terms are cross terms between these two types of elastic strains. The stability of the smectic C structure imposes the following inequalities on the elastic moduli:

$$\begin{gathered} \alpha_{11},\, \alpha_{22} > 0, \qquad \alpha_{22}\alpha_{33} > \alpha_{23}{}^2, \qquad \alpha_{11}\alpha_{44} > \alpha_{14}{}^2 \\ (\alpha_{11}\alpha_{55} - \alpha_{15}{}^2)(\alpha_{11}\alpha_{44} - \alpha_{14}{}^2) > (\alpha_{11}\alpha_{45} - \alpha_{14}\alpha_{15})^2. \end{gathered} \tag{16.70}$$

The elastic energy is used below to discuss some possible types of Fredericksz transitions induced by applying a magnetic field to a smectic C (Rapini, 1972). As in the smectic A case, all transitions involving a distortion of the layers are probably not observable, as the distortion of the molecular alignment increases very slowly with increasing field. Thus for the discussion of the Fredericksz transition we need only retain the first four terms of Eq. (16.69). It is convenient to introduce a vector $\mathbf{n}_\perp = \mathbf{n} - (\mathbf{n}\cdot\boldsymbol{\kappa}_0)\boldsymbol{\kappa}_0$ which lies in the plane normal to $\boldsymbol{\kappa}_0$ and satisfies $\mathbf{n}_\perp{}^2 =$ constant. In vectorial notation the elastic energy density is

$$\begin{aligned} g = {} & \tfrac{1}{2}\alpha_{11}(\nabla\cdot\mathbf{n}_\perp)^2 + \tfrac{1}{2}\alpha_{22}'(\mathbf{n}_\perp\cdot\operatorname{curl}\mathbf{n}_\perp)^2 + \tfrac{1}{2}\alpha_{33}(\boldsymbol{\kappa}_0\cdot\operatorname{curl}\mathbf{n}_\perp)^2 \\ & - \alpha_{23}'(\mathbf{n}_\perp\cdot\operatorname{curl}\mathbf{n}_\perp)(\boldsymbol{\kappa}_0\cdot\operatorname{curl}\mathbf{n}_\perp), \end{aligned} \tag{16.71}$$

where $\alpha_{22}'\sin^2\theta_0 = \alpha_{22}$, $\alpha_{23}'\sin\theta_0 = \alpha_{23}$. The first three terms of Eq. (16.71) are analagous to splay, twist, and bend in nematics, respectively. These types of rotations were first discussed by Saupe (1969). This expression may be generalized to a cholesteric type of smectic C where the tilt angle varies linearly with z by replacing $\mathbf{n}_\perp\cdot\operatorname{curl}\mathbf{n}_\perp$ by $\mathbf{n}_\perp\cdot\operatorname{curl}\mathbf{n}_\perp + t_0\mathbf{n}_\perp{}^2$ where the full pitch is $2\pi/t_0$.

2. *Lagrangian description*

The Orsay group (1971b) has used the Lagrangian method to describe the strains in a smectic C. In this description a vector $\boldsymbol{\Omega}(\mathbf{r})$ whose direction gives the axis of rotation and whose magnitude gives the angle of rotation of the medium at $\mathbf{r}$ is introduced. The elastic energy density can be written in terms of $\boldsymbol{\Omega}$ by noting that the changes in the unit vectors $\boldsymbol{\kappa}$ and $\mathbf{n}$ are related to $\boldsymbol{\Omega}$ by

$$\begin{aligned} \boldsymbol{\kappa} - \boldsymbol{\kappa}_0 &= \boldsymbol{\Omega} \times \boldsymbol{\kappa}_0 \\ \mathbf{n} - \mathbf{n}_0 &= \boldsymbol{\Omega} \times \mathbf{n}_0. \end{aligned} \tag{16.72}$$

The constraints (16.66) can now be written

$$\begin{aligned} \Omega_{xz} &= \Omega_{yz} = 0 \\ \Omega_{xx} - \Omega_{yy} &= 0, \end{aligned} \tag{16.73}$$

where $\Omega_{xy} = \partial\Omega_x/\partial y$ etc. Substituting these results in Eq. (16.69) gives

$$\begin{aligned} g = {} & \tfrac{1}{2}A_{11}\Omega_{xx}{}^2 + \tfrac{1}{2}A_{21}\Omega_{xy}{}^2 + \tfrac{1}{2}A_{12}\Omega_{yx}{}^2 + \tfrac{1}{2}B_1\Omega_{zx}{}^2 + \tfrac{1}{2}B_2\Omega_{zy}{}^2 \\ & + \tfrac{1}{2}B_3\Omega_{zz}{}^2 + B_{13}\Omega_{zx}\Omega_{zz} + C_1\Omega_{xx}\Omega_{zx} + C_2\Omega_{xy}\Omega_{zy} \end{aligned} \tag{16.74}$$

where we have used the notation of the Orsay group for the elastic moduli. The relations between these elastic moduli and the α_{ij} are (with $s = \sin\theta_0$, $c = \cos\theta_0$)

$$\begin{gathered} A_{11} = c^2\alpha_{33} + 2\alpha_{45} + 2c\alpha_{14}, \qquad A_{21} = c^2\alpha_{11} + \alpha_{55} + 2c\alpha_{15}, \\ A_{12} = \alpha_{44}, \qquad B_1 = s^2\alpha_{33}, \qquad B_2 = s^2\alpha_{11}, \qquad B_3 = s^2\alpha_{22}, \\ B_{13} = s^2\alpha_{23}, \qquad C_1 = -s(c\alpha_{33} + \alpha_{14}), \\ C_2 = -s(c\alpha_{11} + \alpha_{15}). \end{gathered} \tag{16.75}$$

L. Fredericksz transition in smectic C

There are a wide variety of geometries in which an experiment to measure the distortion produced by an applied magnetic field (Fredericksz transition) can be made. A number of important cases has been considered by Rapini (1972). The smectic is confined between parallel glass slides, and it is supposed that the boundary conditions at the glass are such that the molecular orientation is fixed at the boundary. Rapini has shown that all transitions requiring a distortion of the layers are probably not observable because the distortion of the molecular alignment increases very slowly with increasing field. The interesting cases thus involve a rotation of the preferred direction $\mathbf{n}$ about the normal to the layers. We denote the three principal susceptibilities of the smectic by χ_i, $i = 1, 2, 3$. χ_3 is the susceptibility along $\mathbf{n}$, χ_1 the susceptibility perpendicular to $\mathbf{n}$ in the xz plane (Fig. 27), and χ_2 is the susceptibility perpendicular to both these directions. The type of Fredericksz transition depends on the relative orders of magnitude of these susceptibilities. We consider three principal geometries in Fig. 27 in which the enclosing glass slides are parallel to the layers.

(a) $\mathbf{H} \parallel \mathbf{n}_0$. If $\chi_2 > \chi_3$ the field will induce a twist of the director $\mathbf{n}$ about the z axis. Introducing $n_{\perp x} = \sin\theta_0\cos\phi(z)$, $n_{\perp y} = \sin\theta_0\sin\phi(z)$ in the elastic energy (16.71), and including the magnetic energy, we find (again $s = \sin\theta_0$, $c = \cos\theta_0$)

$$\begin{aligned} g = {} & \tfrac{1}{2}\alpha_{22}s^2(\partial\phi/\partial z)^2 - \tfrac{1}{2}H^2[\chi_1 s^2c^2(1 - \cos\phi)^2 + \chi_2 s^2\sin^2\phi \\ & \times \chi_3(s^2\cos\phi + c^2)^2]. \end{aligned} \tag{16.76}$$

Retaining only the terms quadratic in ϕ in Eq. (16.76), the critical field is found to be

$$H_c = \frac{\pi s}{d}\left(\frac{\alpha_{22}}{\chi_2 - \chi_3}\right)^{1/2}. \tag{16.77}$$

(b) $\mathbf{H} \perp \mathbf{n}_0$ with H in the xz plane. If $\chi_2 > \chi_1$ the field will induce a twist of $\mathbf{n}$ about the z axis. The critical field may be shown to be

$$H_c = \frac{\pi s}{cd}\left(\frac{\alpha_{22}}{\chi_2 - \chi_1}\right)^{1/2}. \qquad (16.78)$$

(c) $\mathbf{H}$ along y axis. The field can again induce a twist in $\mathbf{n}$ around z. The critical field is

$$H_c = \frac{\pi s}{d}\left(\frac{\alpha_{22}}{\chi_1 c^2 + \chi_3 s^2 - \chi_2}\right)^{1/2}. \qquad (16.79)$$

In general we expect $\chi_3 > \chi_2 \simeq \chi_1$ in which case (a) will not occur and (b) may not occur, or occur only for extremely large fields, and the important case is (c). We refer the reader to the article by Rapini (1972) for a discussion of other geometries in which a Fredericksz transition may occur.

M. Fluctuations in smectic C

The Fourier transforms of the fluctuating quantities n_y, κ_x, and κ_y are introduced in the elastic energy [Eq. (16.69)]:

$$\begin{aligned} G = \tfrac{1}{2} \sum_{\mathbf{q}} [&(\alpha_{11}q_y^2 + \alpha_{22}q_z^2 + \alpha_{33}q_x^2 + 2\alpha_{23}q_xq_z) \mid n_{y\mathbf{q}} \mid^2 \\ &+ \alpha_{44}q_x^2 \mid \kappa_{x\mathbf{q}} \mid^2 + \alpha_{55}q_y^2 \mid \kappa_{y\mathbf{q}} \mid^2 + 2\alpha_{45}q_xq_y\kappa_{x\mathbf{q}}\kappa_{y-\mathbf{q}} \\ &+ 2\alpha_{14}q_xq_y\kappa_{x\mathbf{q}}n_{y-\mathbf{q}} + 2\alpha_{15}q_y^2\kappa_{y\mathbf{q}}n_{y-\mathbf{q}}]. \end{aligned} \qquad (16.80)$$

The constraint (16.66) requires that $\kappa_{x\mathbf{q}} = \kappa_{y\mathbf{q}} = 0$ unless $q_z = 0$. We thus consider the two cases:

(a) $q_z \neq 0$, $\kappa_{x\mathbf{q}} = \kappa_{y\mathbf{q}} = 0$. The only fluctuations that occur are constrained to take place without distortion of the layers. The mean square fluctuations in n_y are

$$\langle \mid n_{y\mathbf{q}} \mid^2 \rangle = \frac{k_BT}{\alpha_{11}q_y^2 + \alpha_{22}q_z^2 + \alpha_{33}q_x^2 + 2\alpha_{23}q_xq_z}. \qquad (16.81)$$

(b) $q_z = 0$. In this case it is possible to have fluctuations in which $\kappa_{x\mathbf{q}}, \kappa_{y\mathbf{q}} \neq 0$. These fluctuations are undulations in the layers and are quite similar to those occurring in a smectic A.

The fluctuations in the dielectric constant are

$$\delta\epsilon_{ij} = \epsilon_a(n_{0i}\delta n_j + n_{0j}\delta n_i), \qquad (16.82)$$

where ϵ_a is the dielectric anisotropy (the structure is assumed approximately uniaxial). The components are given by

$$\begin{aligned} &\delta\epsilon_{xx} = 2\epsilon_a sc\kappa_x, \qquad \delta\epsilon_{yy} = 0, \qquad \delta\epsilon_{zz} = -2\epsilon_a sc\kappa_x \\ &\delta\epsilon_{xy} = \epsilon_a s n_y, \qquad \delta\epsilon_{xz} = \epsilon_a(c^2 - s^2)\kappa_x, \qquad \delta\epsilon_{yz} = \epsilon_a c n_y. \end{aligned} \qquad (16.83)$$

The most interesting fluctuations, special to the tilted smectic C structure, are those involving n_y. These would appear in depolarized light scattering (involving $\delta\epsilon_{xy}$ or $\delta\epsilon_{yz}$). These fluctuations probably explain why the smectic C phase is more turbid in appearance than the A phase, where strong fluctuations and scattering can only occur when $q_z = 0$.

The Rayleigh scattering of light by a smectic C liquid crystal, 4 — 4′ decycloxybenzilidene 3 chloro phenylenediamine, has been observed by the Orsay group (1973). From the observed polarization selection rules the scattering could be attributed to the thermally excited twist fluctuations discussed above. The fluctuations are purely damped as in nematic liquid crystals.

N. Landau theory of smectic A–C transition

The ordered smectic C state can be described by giving the magnitude θ of the tilt angle of the molecular axes with respect to the normal to the smectic planes and the azimuthal angle ψ of the direction of the molecular axes. An appropriate order parameter to describe the order in the smectic C state is thus the complex number $\chi = \sin\theta \exp(i\psi) = \chi_x + i\chi_y$ (de Gennes, 1972b; 1973). Assuming that χ is small near the transition temperature T_{AC} the free energy density is expanded in powers of χ:

$$g = g_{\mathrm{A}} + a \mid \chi \mid^2 + \tfrac{1}{2}b \mid \chi \mid^4, \qquad (16.84)$$

where g_{A} is the free energy density of the A phase and a and b are temperature-dependent parameters. The free energy is independent of the angle ψ. In the presence of spatial variations of the order parameter the distortion free energy density may be taken in the same form as for nematics (de Gennes, 1973) [see Eq. (4.1)]. In the present case the director has the form $\mathbf{n} = (\chi_x, \chi_y, 1)$ and substituting in Eq. (4.1) we find

$$\begin{aligned} g_d = \tfrac{1}{2}k_1(\partial\chi_x/\partial x + \partial\chi_y/\partial y)^2 + \tfrac{1}{2}k_2(\partial\chi_x/\partial y - \partial\chi_y/\partial x)^2 \\ + \tfrac{1}{2}k_3((\partial\chi_x/\partial z)^2 + (\partial\chi_y/\partial z)^2). \end{aligned} \qquad (16.85)$$

It was first pointed out by Parodi (see de Gennes, 1973) that three elastic constants are involved.

De Gennes (1972b) pointed out that the λ transition in ^{4}He is described by a similar two-component order parameter, and he suggested that if the A–C transition is of second order, the critical exponents may be the same as those in ^{4}He. From Eq. (16.84) and the analogy with ^{4}He the following results are obtained:

(a) The tilt angle (order parameter) just below T_{AC} is given by

$$\mid \chi \mid = -a/b \sim (T_{\mathrm{AC}} - T)^{\beta} \qquad (16.86)$$

with $\beta \sim \frac{1}{3}$.

(b) The mean square fluctuations in χ of wave vector $\mathbf{q}$ in the A phase close to T_{AC} are

$$\langle \mid \chi_{\mathbf{q}} \mid^2 \rangle = k_BT/a(T) \sim (T - T_{\mathrm{AC}})^{-\gamma}, \qquad (16.87)$$

with $\gamma \sim 1.3$. The mean square fluctuations in the dielectric constant, $\delta\epsilon_{xz}$ and $\delta\epsilon_{yz}$, are proportional to Eq. (16.87), and a strong divergence in the intensity of depolarized light scattering close to T_{AC} should occur.

(c) If a magnetic field H is applied in the xz plane, to first order in χ, an extra magnetic energy density $-\frac{1}{2}\chi_a H_x H_z(\chi + \chi^*)$ must be included in Eq. (16.84). This field produces a nonzero tilt angle in the A phase (ignoring distortion of the layers)

$$\chi_x = \sin\theta = \tfrac{1}{2}\chi_a H_x H_z / a(T) \sim (T - T_{\mathrm{AC}})^{-\gamma}. \qquad (16.88)$$

For $H = 10^4$ G and $T - T_{\mathrm{AC}} = 1°\mathrm{K}$, de Gennes (1972b) has estimated $\theta \simeq 3.10^{-4}$ rad which may be detectable.

The smectic A–C transition may be more complicated than that considered here: a discontinuous change in the layer spacing may occur; or the fluctuations in the layers and the anisotropy in the fluctuations may be important.

XVII. ELECTROHYDRODYNAMICS

Nematic liquid crystals subjected to dc and ac electric fields exhibit several important effects involving the aligning effects of electric fields, the flow of ions (either ionized impurities or intrinsic charge carriers), and the induced hydrodynamic flows. Compared to the behavior of isotropic liquids under electric fields, liquid crystals exhibit a much larger variety of phenomena which lead to some interesting electro-optical applications.

We have already briefly mentioned the aligning effects produced by an electric field in nematics in Sec. III. The dielectric anisotropy, $\epsilon_a = \epsilon_{||} - \epsilon_{\perp}$, where $\epsilon_{||}$ and $\epsilon_{\perp}$ are the dielectric constants parallel and perpendicular to the director, may be positive or negative. If an electric field is the most important aligning force on the molecules, the axis along which the dielectric constant is a maximum would be expected to become parallel to the applied field; i.e., if $\epsilon_a > 0$, the molecules would align *parallel* to the field; while if $\epsilon_a < 0$, the molecules would align *perpendicular* to the field. This does occur when alternating fields of sufficiently high frequency are used (see below). On the other hand, for dc or low frequency fields PAA, MBBA, and other nematics with negative dielectric anisotropy tend to align with the preferred axis parallel (rather than perpendicular) to the field. This anomalous alignment has been studied extensively by Carr and co-workers (Carr 1967, 1969, and references cited therein). It was first proposed by Zwetkoff and Mikhailov (1938) that the anomalous alignment is due to the anisotropic conductivity of a nematic. Carr (1963) and Carr and Chou (1973) by a study of doped nematics, have shown experimentally that electrical conduction plays an important role in the anomalous alignment of a nematic in an electric field. Above a critical frequency of the field, which is determined by the space charge relaxation time, the behavior in external fields can be explained by considering only the dielectric properties.

The conductivity of a nematic is generally larger parallel to the preferred axis than perpendicular. Exceptions appear to be those nematics which show a smectic C phase at lower temperatures (Rondelez, 1972). The dielectric anisotropy and resistivity anisotropy have been measured in MBBA by Diguet *et al.* (1970) and Rondelez, Diguet, and Durand (1971), and in PAA by Meier and Saupe (1966) and by Sussman (1971). The anisotropy in the conductivity of PAA is in accord with the anisotropy in the viscosity found by Miesowicz (1946) (the viscosity is least for sheared flow parallel to the director in PAA). Helfrich (1969a) has discussed a theoretical model which includes the effects of ion currents in the nematic and the anisotropy in the conductivity and dielectric constant. He showed that the torques on the molecules arising from the ion current may more than offset the torque arising from the electric field thus explaining the anomalous alignment of nematics with $\epsilon_a < 0$ in low frequency fields.

Since the first experiments of Williams (1963), a large amount of work has been devoted to the study of electric instabilities in nematics. These effects have potential applications in display devices (Heilmeier, Zanoni, and Barton, 1968). Three main types of instabilities have been observed in nematics: the first occurs in dc fields, the second in ac fields of low frequency, and the third in ac fields of higher frequency. The most important observations on these instabilities have been summarized by Rondelez (1970) and the Orsay Group (1971c):

(a) dc fields. Williams (1963) studied a nematic confined between two electrodes and observed that there is a threshold voltage (~5 V) above which a convective instability occurs: the nematic breaks up into regular patterns or domains visible in polarized light with direction of polarization parallel to the initial direction of molecular alignment (Teaney and Migliori, 1970). The patterns may be hexagonal, linear, or intermediate and depend on the surface state of the electrodes. These patterns are produced by twin rotating flows of opposite angular momentum (Durand *et al.*, 1970; Penz, 1970)) which may interact to give the observed patterns. At higher voltages the stationary flow patterns give way to turbulence. In the turbulent state the light scattering by the nematic is very strong and has been called "dynamic scattering" by Heilmeier *et al.*, (1968). The scattering of light above the dc threshold has also been studied by Bertolotti *et al.* (1971a,b).

The flow patterns described above persist when the nematic is heated above the nematic-isotropic transition (Koelmans and van Boxtel, 1971). This observation suggests strongly that the mechanism for this instability is not specific to the nematic phase. Convective instabilities in normal liquids have been studied extensively by Felici (1969) and have similar features. The observations of Gruler and Meier (1971) of a voltage threshold for the onset of hydrodynamic flow in nematics with both positive and negative dielectric anisotropy is consistent with this view. The dc instability disappears when blocking electrodes (electrodes separated from the nematic by thin insulating sheets) are used (Rondelez, 1970).

In the presence of a magnetic field two threshold voltages can be distinguished (Orsay Group, 1971c). The threshold voltage for the appearance of hydrodynamic flow is independent of the field up to 20 kG, the highest field used. The threshold voltage for the appearance of the optical patterns increases with the field. For zero field the two thresholds coincide. This field effect can be simply understood: above the threshold for hydrodynamic flow a shear-flow induced torque acts on the molecules; misalignment of the molecules takes place when the shear rate (and thus the applied voltage) is large enough to overcome the aligning effects of the magnetic field and the elastic torque.

(b) Low frequency dc fields. When a low frequency ac field is applied to a nematic with $\epsilon_a < 0$ a threshold voltage (~7 V) above which optical patterns and hydrodynamic flow sets in is observed (Williams, 1963). No threshold voltage is observed if initially the director is parallel to the applied field and $\epsilon_a > 0$ (Gruler and Meier, 1972). The spatial period of the optical patterns and flow are of the order of magnitude of the separation between the electrodes (50–100 μm). In appearance this instability is very much like that occurring with dc fields; it can be distinguished from the dc one through several observations of Rondelez (1970) and the Orsay Group (1971c): (i) the threshold voltage is unaffected when blocking electrodes are used; (ii) there is no convective instability in the isotropic phase of the nematic; and (iii) in the presence of an external magnetic field, the thresholds for the appearance of periodic deformations and hydrodynamic flow increase but they always coincide.

These results show that this instability is characteristic of the nematic phase and that injection of charge carriers at the electrodes is not required. This would indeed be expected to be the case as soon as the period of the field is shorter than the transit time of a charge carrier in the nematic. It is also observed that the voltage at which this instability occurs increases with the frequency of the ac field up to a cutoff frequency ω_c. The cutoff frequency has been shown, by suitably doping the nematic with ionizable molecules, to be proportional to the conductivity of the nematic (Teaney and Migliori, 1970; Heilmeier and Helfrich, 1970). In the Orsay Group experiments with MBBA (1971c), ω_c was varied from 50–3000 Hz.

(c) Higher frequency ac fields. At higher frequencies ($\omega > \omega_c$) and voltages of the applied ac field, another type of instability occurs (Heilmeier and Helfrich, 1970). It is commonly called the "fast turn off mode" for reasons which will be explained below. The onset of instability in this case is observed optically (Orsay Group, 1971c) by the appearance of parallel striations of a short spatial period ($\sim$3 μm). The period of these striations is much shorter than the period of the patterns observed by Williams in the dc and low frequency ac cases ($\sim$50 μm). Slightly above threshold the striations bend and give what the Orsay Group have called "chevrons." This instability has been extensively investigated by them in MBBA (Galerne, 1973). Using samples of different thickness they have shown that the threshold depends on the field rather than the voltage as found in the dc and low frequency ac cases. Again the injection of current carriers at the electrodes is unimportant and the instability is characteristic of the nematic phase and does not exist in the isotropic phase. The field threshold increases with frequency like $\omega^{1/2}$. An applied magnetic field does not change the value of the threshold, but increases the spatial period of the optical striations.

To summarize this discussion of the instabilities in nematics, the observations indicate that the dc instability is not specific to the nematic phase but also occurs in normal liquids. On the other hand, in the two ac regimes the instabilities are closely related to the anisotropic character of the nematic phase.

Helfrich (1969a) has discussed theoretically the effects of the anisotropy in the conductivity and dielectric constant on the dc instability in nematics. The Orsay Group (1970) and Dubois-Violette *et al.* (1971) have extended the Helfrich model to the ac case and discussed the ac instabilities. A simple discussion has been given by de Gennes (1970a). In the remainder of this section, in subsection A, by way of introduction we first discuss the convective instability in normal liquids. In B the Helfrich model for electrohydrodynamic effects in nematics is presented. In C this model is used to discuss the dc instability and (in D.E.F.) the ac instabilities in nematics (for $\epsilon_a < 0$). In G the case $\epsilon_a > 0$ is considered, and in H instabilities of cholesterics and thermal instabilities are briefly discussed.

A. Convective instability in a normal liquid

A nonpolar liquid or nematic in the isotropic state is confined between two parallel plane electrodes of infinite extent (to avoid any edge effects) separated by a distance d. Electrons or ions are injected into the liquid from one electrode (we only consider the case of unipolar injection) giving rise to a gradient in charge across the sample such that the charge density is greatest at the injecting electrode. As the voltage across the electrode is increased, the apparent mobility of the ions increases and above a critical voltage V_{0c} cellularlike hydrodynamic flow can be observed in the liquid. This effect has been studied theoretically by Felici (1969) and experimentally by Filippini *et al.* (1969). It can be understood as follows: suppose a fluctuation increases the charge density q in a region to $q + \delta q$: then this region will be dragged by the field and at the same time the charge fluctuation will tend to decay to the local charge density. For voltages $V < V_{0c}$ the motion of the charge fluctuation is sufficiently slow that it has time to decay to the local charge density. When $V > V_{0c}$ the motion of the charge fluctuation relative to the gradient of the local charge density is sufficiently rapid that the fluctuation never decays to the local value. Convective flow of the fluid is set up. The critical voltage for this to occur has been calculated by Atten and Moreau (1969, 1970). We will give a simplified derivation.

We begin by discussing the hydrodynamic equations in the presence of electric fields. The current of the injected ions is given by

$$\mathbf{J}^{(i)} = q(K\mathbf{E} + \mathbf{v}), \qquad (17.1)$$

where q is the ion charge density, K is the ion mobility, $\mathbf{E}$ is the electric field acting on the ions in the fluid, and $\mathbf{v}$ is the fluid velocity. The last term of Eq. (17.1) arises because the ions will relax by collisions with the molecules of the fluid to the local fluid velocity. The ions will satisfy an equation of continuity

$$(\partial q/\partial t) + \nabla\cdot\mathbf{J}^{(i)} = 0. \qquad (17.2)$$

The electric displacement $\mathbf{D}$ in the nonpolar fluid satisfies Poisson's equation

$$\nabla\cdot\mathbf{D} = 4\pi q. \qquad (17.3)$$

The equation of motion of the fluid (which we regard as incompressible) is

$$(\partial/\partial t)(\rho\mathbf{v}) + (\partial/\partial x_j)T_{ij} = 0, \qquad (17.4)$$

where ρ is the fluid density and T_{ij} is the stress tensor. For a simple incompressible fluid the stress tensor is

$$T_{ij} = P\delta_{ij} + \rho v_i v_j - \eta(\partial v_i/\partial x_j + \partial v_j/\partial x_i) + T_{ij}^{(e)}, \tag{17.5}$$

where P is the pressure, η is the shear viscosity, and $T_{ij}^{(e)}$ is the stress arising from the electric fields and is given by (Landau and Lifshitz, 1960)

$$T_{ij}^{(e)} = -(1/8\pi)(D_i E_j + D_j E_i - \mathbf{D}\cdot\mathbf{E}\delta_{ij}), \tag{17.6}$$

where $D_i = \epsilon E_i$ is the electric displacement. We take this tensor in symmetrical form and neglect a term arising from the variation of ϵ with density. In a nearly incompressible fluid this term can always be included in the pressure in Eq. (17.5).

The complete set of hydrodynamic equations is (17.2)-(17.4). When we introduce the electric potential Ψ such that $\mathbf{E} = -\nabla\Psi$, these equations become

$$(dq/dt) - K\nabla\cdot(q\nabla\Psi) = 0, \tag{17.7}$$

$$\epsilon\nabla^2\Psi = -4\pi q, \tag{17.8}$$

$$\rho(dv_i/dt) + \nabla_i P - \eta\nabla^2 v_i + q\nabla_i\Psi = 0, \tag{17.9}$$

where $d/dt = (\partial/\partial t) + \mathbf{v}\cdot\nabla$ is the substantial derivative. The force exerted on the fluid by the electric field is given by the last term of Eq. (17.9). We first investigate the static solution of (17.7)-(17.9).

1. Static Solution

At low voltages the fluid is stationary and a steady ion current flows. Let the first electrode lie in the plane $z = 0$ and be at a voltage V_0, while the second electrode is in the plane $z = d$ and is at zero potential. Equations (17.7)-(17.9) reduce to

$$\begin{aligned}&(\partial/\partial z)(q_0(\partial/\partial z)\Psi_0) = 0,\\ &\epsilon(\partial^2/\partial z^2)\Psi_0 = -4\pi q_0,\\ &\partial P_0/\partial z + q_0(\partial/\partial z)\Psi_0 = 0,\end{aligned} \tag{17.10}$$

where the subscript 0 indicates the steady value of a quantity. The solutions of Eq. (17.10) satisfying the boundary conditions are

$$\begin{aligned}\Psi_0 &= V_0[1 - (z/d)^{3/2}],\\ q_0 &= (3\epsilon/16\pi)(V_0/d^{3/2}z^{1/2}),\\ P_0 &= (9\epsilon/32\pi)(V_0/d^3) + \text{constant}.\end{aligned} \tag{17.11}$$

There is a uniform current in the fluid given by

$$J_{0z}^{(i)} = (9\epsilon/32\pi)(V_0^2/d^3)K. \tag{17.12}$$

2. Convective instability

Linearize Eqs. (17.7)-(17.9) about the static solution (17.11) by setting

$$\begin{aligned}q &= q_0 + q_1,\\ \Psi &= \Psi_0 + \Psi_1,\\ P &= P_0 + P_1,\end{aligned} \tag{17.13}$$

where q_1, Ψ, and P_1 are small quantities. The fluid velocity $\mathbf{v}$ is also regarded as a small quantity. Substituting Eq. (17.13) in (17.7)-(17.9) and neglecting quantities of second order in these small quantities, we get the linearized equations

$$\begin{aligned}\partial q_1/\partial t + \mathbf{v}\cdot\nabla q_0 + (8\pi K/\epsilon)q_0 q_1 - K(\nabla q_1)\cdot(\nabla\Psi_0)&\\ - K(\nabla q_0)\cdot(\nabla\Psi_1) = 0,&\end{aligned} \tag{17.14}$$

$$\epsilon\nabla^2\Psi_1 = -4\pi q_1, \tag{17.15}$$

$$\rho(\partial v_i/\partial t) + \nabla_i P_1 - \eta\nabla^2 v_i + q_0\nabla_i\Psi_1 + q_1\nabla_i\Psi_0 = 0. \tag{17.16}$$

These equations are difficult to solve because q_0 and Ψ_0 depend on the z coordinate. Atten and Moreau (1969, 1970) have used numerical methods. We will only give an approximate discussion. Thus neglecting terms which are qualitatively unimportant, we replace Eqs. (17.14) and (17.16) by

$$\partial q_1/\partial t + v_z(\partial q_0/\partial z) + (2/\tau)q_1 = 0 \tag{17.17}$$

$$\eta\nabla^2 v_z = q_1(\partial/\partial z)\Psi_0, \tag{17.18}$$

where $\tau^{-1} = 4\pi K q_0/\epsilon$. We will approximate further by replacing q_0 by a constant average value and use the approximations

$$\partial q_0/\partial z \simeq -q_0/d, \qquad \partial\Psi_0/\partial z = -V_0/d \tag{17.19}$$

which follow from Eq. (17.11). We now assume a solution of Eqs. (17.17) and (17.18) with q_1 and v_z varying like $\exp(ikx)$, where $k = 2\pi/d$ is the smallest wave vector for a fluctuation. From Eq. (17.18) we find

$$v_z = (V_0 d/4\pi^2\eta)q_1. \tag{17.20}$$

Substituting in Eq. (17.17) we find

$$\partial q_1/\partial t + (2/\tau - V_0 q_0/4\pi^2\eta)q_1 = 0. \tag{17.21}$$

The static solution (17.11) thus becomes unstable at a critical voltage given approximately by

$$\begin{aligned}V_{0c} &= 8\pi^2\eta/q_0\tau\\ &= 32\pi^3\eta K/\epsilon.\end{aligned} \tag{17.22}$$

An exact calculation of V_{0c} has been given by Atten and Moreau (1969, 1970). When the voltage exceeds this value, any long wavelength fluctuation q_1 will tend to grow and, from Eq. (17.20), convection will be set up. For $\eta = 0.1$ P, $\epsilon = 3$, and an ion mobility $K = 10^{-5}$–10^{-6} cm^2 sec$^{-1}\cdot$V^{-1} this critical voltage is $V_{0c} \simeq 5$ V.

The determination of the flow velocity and ion current in the fluid above the instability requires a consideration of the nonlinear terms in the hydrodynamic equations which may have the effect of stabilizing the system or may give rise to turbulence. This is a complicated problem and we will be content with locating the position of the instability, which can be accomplished by a linear analysis.

The nature and origin of the mobility K of the charge carriers is not well understood. In MBBA it is of order 10^{-5}–10^{-6} cm^2 sec$^{-1}\cdot$V^{-1} (Brière *et al.*, 1972). It has been suggested by de Gennes (1970a) that it arises from a lag of the polarization cloud produced in the solvent by the ion. In a polar solvent like water the slow relaxation of the dipole moments of the water molecules is the most important contribution to the relaxation of the polarization cloud (Zwanzig, 1963). In organic liquids like MBBA, de Gennes (1970a) has suggested that the anisotropic dielectric constant and its slow relaxation is an important factor in the mobility. The dielectric relaxation time is of order 1–10 MHz in MBBA (Rondelez *et al.*, 1971).

B. Electrohydrodynamics of nematics

The mobility of ions in a nematic is a second rank tensor and is given by

$$K_{ij} = K_\perp \delta_{ij} + K_a n_i n_j, \qquad (17.23)$$

where $K_a = K_{||} - K_\perp$ and $K_{||}$ and $K_\perp$ are the mobilities parallel and perpendicular to the preferred axis.

This tensor has exactly the same form as the dielectric tensor

$$\epsilon_{ij} = \epsilon_\perp \delta_{ij} + \epsilon_a n_i n_j, \qquad (17.24)$$

where ϵ_a is the dielectric anisotropy. The ion current in a nematic is now

$$J_i^{(i)} = q(K_{ij}E_j + v_i) \qquad (17.25)$$

and as before satisfies the equation of continuity (17.2). Likewise the electric displacement $\mathbf{D}$ satisfies Poisson's equation (17.3) but now D is related to the electric field E by the more complicated relation

$$D_i = \epsilon_{ij} E_j. \qquad (17.26)$$

The equation of motion of the fluid (regarded as incompressible) is

$$\rho(d/dt)v_i + \partial/\partial x_j(t_{ij} + T_{ij}^{(e)}) = 0, \qquad (17.27)$$

where t_{ij} is given by Eq. (6.11) and $T_{ij}^{(e)}$ is given by Eq. (17.6). Finally we have the equation for the director (6.8). In this equation we will neglect inertial effects, but we must include the torque on the director due to the electric and magnetic fields. The director equation is then

$$\gamma_1(dn_i/dt - \omega_{ij}n_j) + \gamma_2 d_{ij}n_j - (\epsilon_a/4\pi)(\mathbf{n}\cdot\mathbf{E})E_i - \chi_a(\mathbf{n}\cdot\mathbf{H})H_i + (\partial/\partial x_j)\Pi_{ij} = -\gamma n_i, \qquad (17.28)$$

where Π_{ij} is the elastic restoring force [Eq. (3.21)] and we have only included the part of f_i in Eq. (3.24) which involves the electric and magnetic fields. The other terms are quadratic in the curvature components. The coefficient γ in Eq. (17.28) is the usual Lagrange multiplier and is determined by the condition $\mathbf{n}^2 = 1$.

The electrohydrodynamic equations for nematics are thus provided by Eqs. (17.2), (17.27), and (17.28), and Poisson's equation (17.3). We now make use of these equations for a discussion of electrohydrodynamic instabilities in nematics.

C. dc instability in nematics

The most interesting case is where the dielectric anisotropy is negative, i.e., $\epsilon_a < 0$. The anisotropy in the ion mobility is taken to be positive, i.e., $K_a > 0$. The molecules will then prefer to lie perpendicular to an applied field, i.e., along x in Fig. 28. There is then a static solution of Eqs. (17.2), (17.27), and (17.28) of exactly the same form as (17.11) except that ϵ and K are now replaced by $\epsilon_\perp$ and $K_\perp$.

We now examine the stability of this solution following the discussion of de Gennes (1970a). Suppose that there is a fluctuation in charge δq in a region (denoted by A in Fig. 28). If $\epsilon_a < 0$, the molecules are initially aligned along x. Owing to the charge fluctuation, the electric field will have components along x as shown in Fig. 28a. The molecules, which prefer to be perpendicular to the field, will have the orientations shown. The gradient in flow velocity produced by the motion of A will tend to rotate the molecules in the same way as the field. These torques on the molecules will be opposed by elastic restoring forces. The current will also have a component along x, the direction of which will be to increase the amount of charge in the fluctuation. We see then that the nematic alignment tends to favor hydrodynamic instability when $\epsilon_a < 0$. The opposite case when $\epsilon_a > 0$ is illustrated in Fig. 28b. The molecules now prefer to lie parallel to the applied field as shown. The effects of gradients in the hydrodynamic velocity are now small. The direction of the transverse current is now such as to tend to deplete the charge fluctuation. The nematic alignment thus tends to favor hydrodynamic stability in the case $\epsilon_a > 0$.

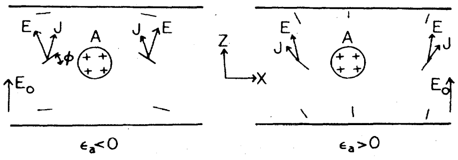

FIG. 28. Charge fluctuation in nematics. (a) $\epsilon_a < 0$ the molecules lie perpendicular to resultant field and the transverse current feeds the fluctuation. (b) $\epsilon_a > 0$ the molecules lie parallel to the resultant field and the transverse current depletes the fluctuation.

We now make a more detailed investigation of the dc instability in nematics. As in Sec. XVII,A, we linearize the hydrodynamic equations (17.2), (17.27), and (17.28) by setting

$$\begin{aligned} q &= q_0 + q_1, \\ E &= \mathbf{E}_0 + \mathbf{E}_1, \\ n_x &= 1, \qquad n_z = \phi, \\ P &= P_0 + P_1, \end{aligned} \tag{17.29}$$

where q_0, $\mathbf{E}_0$, and P_0 are the static values of the charge, field, and pressure, given by Eq. (17.11) with ϵ and K replaced by $\epsilon_\perp$ and $K_\perp$. The small quantities q_1, $\mathbf{E}_1$, and P_1 are the fluctuations in the charge, field, and pressure, respectively. For simplicity we will neglect the small modification in the z component of the field so that $\mathbf{E}_1$ is along x, and we will denote it by E_x. As before, we only examine fluctuations in the xz plane and neglect any dependence on the y coordinate. Then ϕ represents the bending of the director in the z direction. Using Eqs. (17.24) and (17.26), the electric displacement is related to the electric field by (retaining terms linear in E_x and ϕ only)

$$\begin{aligned} D_x &= \epsilon_{||} E_x + \epsilon_a \phi E_0 \\ D_z &= \epsilon_\perp E_0. \end{aligned} \tag{17.30}$$

Substituting in Poisson's equation (17.3) we get

$$\epsilon_{||}(\partial E_x/\partial x) = -\epsilon_a E_0 \psi + 4\pi q_1, \tag{17.31}$$

where $\psi = \partial\phi/\partial x$ and is the component of bend. From Eqs. (17.23) and (17.25) the components of the current are

$$\begin{aligned} J_x &= q_0(K_{||} E_x + K_a \phi E_0 + v_x) \\ J_z &= J_0 + q_0 v_z + q_1 K_\perp E_0. \end{aligned} \tag{17.32}$$

When these are substituted into the equation of continuity (17.2), we get [with the same approximations as in Eq. (17.17)]

$$\partial q_1/\partial t + q_1/\tau + v_z(\partial q_0/\partial z) + \sigma_H E_0 \psi = 0, \tag{17.33}$$

where

$$\tau^{-1} = 4\pi q_0[(K_{||}/\epsilon_{||}) + (K_\perp/\epsilon_\perp)] \tag{17.34}$$

and

$$\sigma_H = q_0[K_a - \epsilon_a(\mathrm{K}_{||}/\epsilon_{||})]. \tag{17.35}$$

The next-to-last term of Eq. (17.33) is the convective part of the ion current. The last term gives the effect of nematic ordering, through the anisotropy in the mobility and dielectric constant, on the ion current.

The director equation follows from Eq. (17.28). Only the z component of this equation is relevant, and then γ may be set equal to $\chi_a(\mathbf{n}\cdot\mathbf{H})^2$ where the field H is applied in the x direction. After linearization of this equation, we find

$$\begin{aligned} &\gamma_1(\partial\phi/\partial t) - \tfrac{1}{2}(\gamma_1 - \gamma_2)(\partial v_z/\partial x) + \tfrac{1}{2}(\gamma_1 + \gamma_2)(\partial v_x/\partial z) \\ &\quad - (\epsilon_a/4\pi) E_0(E_x + \phi E_0) - [k_{11}(\partial^2/\partial z^2) \\ &\quad + k_{33}(\partial^2/\partial x^2) - \chi_a H_i]\phi = 0. \end{aligned} \tag{17.36}$$

After differentiating Eq. (17.36) with respect to x and eliminating E_x by means of Eq. (17.31) we find

$$\begin{aligned} &\gamma_1(\partial\psi/\partial t) - \tfrac{1}{2}(\gamma_1 - \gamma_2)(\partial^2 v_z/\partial x_i^2) \\ &\quad + \tfrac{1}{2}(\gamma_1 + \gamma_2)(\partial^2 v_x/\partial x\partial z) - (\epsilon_a/\epsilon_{||}) E_0 q_1 \\ &\quad - [(\epsilon_a\epsilon_\perp/4\pi\epsilon_{||}) E_0^2 + k_{11}(\partial^2/\partial z^2) + k_{33}(\partial^2/\partial x^2) \\ &\quad - \chi_a H^2]\psi = 0. \end{aligned} \tag{17.37}$$

In this equation the term proportional to $E_0 q_1$ is the force producing the curvature in the nematic, and the opposing forces are contained in the last term, which consists of a restoring force due to the dielectric anisotropy, the elastic forces, and the effect of the applied magnetic field. In the time-dependent case these terms also lead to a relaxation effect.

Finally, the momentum equation follows from Eq. (17.27). We will only require the z component of this equation. The x component of this equation together with the incompressibility condition determine the pressure. The required components of the nematic stress tensor (6.11) are

$$\begin{aligned} t_{zx} &= -\alpha_2\dot{\phi} - \tfrac{1}{2}(\alpha_4 + \alpha_5 - \alpha_2)(\partial v_z/\partial x) \\ &\quad - \tfrac{1}{2}(\alpha_4 + \alpha_5 + \alpha_2)(\partial v_x/\partial z) \\ t_{zz} &= P_0 + P_1 - \alpha_4(\partial v_z/\partial z). \end{aligned} \tag{17.38}$$

The electromagnetic part of the stress tensor from Eq. (17.6) and (17.30) are

$$\begin{aligned} T_{zx}^{(e)} &= -(1/8\pi)[(\epsilon_{||} + \epsilon_\perp) E_0 E_x + \epsilon_a \phi E_0^2] \\ T_{zz}^{(e)} &= -(\epsilon_\perp/8\pi) E_0^2. \end{aligned} \tag{17.39}$$

Substituting these results in Eq. (17.27) and using Eq. (17.31) to eliminate $\partial E_x/\partial x$, and the incompressibility condition to eliminate v_x, we find

$$\begin{aligned} &\rho(\partial v_z/\partial t) + \partial P_1/\partial z - \alpha_2(\partial\psi/\partial t) - \tfrac{1}{2}(\alpha_4 - \alpha_2 - \alpha_5) \\ &\quad \times (\partial^2 v_z/\partial z^2) - \eta_2(\partial^2 v_z/\partial x^2) + (\epsilon_a\epsilon_\perp/8\pi\epsilon_{||}) E_0^2\psi \\ &\quad - \tfrac{1}{2}(1 + \epsilon_\perp/\epsilon_{||}) q_1 E_0 = 0, \end{aligned} \tag{17.40}$$

where η_2 is given by Eq. (7.13). The electric forces acting on the fluid are provided by the last two terms of Eq. (17.40).

The small fluctuations in the charge density, the director, and the fluid velocity are described by Eqs. (17.33), (17.37), and (17.40). The equations will be used for a discussion of fluctuations and instabilities in both dc and ac fields.

To investigate the dc instability we again make the approximations (17.19) and assume that the voltage across the sample is related to the field by $V_0 = E_0 d$. The fluctuating quantities q_1, ψ, and v_z are assumed proportional to $\exp(ikx)$ with $k \sim 2\pi/d$. The domain size has been measured by Penz (1971) and Lacroix *et al.* (1972) and found to be close to $2d$. A more complete treatment of the boundary value problem has been given by Penz and Ford (1972).

From the momentum equation (17.40), omitting the pressure term and the time derivative, we get

$$\eta_2(\partial^2 v_z/\partial x^2) = (\epsilon_a\epsilon_\perp/8\pi\epsilon_{||})E_0^2\psi - \tfrac{1}{2}(1+\epsilon_\perp/\epsilon_{||})q_1E_0. \tag{17.41}$$

From the director equation (17.37) in the static case we get (assuming for simplicity that $\gamma_2 = -\gamma_1$)

$$\gamma_1(\partial^2 v_z/\partial x^2) = -(\epsilon_a/\epsilon_{||})E_0q_1 - [(\epsilon_a\epsilon_\perp/4\pi\epsilon_{||})E_0^2 - k_{33}k^2 - \chi_aH^2]\psi. \tag{17.42}$$

Then using these two equations to eliminate v_z and ψ from the charge equation (17.33), we find

$$\partial q_1/\partial t + q_1/\tau - \frac{q_0V_0}{2\pi^2(\gamma_1+2\eta_2)} \times \left(\frac{V_0^2+V_b^2+V_0V_n}{V_0^2+V_a^2}\right)q_1 = 0, \tag{17.43}$$

where

$$V_n = -(8\pi^3\epsilon_{||}/\epsilon_a\epsilon_\perp)[\gamma_1(1+\epsilon_\perp/\epsilon_{||}) - 2\eta_2(\epsilon_a/\epsilon_{||})] \times [K_a - \epsilon_a(K_{||}/\epsilon_{||})], \tag{17.44}$$

$$V_a^2 = -(16\pi^3\epsilon_{||}/\epsilon_a\epsilon_\perp)[2\eta_2/(\gamma_1+2\eta_2)] \times [k_{33} + (d^2/4\pi^2)\chi_aH^2],$$

$$V_b^2 = \tfrac{1}{2}V_a^2(1+\epsilon_\perp/\epsilon_{||})(1+\gamma_1/2\eta_2). \tag{17.45}$$

The instability now sets in at a critical voltage, V_{0c}, determined by

$$V_{0c} = [(V_i - V_n)V_{0c}^2 + V_iV_a^2]/(V_{0c}^2 + V_b^2), \tag{17.46}$$

where

$$V_i = 8\pi^3(\gamma_1+2\eta_2)[(K_{||}/\epsilon_{||}) + (K_\perp/\epsilon_\perp)]. \tag{17.47}$$

For MBBA at 25°C $\epsilon_{||} = 4.7$, $\epsilon_\perp = 5.2$, and $k_{33} \simeq 10^{-6}$ dyn, and assuming $\eta_2 \sim \gamma_1 \simeq 0.1$ P, we find $V_a \sim V_b \sim 6$ V. V_i and V_n are of the same order of magnitude as the critical voltage (17.22) in a normal liquid; i.e., for $K \sim 10^{-5}$–10^{-6} cm^2 sec$^{-1}\cdot$V^{-1} we have $V_i \sim V_n \sim 5$ V. There are two types of solutions to Eq. (17.46), depending on the relative magnitudes of V_i and V_n.

(a) $V_i > V_n$. The solution of Eq. (17.46) is approximately

$$V_{0c} \simeq V_i(V_a^2/V_b^2), \qquad V_b > V_i \tag{17.48}$$

$$V_{0c} \simeq V_i - V_n, \qquad V_b < V_i. \tag{17.49}$$

In each case the instability is of the Felici type of convective instability. In the case (17.48) the dielectric and mobility anisotropy do not play a role. The inequality $V_b > V_i$ can be realized if the applied magnetic field or elastic energy is large enough. In the case (17.49) the magnetic field and elastic energy are not important. $V_i - V_n$ can be written

$$V_i - V_n = 32\pi^3[\eta_2(K_\perp/\epsilon_\perp) + (\gamma_1/2)(K_a/\epsilon_a)]. \tag{17.50}$$

The second term here represents the effect of the dielectric and mobility anisotropy. For $\epsilon_a < 0$ and $K_a > 0$ the critical voltage is reduced, whereas for $\epsilon_a > 0$, $K_a > 0$ it is increased.

(b) $V_n > V_i > V_a$. This case generally only occurs when $\epsilon_a < 0$ [see Eq. (17.44)]. The solution of Eq. (17.46) is approximately

$$V_{0c} = V_a[V_i/(V_n - V_i)]^{1/2}. \tag{17.51}$$

The elastic properties of the nematic now play an important role. This is the case considered by Helfrich (1969a) and the instability is now essentially one of the director.

The magnetic field has the effect of opposing any director motion. In the limit of a very strong field when the director motion is frozen out, we thus obtain the solution (17.48) corresponding to the convective Felici instability. At lower fields, if Eq. (17.51) applies, the critical voltage will increase approximately linearly with H [when the magnetic energy χ_aH^2 exceeds the elastic energy $k_{33}(2\pi/d)^2$].

Experimentally, the Orsay Group (1971c) has observed two thresholds in the presence of a magnetic field in the nematic MBBA. The first threshold, corresponding to hydrodynamical motion, is independent of the field up to 20 kG. This threshold presumably corresponds to the usual convective Felici instability as in Eq. (17.48). This instability also persists in the isotropic phase of MBBA. The second threshold observed by the Orsay Group corresponds to the appearance of optical patterns in the nematic. This threshold increases with H and is not dependent on the orientation of the field. From our linearized equations we are only able to determine the first or lowest threshold corresponding to the onset of hydrodynamic flow.

D. ac instabilities in nematics

Two types of instabilities have been observed in nematics in ac fields. (a) For frequencies ω less than a certain critical frequency there exists a critical voltage $V_{0c}(\omega)$, depending on frequency, above which the nematic breaks up into domains (Williams, 1963). The spatial periodicity of the domains is comparable to d, the separation of the electrodes (Penz, 1971). (b) For frequencies $\omega > \omega_c$ another type of instability occurs, first reported by Heilmeier and Helfrich (1970), called the "fast turn off mode." The onset of instability manifests itself in the appearance of a chevron structure which can be observed optically (Orsay Group, 1971c). The spatial period of this structure is much smaller than d.

Both these instabilities have been investigated by the Orsay Group (1970) and DuBois-Violette *et al.*, (1971). The time-dependent equations of the Orsay group follow from Eqs. (17.33), (17.37), and (17.40). We neglect convective effects and then the charge equation (17.33) becomes

$$(\partial q_1/\partial t)+(q_1/\tau)+\sigma_H E_0\psi=0. \tag{17.52}$$

We again will consider fluctuations which vary as e^{ikx} and then from the momentum equation (17.40) (omitting the inertial and pressure effects) we get

$$\eta_2(\partial^2 v_2/\partial x^2)=-\alpha_2(\partial\psi/\partial t)+(\epsilon_a\epsilon_\perp/8\pi\epsilon_{||})E_0{}^2\psi$$
$$-\tfrac{1}{2}(1+\epsilon_\perp/\epsilon_{||})q_1E_0. \tag{17.53}$$

When this is substituted in the director equation (17.37), we obtain

$$(\partial\psi/\partial t)+(1/T)\psi+(q_1E_0/\eta)=0, \tag{17.54}$$

where

$$1/T=\alpha E_0{}^2+\beta \tag{17.55}$$

$$\frac{1}{\eta}=\left(\frac{\gamma_1-\gamma_2}{4\eta_2}\left(1+\frac{\epsilon_\perp}{\epsilon_{||}}\right)-\frac{\epsilon_a}{\epsilon_{||}}\right)\frac{1}{\eta'}. \tag{17.56}$$

In Eqs. (17.55) and (17.56)

$$\alpha=-(\epsilon_a\epsilon_\perp/4\pi\epsilon_{||}\eta')[1+(\gamma_1-\gamma_2)/4\eta_2], \tag{17.57}$$

$$\beta=(k_{33}k^2+\chi_aH^2)/\eta', \tag{17.58}$$

$$\eta'=\gamma_1+(\alpha_2/2\eta_2)(\gamma_1-\gamma_2). \tag{17.59}$$

It can be shown from the inequalities [Eq. 6.61] that η' is positive. For materials with $\epsilon_a<0$ we see that η, α, and β are always positive. For materials in which $\epsilon_a/\epsilon_{||}\gg 0$ it is possible for η to be negative and α will also be negative. These two cases will be examined below.

The equations describing the coupled charge density and director fluctuations are Eqs. (17.52) and (17.54). The coupling of the charge and director is of a parametric type and is via the electric field. In the absence of any field the charge density fluctuations decay in a time τ and the director fluctuations in a time T. In the presence of an ac field $E_0=E_m\cos\omega t$ the equations have very different types of solutions which depend on the frequency ω.

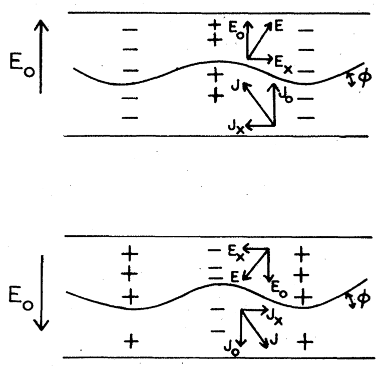

FIG. 29. Conduction mode. (a) E_0 is up. (b) E_0 is down. The director is approximately stationary and in each part of the cycle is perpendicular to the resultant field.

E. Conduction mode ($\omega\tau<1$)

In general the relaxation time τ of the charge is much shorter than the relaxation time T for the director. If the frequency of excitation is such that $\omega T\gg 1$, then the solution of Eqs. (17.52) and (17.54) may be approximately taken in the form

$$\psi=\psi^{(0)}$$
$$q_1=q^{(1)}\sin\omega t+q^{(2)}\cos\omega t \tag{17.60}$$

so that the charge density oscillates while the director is stationary. The nature of this mode is illustrated in Fig. 29. Substituting Eq. (17.60) in (17.52) and (17.54) and neglecting harmonics we obtain

$$\omega q^{(1)}+q^{(2)}/\tau+\sigma_H E_m\psi^{(0)}=0,$$
$$\omega q^{(2)}-q^{(1)}/\tau=0,$$
$$\tfrac{1}{2}(\alpha E_m{}^2+\beta)\psi^{(0)}+E_m/2\eta q^{(2)}=0. \tag{17.61}$$

From these equations we obtain the secular equation for this mode

$$(\tfrac{1}{2}\alpha E_m{}^2+\beta)(1+\omega^2\tau^2)-(\sigma_H\tau/2\eta)E_m{}^2=0. \tag{17.62}$$

The critical field E_{mc} for the onset of this mode is

$$\frac{E_{mc}{}^2}{2}=\frac{E_a{}^2(1+\omega^2\tau^2)}{\zeta^2-(1+\omega^2\tau^2)}, \tag{17.63}$$

where

$$E_a{}^2=\beta/\alpha,\qquad \zeta^2=\sigma_H\tau/\eta\alpha. \tag{17.64}$$

From Eqs. (17.34), (17.35), (17.56), and (17.57) we have (putting $\gamma_2=-\gamma_1$)

$$\zeta^2=\frac{1-\lambda}{(1+\lambda)}\frac{[1-(\epsilon_{||}/\epsilon_a)(\gamma_1/2\eta_2)(1+\epsilon_\perp/\epsilon_{||})]}{(1+\gamma_1/2\eta_2)}, \tag{17.65}$$

where $\lambda=(\epsilon_{||}/\epsilon_\perp)(K_\perp/K_{||})$. Apart from the denominator (which is close to unity), this is identical with the parameter introduced by DuBois-Violette *et al.* A closely related parameter θ_H has been introduced by Helfrich (1969)

$$\theta_H = -\epsilon_a(\zeta^2 - 1). \tag{17.66}$$

From Eqs. (17.63), (17.64), and (17.57) we note that if $\theta_H > 0$ a real critical field for the onset of the instability exists, while if $\theta_H < 0$, there is no instability.

For MBBA $K_{||}/K_{\perp} = 1.5$, $\epsilon_{||} = 4.7$, $\epsilon_{\perp} = 5.2$ (Diguet *et al.*, 1970), and taking $\gamma_1/2\eta_2 \simeq 0.7$ we find $\zeta^2 = 2$. Recently a case where $\zeta^2 = 1$ and no instability was found has been reported by Gosczianski *et al.*, (1974). We also note that $\zeta^2 = V_n/V_i$ and $E_a{}^2 = V_a{}^2/d^2$, where V_n, V_i, and V_a are given in Eqs. (17.44)–(17.47). In the dc case, apart from a factor of 2, Eq. (17.63) reduces to (17.51).

We can make the following observations from (17.63): (1) A cutoff frequency

$$\omega_c = (\zeta^2 - 1)^{1/2}/\tau \tag{17.67}$$

at which $E_{mc} \rightarrow \infty$ exists. ω_c is proportional to the conductivity and typically $\omega_c \sim \tau^{-1} \sim 10^2$ sec^{-1}. From Eq. (17.61), $q^{(2)}/q^{(1)} = (\omega\tau)^{-1} > 1$. When Eq. (17.60) is substituted in (17.53) we see that associated with the charge fluctuations is a steady flow. (2) The condition, $\omega_c T > 1$, for the solution (17.63) has been investigated in detail by DuBois-Violette *et al.*, (1971). From Eqs. (17.55) and (17.63) assuming $\alpha E_a{}^2/\omega_c \ll 1$, this condition is

$$1/\omega_c T \simeq (k_{33}k^2 + \chi_a H)\tau/\eta' < 1. \tag{17.68}$$

For $H = 0$ and $k = 2\pi/d$ this requires that $d > d_c$ where

$$d_c = 2\pi(k_{33}\tau/\eta')^{1/2}. \tag{17.69}$$

For $k_{33} = 10^{-6}$ dyn, $\tau = 10^{-2}$ sec, and $\eta' = 0.1$ P we have $d_c = 10^{-3}$ cm. With the condition $d > d_c$ it can be shown that Eq. (17.63) is valid for practically the whole frequency range $0 - \omega_c$.

(3) From Eqs. (17.63), (17.57), and (17.58) the threshold voltage $V_{mc} = (1/\sqrt{2})E_{mc}d$ is

$$V_{mc}{}^2 = V_a{}^2(1 + \omega^2\tau^2)/[\zeta^2 - (1 + \omega^2\tau^2)], \tag{17.70}$$

where $V_a{}^2$ is given by Eq. (17.45). For small magnetic fields, $\xi > d$, where ξ is the magnetic coherence length ($\xi^2 = k_{33}/\chi_a H^2$), V_a is independent of d and a voltage threshold exists. For large fields, $\xi > d$, V_a is proportional to d, i.e., a field threshold proportional to H exists. These results are in reasonable agreement with the observations of the Orsay Group (1971c).

F. Dielectric mode ($\omega\tau > 1$)

At high frequencies when $\omega\tau$ is large, the charge will be approximately stationary. The solution of Eqs. (17.52) and (17.54) may now be taken approximately in the form

$$q_1 = q^{(0)}$$
$$\psi = \psi^{(1)} \sin\omega t + \psi^{(2)} \cos\omega t \tag{17.71}$$

so that in this mode the director fluctuates while the distribution of charge is stationary. The nature of this mode is illustrated in Fig. 30. Substituting Eq. (17.71) in (17.52) and (17.54) and neglecting harmonics we obtain

$$(q^{(0)}/\tau) + \tfrac{1}{2}\sigma_H E_m \psi^{(2)} = 0,$$
$$\omega\psi^{(1)} + [(\alpha/2)E_m{}^2 + \beta]\psi^{(2)} + q^{(0)}E_m/\eta = 0,$$
$$-\omega\psi^{(2)} + [(\alpha/2)E_m{}^2 + \beta]\psi^{(1)} = 0. \tag{17.72}$$

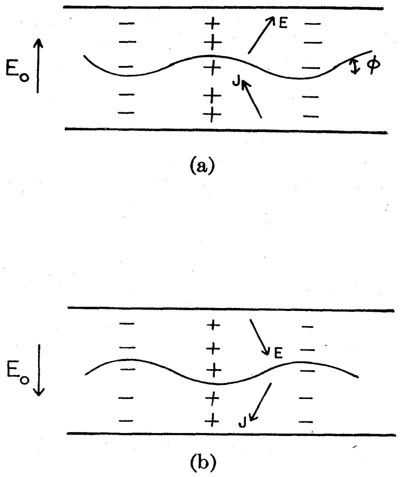

FIG. 30. Dielectric mode. (a) E_0 is up. (b) E_0 is down. The charge density is approximately stationary and in each part of the cycle the director is perpendicular to the resultant field.

Setting the determinant of the coefficients in these equations equal to zero leads to the secular equation

$$\omega^2 = \tfrac{1}{4}\alpha^2(E_m{}^2 + E_a{}^2)^2[\zeta^2 E_m{}^2/(E_m{}^2 + E_a{}^2) - 1]. \tag{17.73}$$

This equation determines the threshold field E_m at which instability arises for a fixed value of ω. The optimum wave vector k for the fluctuations at threshold is determined by minimizing E_m with respect to k (which enters into E_a). This leads to the equation determining the wave vector,

$$(k_{33}k^2 + \chi_a H^2) = 2\omega\eta'[(\zeta^2 - 2)/\zeta^2]. \tag{17.74}$$

When this result is substituted back in Eq. (17.73), we find that the threshold field is given by

$$E_{mc}{}^2 = (\omega/\alpha)(4/\zeta^2). \tag{17.75}$$

DuBois-Violette *et al.* (1971) have obtained a more exact solution for the threshold field:

$$E_{mc} = (\omega/\alpha)C_1(\zeta^2) + \text{constant}, \tag{17.76}$$

where $C_1(\zeta^2)$ is tabulated and the constant is independent of ω.

The mode described by Eq. (17.71) is a propagating orientational mode (in the absence of charges it would be overdamped). The threshold field is large, and correspondingly the relaxation time T [Eq. (17.55)] is short. For $\omega = 10^2\ \mathrm{sec}^{-1}$, $\eta' = 0.1$ P, $E_{mc} \sim 10^3$–10^4 V/cm, and $T \sim 10^{-2}$ sec. This is the origin of the name "fast turn off" for this mode. The director fluctuations scatter light strongly, as first observed by Heilmeier and Helfrich (1970).

From Eqs. (17.74) and (17.76) we note the following results.

(1) The field threshold is independent of wave vector k and sample thickness and varies with frequency as $\omega^{1/2}$. This is quite different from the charge density mode and confirmed by the observations (Orsay Group, 1971c).

(2) The spatial periodicity of the director fluctuations is determined by Eq. (17.74). A more exact result (DuBois-Violette *et al.*, 1971) is

$$k_{33}k^2 + \chi_a H^2 = \omega\eta' C_2(\zeta^2) + \text{constant}, \tag{17.77}$$

where C_2 is tabulated and the constant is independent of ω. This result shows that (a) for fixed H, k^2 depends linearly on ω; and (b) for fixed ω, $k_{33}k^2 + \chi_a H^2$ is a constant. Both these results have been confirmed by the Orsay Group (1971c) in MBBA.

It should be noted that the above discussion is valid for $\omega\tau > 1$ or $\omega > \omega_c$ where ω_c is the cutoff frequency (17.67). A numerical investigation of the region $\omega \sim \omega_c$ has been carried out by DuBois-Violette (1972), who showed that the voltage threshold for the onset of the conduction regime is an S-shaped curve. Thus in a certain range of frequencies $\omega_1 < \omega < \omega_2$ Williams domains appear at a voltage threshold, while at higher voltages turbulence and dynamic scattering occur. When the voltage is further increased, the turbulence diminishes and finally the flow patterns disappear completely. The threshold for chevrons (dielectric regime) occurs at higher voltages. Such effects have been observed by the Orsay Group (1972) and de Jeu and van der Veen (1973).

G. Dependence of instability threshold on ϵ_a

By mixing suitable nematic components, it is possible to vary the dielectric anisotropy and even change its sign (Kashnow and Cole, 1972; Alder and Raynes, 1973). The instability threshold for the charge fluctuation or conduction mode (17.63) is conveniently written

$$\tfrac{1}{2}E_{mc}^2 = D^2(1 + \omega^2\tau^2)/[\epsilon_a(1 + \omega^2\tau^2 - \zeta^2)], \tag{17.78}$$

where

$$D^2 = (4\pi\epsilon_{||}/\epsilon_\perp)[(k_{33}k^2 + \chi_a H^2)/(1 + \gamma_1/2\eta_2)].$$

It is assumed that the director is initially in the plane of the electrodes. The dependence of ζ^2 [Eq. (17.65)] on ϵ_a for MBBA is shown in Fig. 31; for this case $\zeta^2 = 1$ at $\epsilon_a = \epsilon_{a0} \simeq -2$, and $\zeta^2 < 1$ for $\epsilon_a > 0$. From Eq. (17.78) the following behavior occurs on increasing ϵ_a:

(a) $\epsilon_a < \epsilon_{a0}$. No threshold field exists and the nematic is stable at all fields and frequencies. A nematic with $\epsilon_a \simeq -5$ has been investigated by de Jeu *et al.*, (1973) and found to have a conduction mode instability. Even for this case it appears that $\epsilon_a > \epsilon_{a0}$.

(b) $\epsilon_{a0} < \epsilon_a < 0$. This is the case considered in Sec. XVII,D. The conduction regime exists for $\omega < \omega_c$ and the dielectric regime for $\omega > \omega_c$.

(c) $\epsilon_a > 0$. The conduction regime exists at all frequencies. At the values ϵ_{a1} and ϵ_{a2} where $\zeta^2 = 0$ the threshold field is independent of frequency. When $\zeta^2 = 0$, the torques due to the anisotropy of the dielectric constant and conductivity just cancel. When $\zeta^2 < 0$, the threshold field is an increasing function of ω, and when $\zeta^2 > 0$, it is a decreasing function of ω. Some results in the case $\epsilon_a > 0$ have been obtained by Gruler and Meier (1971) and de Jeu and Gerritsma (1972).

H. Other instabilities

The instabilities of cholesterics in electric fields parallel to the pitch axis have been studied theoretically by Helfrich (1971a) and by Hurault (1973), who has extended the theoretical model of DuBois-Violette *et al.*, (1971) to the cholesteric case. The predicted and observed behavior (Rondelez *et al.*, 1972; Arnould and Rondelez, 1974) is very similar to that of nematics. For $\epsilon_a > 0$, a single threshold for the formation of domains is observed, while for $\epsilon_a < 0$, a conduction and dielectric regime are observed. A memory effect above the threshold for the conduction mode has been observed by Heilmeier *et al.* (1969).

Hydrodynamic instabilities in nematics and cholesterics under thermal gradients have been studied theoretically by DuBois-Violette (1971, 1973). The instabilities are similar to the Benard instability in normal liquids. The anisotropy in the thermal conductivity plays an important role in the liquid crystal, and the threshold thermal gradient is much lower in the ordered phase than in the isotropic phase. Convective instabilities have been observed in nematics subjected to a temperature difference of only a few degrees (Guyon and Pieranski, 1972; Pieranski, DuBois-Violette, and Guyon, 1973).

XVIII. OPTICAL PROPERTIES OF CHOLESTERIC LIQUID CRYSTALS

Cholesteric liquid crystals have some unusual optical properties, the best known of which are the color effects seen in reflection under white light. These effects have their origins in the interactions of the light with the twisted arrangement of the molecules and the concomitant spatial variation of the dielectric constant.

The optical properties of uniformly twisted structure have been discussed by Mauguin (1911), Oseen (1933), de Vries (1951), and Dreher *et al.* (1971) for the case of light incident parallel to the twist axis. The case of oblique incidence has been considered by Conners (1968), Taupin (1969), and Berreman and Scheffer (1970a,b; 1972). In Sec. XVIII,A we will outline some general considerations relevant to this problem; in Sec. XVIII,B we consider the solutions of the wave equation for the special case of propagation parallel to the cholesteric axis.

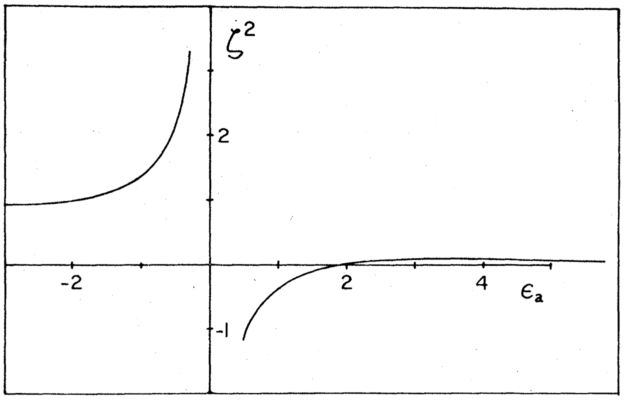

FIG. 31. Dependence of ζ^2 [Eq. (17.65)] on ϵ_a. The parameters used were $K_{||}/K_\perp = 1.5$, $\gamma_1/2\eta_2 = 0.7$, $\frac{1}{2}(\epsilon_{||} + \epsilon_\perp) = 5.05$, and $\epsilon_a = -.07$ and are appropriate for MBBA.

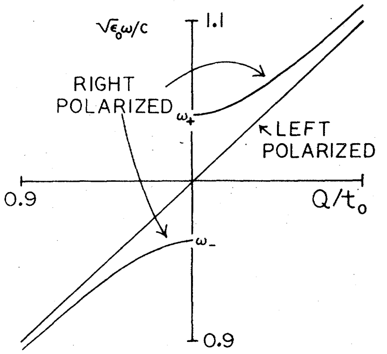

FIG. 32. Dispersion of light in a right-hand twisting cholesteric. The right-hand circularly polarized wave is strongly affected when its wavelength is comparable to the pitch. The left-hand circularly polarized wave of the same wavelength is unaffected. This figure and Fig. 33 were drawn for the case $n_e = 1.57$, $n_0 = 1.51$.

A. General properties of the cholesteric structure

The variation in dielectric constant through the medium is small ($\Delta n/n \sim 0.03$; see, for example, Teucher *et al.*, 1972), and consequently we will imagine (and verify in the next section) that the normal form of waves propagating through the medium is not very different from ordinary circularly polarized waves. Such a wave will be strongly affected only if its half-wavelength nearly matches the periodicity length (or its projection on the wave vector) and if the sense of its rotation is the same as that of the twisted structure. The effect on the dispersion relation of the wave should otherwise be the same as encountered in other cases of waves in periodic structures; in particular, a "band gap" should appear at the matching wavelength

$$\lambda_0 = p \sin\theta. \tag{18.1}$$

The factor of 2 usually encountered in the Bragg formula is missing: the periodicity length is one-half the pitch because **n** and **−n** are indistinguishable optically. Figure 32 is an illustration of the form of the dispersion relation near λ_0. The size of the band gap is determined by the strength of the periodic perturbation. Light having exactly the wavelength λ_0 can travel at two distinct speeds by having its electric vector aligned with the principal axes of the dielectric constant. These two waves determine the extrema of the band gap so that

$$\omega_+ = 2\pi c/n_-\lambda_0, \qquad \omega_- = 2\pi c/n_+\lambda_0, \tag{18.2}$$

where n_+, n_-, are the greater and lesser, respectively, of the indices of refraction. Frequencies between ω_- and ω_+ do not correspond to a propagating wave; if light of frequency in this range and of the appropriate circular polarization to match the sense of the twist is directed at the liquid crystal, it is totally reflected. The polarization of the reflected light also matches the sense of the twist (so that the reflection process is time-reversible); thus right-polarized light is reflected as right-polarized light[11] by a right-hand cholesteric. Left-polarized light of the same frequency suffers only the weak reflection usually encountered at dielectric surfaces.

The reflected band is typically narrow ($\Delta\omega/\omega \sim \Delta n/n \sim 0.03$), so that a pure color is reflected, which depends on the angle of incidence relative to the cholesteric axis, as well as the pitch, which may in turn be strongly dependent on temperature and other environmental considerations.

Plane polarized light incident on a layer of liquid crystal traverses it as a superposition of the two circularly polarized waves having the same frequency. Since the wavelengths of these waves can be substantially different, a large phase difference develops in a short distance, which implies a large rotary power

$$\text{R.P.} = \pi(\lambda_R^{-1} - \lambda_L^{-1}) \tag{18.3}$$

which can amount to a hundred revolutions per mm [for example, see Landolt-Bornstein (1962), and Teucher *et al.* (1972)]. It is also evident from Fig. 32 that the rotary power has opposite signs on the two sides of the reflection band: below ω_-, $\lambda_R < \lambda_L$; above ω_+, $\lambda_R > \lambda_L$.

B. The wave equation in a twisted structure

It will be assumed here that the cholesteric structure can be represented adequately by a regular precession of the principal axes of the dielectric constant along the twist axis, thus ignoring any fluctuations in the pitch; and only the special case of propagation parallel to the twist axis will be treated. The precessing dielectric tensor has the form

$$\epsilon_{ij} = \epsilon_0\delta_{ij} + \epsilon_a(n_i n_j - \tfrac{1}{2}\delta_{ij}), \tag{18.4}$$

where n_i are the components of the director. These are given by

$$n_x = \cos t_0 z, \qquad n_y = \sin t_0 z, \tag{18.5}$$

where the pitch is $2\pi/t_0$ (this is a right-hand twisting structure).

Anticipating that waves of circular polarization give the more convenient representation, we shall write the electric

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[11] In contrast ordinary isotropic mirrors reverse the sense of circular polarization on reflection.

field as a superposition of a right-hand circularly polarized wave with an amplitude E_R, and a left-hand circularly polarized wave with an amplitude E_L:

$$\mathbf{E} = \mathrm{Re}[E_R(\mathbf{x} + i\mathbf{y}) + E_L(\mathbf{x} - i\mathbf{y})] \tag{18.6}$$

and similarly for **D**. The coefficients D_R, D_L are related to E_R, E_L by

$$\begin{aligned} D_R &= \epsilon_0 E_R + \tfrac{1}{2}\epsilon_a \exp(-2it_0z) E_L, \\ D_L &= \epsilon_0 E_L + \tfrac{1}{2}\epsilon_a \exp(2it_0z) E_R. \end{aligned} \tag{18.7}$$

The wave equation is

$$c^2(\partial^2\mathbf{E}/\partial z^2) = \partial^2\mathbf{D}/\partial t^2, \tag{18.8}$$

where the small magnetic susceptibility has been neglected. Substituting from Eq. (18.7), and assuming the wave has frequency ω,

$$\begin{aligned} [c^2(\partial^2/\partial z^2) + \epsilon_0\omega^2]E_R &= -\tfrac{1}{2}\epsilon_a\omega^2 \exp(-2it_0z) E_L \\ [c^2(\partial^2/\partial z^2) + \epsilon_0\omega^2]E_L &= -\tfrac{1}{2}\epsilon_a\omega^2 \exp(2it_0z) E_R. \end{aligned} \tag{18.9}$$

These equations describe a wave of one polarization weakly coupled to one of the reverse polarization and different wavelength. They have such structure that if (E_R, E_L) is a solution, then $(E_L{}^*, E_R{}^*)$ is also. We might then seek a solution of the form

$$E_R = A \exp[-i(Pz - \omega t)] + B \exp[i(Qz - \omega t)] \tag{18.10}$$

and correspondingly for $E_L = E_R{}^*$. Equation (18.9) becomes

$$\begin{aligned} &A(c^2P^2 - \epsilon_0\omega^2) \exp[-i(Pz - \omega t)] + B(c^2Q^2 - \epsilon_0\omega^2) \\ &\qquad \times \exp[i(Qz - \omega t)] \\ &\quad = \tfrac{1}{2}\epsilon_a\omega^2\{A^* \exp[-i(2t_0z - Pz + \omega t)] \\ &\qquad + B^* \exp[-i(2t_0z + Qz - \omega t)]\}. \end{aligned} \tag{18.11}$$

If P and Q are related by

$$P - Q = 2t_0, \tag{18.12}$$

then only two independent waveforms occur. Combining the coefficients of these,

$$\begin{aligned} A(c^2P^2 - \epsilon_0\omega^2) &= \tfrac{1}{2}\epsilon_a\omega^2 B^* \\ B(c^2Q^2 - \epsilon_0\omega^2) &= \tfrac{1}{2}\epsilon_a\omega^2 A^*. \end{aligned} \tag{18.13}$$

The complex conjugates of these equations are found by consideration of the equation for E_L. The equations are self-consistent only for

$$(P^2c^2 - \epsilon_0\omega^2)(Q^2c^2 - \epsilon_0\omega^2) = \tfrac{1}{4}\epsilon_a{}^2\omega^4 \tag{18.14}$$

which may be solved for ω^2 to give

$$\omega^2 = \frac{c^2}{2}\,\frac{\epsilon_0(P^2 + Q^2) \pm [\epsilon_0{}^2(P^2 - Q^2)^2 + \epsilon_a{}^2P^2Q^2]^{1/2}}{\epsilon_0{}^2 - \frac{1}{4}\epsilon_a{}^2}. \tag{18.15}$$

The form of the normal waves is given by Eq. (18.6) with

$$\begin{aligned} E_R = {} & Ae^{-i(Pz-\omega t)} + 2[(P^2c^2 - \epsilon_0\omega^2)/\epsilon_a\omega^2] \\ & \times A^* \exp[-i(2t_0z - Pz - \omega t)] \end{aligned} \tag{18.16}$$

which may also be written

$$\begin{aligned} E_R = {} & Be^{i(Qz-\omega t)} + 2[(Q^2c^2 - \epsilon_0\omega^2)/\epsilon_a\omega^2] \\ & \times B^* \exp[-i(2t_0z + Qz - \omega t)] \end{aligned} \tag{18.17}$$

and $E_L = E_R{}^*$.

Discussion of these results must be divided into three cases:

(a) $P > 2t_0$ — $(Q > 0)$

The two solutions (18.15) are approximately $\omega^2 = c^2P^2/\epsilon_0$ and $\omega^2 = c^2Q^2/\epsilon_0$; the corresponding waveforms are a right-polarized wave with a small left-polarized component [the coefficient of the second term of Eq. (18.16) is small], and a left-polarized wave with a small right-polarized component [the coefficient of the second term of Eq. (18.17) is small]. The dispersion relation for this latter solution has been plotted in Fig. 32 for Q near t_0.

(b) $P < 0$ — $(Q < -2t_0)$

Reference to Eq. (18.10) shows this to correspond to waves propagating in the backward direction. Interpretation is the same as in the previous case, except that P and Q have interchanged roles.

(c) $0 < P < 2t_0$ — $(-2t_0 < Q < 0)$

The waveform in this case consists of a sum of forward- and backwards-travelling waves, both having the same helicity as the cholesteric structure itself. At $P = t_0 = -Q$ there are two solutions for ω^2

$$\omega_\pm{}^2 = c^2t_0{}^2/(\epsilon_0 \pm \tfrac{1}{2}\epsilon_a) \tag{18.18}$$

which define the band gap [compare Eq. (18.2)]. The general solution for this case has also been plotted in Fig. 32.

Except near the band gap, $Pc = (\epsilon_0\omega)^{1/2}$ and $Qc = (\epsilon_0\omega)^{1/2}$ are good approximations to the forward-going wave solutions of (18.14), and by expansion we may give the correction terms

$$\epsilon_0{}^{-1/2}cq_\pm = \omega + (\epsilon_a{}^2\omega^3/32ct_0\epsilon_0)[t_0c \mp \omega(\epsilon_0)^{1/2}]^{-1}, \tag{18.19}$$

TABLE II. Properties of PAA near 125°C and of MBBA near 25°C.[a]

Properties	of PAA near 125°C	of MBBA near 25°C
Specific gravity	1.168 (1)	1.088 (2)
Melting point	117.5°C	16°C
Clear point	135°C	46°C
Magnetic anisotropy χ_a	1.18×10^{-7} (3)	0.97×10^{-7} (4)
Zero frequency		
Dielectric $\epsilon_{\|\|}$	5.538 (5)	4.7 (6)
Constants $\epsilon_{\perp}$	5.705 (5)	5.4 (6)
Optical		
Constants n_0	1.565 (7)	1.54 (2)
(Na D line) n_e	1.829 (7)	1.75
Surface tension	38 dyn/cm (8)	40 dyn/cm (8)
Sound velocity	1.34×10^{5} cm/sec (9)	1.54×10^{5} cm/sec (10)
Frank constants:		
k_{11} (dyne)	4.5×10^{-7}	6×10^{-7}
k_{22}	2.9×10^{-7} (11)	4×10^{-7} (12)
k_{33}	9.5×10^{-7}	7.5×10^{-7}
Viscosity coefficients (See Table I)		
γ_1 (centipoise)	6.7 (13); 5.8 (14)	77 (15)
γ_2	−7.0 (13); −7 (14)	−80 (15)
α_1	4.3 (13);	6.5 (15)
α_2	−6.9 (13); −6.4 (14)	−77.5 (15)
α_3	−.2 (13); −.6 (14)	−1 (15)
α_4	6.8 (13); 8.3 (14)	83 (15)
α_5	4.7 (13); 2.5 (14)	46 (15)
α_6	−2.3 (13); −4.5 (14)	−35 (15)
η_1	2.4 (16); 1.5 (14)	16.3 (17); 24 (15)
η_2	9.2 (16); 8.6 (14)	25.2 (17); 103 (15)
η_3	3.4 (18); 4.1 (14)	16.1 (17); 41 (15)
θ_0	9.1° (13); 20° (19)	7° (15); 19° (19)
$\beta_{\|\|}$ (cal $\text{cm}^{-1}\cdot\text{sec}^{-1}$		5×10^{-4} (20)
$\beta_{\perp}$ $\cdot\text{deg}^{-1}$		3×10^{-4} (20)

[a] (1) Schenk (1898) as cited by Hoyer and Nolle (1956). (2) Haller, Huggins, and Freiser (1972). (3) Zwetkoff (1939b); Gasparoux and Prost (1971). (4) Gasparoux and Prost (1971); see also Landolt-Bornstein (1959). (5) Maier, Barth, and Wiehl (1954). (6) Diguet, Rondelez, and Durand (1970). (7) Chatelain and Germain (1964); Brunet-Germain (1970). (8) Langevin (1972). (9) Kemp and Letcher (1971). (10) Mullen, Lüthi, and Stephen (1972). (11) Zwetkoff (1937, 1943); Orsay Group (1969b). (12) Haller (1972). (13) From a data review by Tseng, Silver, and Finlayson (1972) based on the work of Miesowicz (1936, 1946), Zwetkoff (1939a), and Marinin and Zwetkoff (1939). (14) Orsay Group (1971a). (15) Gähwiller (1971). (16) Miesowicz (1946). (17) Langevin (1972). (18) Miesowicz (1946). According to Tseng, Silver, and Finlayson (1972), the viscosity in the absence of an ordering field (rather than the viscosity with director oriented in the direction of flow) is being quoted here, and the true value of η_3 is closer to 3 centipoise. (19) Meiboom and Hewitt (1973). (20) Pieranski, Brochand, and Guyon (1972).

where q_+ and q_- are, respectively, the wave vectors of P and Q type corresponding to the same frequency; in terms of these the specific rotary power may be written

$$\text{R.P.} = q_+ - q_- = (\epsilon_a{}^2\omega^4/32t_0c^2)(c^2t_0{}^2 - \epsilon_0\omega^2)^{-1}. \tag{18.20}$$

The rotary power has opposite signs on the two sides of the band gap centered on $\omega = ct_0/(\epsilon_0)^{1/2}$. Most of the rotary power is due to the large dispersion of the q_+ branch of Eq. (18.19) (compare Fig. 32).

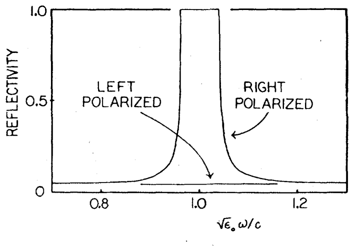

FIG. 33. Reflectivity of a semi-infinite slab of a right-hand twisting cholesteric with $n_e = 1.57$, $n_0 = 1.51$.

C. Reflection from a thick slab

We will consider a plane-faced slab with the cholesteric axis perpendicular to the face; the medium is bounded by glass of index of refraction n. Light is incident on the surface perpendicular to it.

The waveforms (18.16) and (18.17) are such that in any plane of constant z the wave is elliptically polarized; but since two wavelengths are involved, the axis of the ellipse precesses through the liquid crystal. Light entering the medium will in general excite both normal waves of the same frequency, unless its polarization is in proper correspondence to the ellipticity of one normal wave at the surface. The general reflectivity is a combination of the reflectivities measured under the conditions that excite only one normal wave.

Let us assume that only one normal wave is excited; let its form be given by Eq. (18.16) with $A = 1$. In the glass there are both incident and reflected waves whose polarization must be determined: let $\mathbf{E}$ have the form (18.6), where

$$E_R = S \exp[-i(qz - \omega t)] + T \exp[i(qz - \omega t)] + U \exp[i(qz + \omega t)] + V \exp[-i(qz + \omega t)] \tag{18.21}$$

and $E_L = E_R{}^*$, and where $cq = n\omega$. The condition of continuity of E at the surface $z = 0$ is

$$S + U = 1; \qquad T + V = 2[(P^2c^2 - \epsilon_0\omega^2)/(\epsilon_a\omega^2)]; \tag{18.22}$$

continuity of dE/dz gives

$$\begin{aligned} &qS - qU = P; \\ &-qT + qV = 2[(P^2c^2 - \epsilon_0\omega^2)(2t_0 - P)/(\epsilon_a\omega^2)]. \end{aligned} \tag{18.23}$$

This set may be solved to give

$$\begin{aligned} S &= \frac{q + P}{2q} \qquad T = 2\frac{P^2c^2 - \epsilon_0\omega^2}{\epsilon_a\omega^2}\left(\frac{q + P - 2t_0}{2q}\right) \\ U &= \frac{q - P}{2q} \qquad V = 2\frac{P^2c^2 - \epsilon_0\omega^2}{\epsilon_a\omega^2}\left(\frac{q + 2t_0 - P}{2q}\right). \end{aligned} \tag{18.24}$$

The reflectivity is the ratio of the reflected intensity to that incident

$$\begin{aligned} R &= \frac{U^2 + V^2}{S^2 + T^2} \\ &= \frac{(q - P)^2\omega^4\epsilon_a{}^2 + 4(q + 2t_0 - P)^2(P^2c^2 - \epsilon_0\omega^2)^2}{(q + P)^2\omega^4\epsilon_a{}^2 + 4(q - 2t_0 + P)^2(P^2c^2 - \epsilon_0\omega^2)^2}. \end{aligned} \tag{18.25}$$

The behavior of this function for the special case $n^2 = 1$ is shown in Fig. 33.

For the uniformly twisted cholesteric, and for normal incidence, there is only one reflection band. At oblique incidence higher-order reflection bands appear. If the cholesteric is distorted (e.g., by a magnetic field) higher-order reflection bands also occur for normal incidence (Chou, Cheung, and Meyer, 1972; Dreher, 1973).

XIX. PHYSICAL PROPERTIES OF PAA AND MBBA

We have collected here some measured values for the physical parameters of the common liquid crystals para-azoxy anisole (PAA:MW = 258) and *p*-methoxy benzilidene *p*-*n*-butylanaline (MBBA:MW = 267) (see also Fig. 1). Our intention is to provide some idea of the magnitude of these quantities; we have not attempted to review the experiments critically (see Table II).

Both of these substances are somewhat labile (Denat, Gosse, and Gosse, 1973): Langevin (1972) and Haller (1972) both report considerable decrease of T_c in MBBA over a time period of several days. The physical constants reported depend considerably on purity and temperature. This makes it difficult to compare the results of different workers, and so we have preferred where possible to choose sets of data from a single source.

ACKNOWLEDGMENTS

The authors would like to thank the National Science Foundation for support; G. B. Benedek (Massachusetts Inisitute of Technology) and F. R. N. Nabarro (University of Witwatersrand) for their hospitality; and Dr. Johanna Stephen and Dr. Susan Straley for their encounragement.

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