

# I. LIQUID CRYSTALS

## ON THE THEORY OF LIQUID CRYSTALS

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A general theory of curvature-elasticity in the molecularly uniaxial liquid crystals, similar to that of Oseen, is established on a revised basis. There are certain significant differences: in particular one of his coefficients is shown to be zero in the classical liquid crystals. Another, which he did not recognize, does not interfere with the determination of the three principal coefficients. The way is therefore open for exact experimental determination of these coefficients, giving unusually direct information regarding the mutual orienting effect of molecules.

### 1. INTRODUCTION

One of the principal purposes of this paper is to urge the revival of experimental interest in its subject. After the Society's successful Discussion on liquid crystals in 1933, too many people, perhaps, drew the conclusion that the major puzzles were eliminated, and too few the equally valid conclusion that quantitative experimental work on liquid crystals offers powerfully direct information about molecular interactions in condensed phases.

The first paper in the 1933 Discussion was one by Oseen,<sup>1</sup> offering a general structural theory of the classical liquid crystals, i.e. the three types, smectic, nematic and cholesteric, recognized by Friedel<sup>2</sup> (1922). In the present paper Oseen's theory (with slight modification) is refounded on a securer basis. As with Oseen, this is a theory of the molecularly uniaxial liquid crystals, that is to say, those in which the long-range order governs the orientation of only one molecular axis. This certainly embraces the classical types, though in the smectic class one translational degree of freedom is also crystalline. Other types of liquid crystal may exist, but are at least relatively rare: presumably because ordering of one kind promotes ordering of another—it is already exceptional for *one* orientational degree of freedom to crystallize without simultaneous crystallization of the translational degrees of freedom. Fluidity (in the sense that no shear stress can persist in the absence of flow) is in principle compatible with biaxial orientational order, with or without translational order in one dimension. It is very unlikely that translational order in two dimensions, and not in the third, can occur as an equilibrium situation. The existence of a three-dimensional lattice is not compatible with true fluidity. A dilute solution with lattice order, which appeared to be fluid, would not be considered a liquid crystal from the present viewpoint, but rather a solid with a very low plastic yield stress.

The Oseen theory embraces smectic mesophases, but is not really required for this case. The interpretation of the equilibrium structures assumed by smectic substances under a particular system of external influences may be carried out by essentially geometric arguments alone. The structures are conditioned by the existence of layers of uniform thickness, which may be freely curved, but in ways which do not require a breach of the layering in regions of greater extension than lines. These conditions automatically require the layers to be Dupin cyclides and the singular lines to be focal conics. Nothing, essentially, has been added

to the account of these given by Friedel, and not much appears to be needed, though a few minor features (the scalloped edges of Grandjean terraces, and scalloped frills of battonets) have not been fully interpreted.

The case is quite different for the nematic and cholesteric liquid crystals. This is particularly clear for the former. In a thin film, say, of a nematic substance, particular orientations are imposed at the surfaces, depending on the nature or prior treatment of the materials at these surfaces; if the imposed orientations are not parallel some curved transition from one orientation to the other is required. Curvature may also be introduced when, say, the orienting effect of a magnetic field conflicts with orientations imposed by surface contacts. Something analogous to elasticity theory is required to define the equilibrium form of such curvatures. It is, however, essentially different from the elasticity theory of a solid. In the latter theory, when we calculate equilibrium curvatures in bending, we treat the material as having undergone homogeneous strains in small elements: restoring forces are considered to oppose the change of distance between neighbouring points in the material. In a liquid, there are no permanent forces opposing the change of distance between points: in a bent liquid crystal, we must look for restoring torques which directly oppose the curvature. We may refer to these as torque-stresses, and assume an equivalent of Hooke's law, making them proportional to the curvature-strains, appropriately defined, when these are sufficiently small. It is an equivalent procedure to assume that the free-energy density is a quadratic function of the curvature-strains, in which the analogues of elastic moduli appear as coefficients: this is the procedure we shall actually adopt.

Oseen likewise proceeded by setting up an expression for energy density, in terms of chosen measures of curvature. However, he based his argument on the postulate that the energy is expressible as a sum of energies between molecules taken in pairs. This is analogous to the way in which Cauchy set up the theory of elasticity for solids, and in that case it is known that the theory predicted fewer independent elastic constants than actually exist, and we may anticipate a similar consequence with Oseen's theory.

It is worth remarking that the controversial conflict between the "swarm theory" and the "continuum theory" of liquid crystals is illusory. The swarm theory was a particular hypothetical and approximative approach to the statistical mechanical problem of interpreting properties which can be well defined in terms of a continuum theory. This point is seen less clearly from Oseen's point of departure than from that of the present paper.

## 2. BASIC THEORY

We first require to define the components of curvature. Let  $\mathbf{L}$  be a unit vector representing the direction of the preferred orientation in the neighbourhood of any point. The sign of this vector is without physical significance, at least in most cases. If so, it must be chosen arbitrarily at some point and defined by continuity from that point throughout the region in which  $\mathbf{L}$  varies slowly with position. In multiply-connected regions it may be necessary to introduce arbitrary surfaces of mathematical discontinuity, where this sign changes without any physical discontinuity. At any point we introduce a local system of Cartesian co-ordinates,  $x, y, z$ , with  $z$  parallel to  $\mathbf{L}$  at the origin,  $x$  chosen arbitrarily perpendicular to  $z$ , and  $y$  perpendicular to  $x$  so that  $x, y, z$  form a right-handed system. Referred to these axes, the six components of curvature at this point are (see fig. 1):

$$\left. \begin{aligned} \text{"splay"}: s_1 &= \partial L_x / \partial x, \quad s_2 = \partial L_y / \partial y; \\ \text{"twist"}: t_1 &= -\partial L_y / \partial x, \quad t_2 = \partial L_x / \partial y; \\ \text{"bend"}: b_1 &= \partial L_x / \partial z, \quad b_2 = \partial L_y / \partial z. \end{aligned} \right\} \quad (1)$$

Then, putting

$$\left. \begin{aligned} L_x &= a_1x + a_2y + a_3z + 0(r^2), \\ L_y &= a_4x + a_5y + a_6z + 0(r^2), \\ L_z &= 1 + 0(r^2), \quad (r^2 = x^2 + y^2 + z^2), \end{aligned} \right\} \quad (2)$$

we have

$$s_1 = a_1, \quad t_2 = a_2, \quad b_1 = a_3, \quad -t_1 = a_4, \quad s_2 = a_5, \quad b_2 = a_6. \quad (3)$$

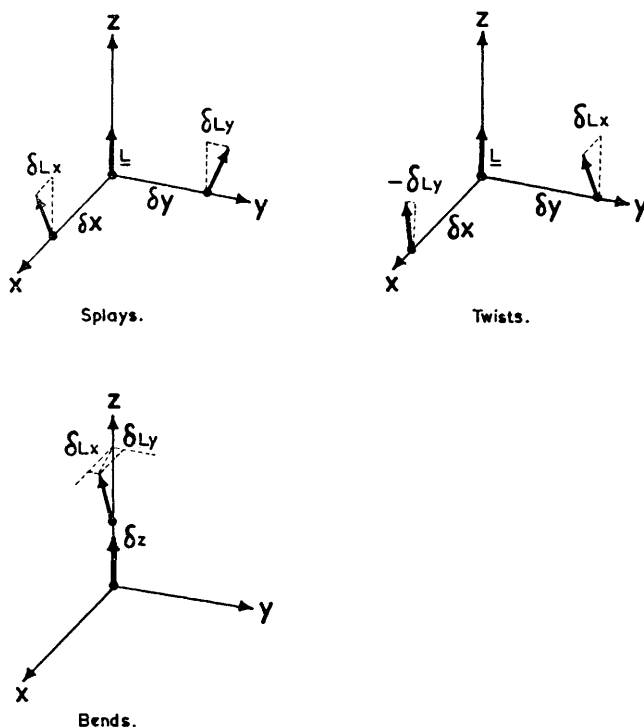


FIG. 1.

We postulate that the free energy  $G$  of a liquid crystal specimen in a particular configuration, relative to its energy in the state of uniform orientation, is expressible as the volume integral of a free-energy density  $g$  which is a quadratic function of the six differential coefficients which measure the curvature :

$$G = \int_v g d\tau, \quad (4)$$

$$g = k_i a_i + \frac{1}{2} k_{ij} a_i a_j, \quad (i, j = 1 \dots 6, \quad k_{ij} = k_{ji}), \quad (5)$$

where summation over repeated suffixes is implied.

In so far as there was arbitrariness in our choice of the local co-ordinate system  $(x, y, z)$ , we require that when we replace this by another equally permissible one  $(x', y', z')$  in which we have new curvature components  $a'_i$ ,  $g$  shall be the same function as before of these curvature components :

$$g = k_i a'_i + \frac{1}{2} k_{ij} a'_i a'_j. \quad (6)$$

This requirement will impose restrictions on the moduli,  $k_i, k_{ij}$ .

The choice of the  $x$ -direction was arbitrary, apart from the requirement that it should be normal to  $z$ , which is parallel to the physically significant direction  $\mathbf{L}$  :

hence any rotation of the co-ordinate system around  $z$  is a permissible one. Putting  $z' = y$ ,  $y' = -x$ ,  $z' = z$ , gives us the equations :

$$\left. \begin{aligned} k_1 &= k_5, k_2 = -k_4, k_3 = k_6 = 0, \\ k_{11} &= k_{55}, k_{22} = k_{44}, k_{33} = k_{66}, \\ k_{12} &= -k_{45}, k_{14} = -k_{25}, \\ k_{13} &= k_{16} = k_{23} = k_{26} = k_{34} = k_{35} = k_{36} = k_{46} = k_{56} = 0 \end{aligned} \right\} \quad (7)$$

The working is omitted here : the simpler examples of eqn. (13-17) below exhibit the principle.

A rotation of  $45^\circ$  gives a further equation

$$k_{11} - k_{15} - k_{22} - k_{24} = 0, \quad (8)$$

and rotation by another arbitrary angle just one more

$$k_{12} + k_{14} = 0, \quad (9)$$

which with those obtained previously gives

$$k_{12} = -k_{14} = k_{25} = -k_{45}. \quad (10)$$

Thus, of the six hypothetical moduli  $k_i$  two are zero and only two are independent :

$$k_i = (k_1 \ k_2 \ 0 \ -k_2 \ k_1 \ 0), \quad (11)$$

while of the thirty-six  $k_{ij}$  eighteen are zero and only five are independent :

$$k_{ij} = \left\{ \begin{array}{cccccc} k_{11} & k_{12} & 0 & -k_{12} & (k_{11} - k_{22} - k_{24}) & 0 \\ k_{12} & k_{22} & 0 & k_{24} & k_{12} & 0 \\ 0 & 0 & k_{33} & 0 & 0 & 0 \\ -k_{12} & k_{24} & 0 & k_{22} & -k_{12} & 0 \\ (k_{11} - k_{22} - k_{24}) & k_{12} & 0 & -k_{12} & k_{11} & 0 \\ 0 & 0 & 0 & 0 & 0 & k_{33} \end{array} \right\} \quad (12)$$

If the molecules are non-polar with respect to the preferentially oriented axis, or, if polar, are distributed with equal likelihood in both directions, the choice of sign of  $\mathbf{L}$  is arbitrary. It is a significant convention in our definition of curvature components that  $z$  is positive in the positive direction of  $\mathbf{L}$  : and if  $z$  changes sign, one of  $x$  and  $y$  should change sign also to retain right-handed co-ordinates. Hence a permissible transformation in the absence of physical polarity is  $\mathbf{L}' = -\mathbf{L}$ ,  $x' = x$ ,  $y' = -y$ ,  $z' = -z$ . This gives us

$$\left. \begin{aligned} L'_x &= -a_1 x' + a_2 y' + a_3 z' + 0(r^2), \\ L'_y &= a_4 x' - a_5 y' - a_6 z' + 0(r^2). \end{aligned} \right\} \quad (13)$$

Since, compared with (2), the coefficients with indices 1, 5 and 6 have changed sign, the required invariance of (6) gives us the equations

$$k_1 = 0, k_5 = 0, k_6 = 0, \quad (14)$$

and (from the second order terms in which only one factor has changed sign) :

$$k_{12} = k_{13} = k_{14} = k_{25} = k_{26} = k_{35} = k_{36} = k_{45} = k_{46} = 0. \quad (15)$$

Some of this information is already contained in eqn. (7-10). The effect upon (11) and (12) is that  $k_1$  and  $k_{12}$  vanish.

There is a further element of arbitrariness in our insistence on right-handed co-ordinates, unless the molecules are enantiomorphic, or enantiomorphically

arranged. Empirically, it appears that enantiomorphy does not occur in liquid crystals unless the molecules are themselves distinguishable from their mirror images, and that it also vanishes in racemic mixtures. In the absence of enantiomorphy, a permissible transformation is  $x' = x$ ,  $y' = -y$ ,  $z' = z$ , giving

$$\left. \begin{aligned} L_{x'} &= a_1x' - a_2y' + a_3z' + 0(r^2), \\ L_{y'} &= -a_4x' + a_5y' - a_6z' + 0(r^2), \end{aligned} \right\} \quad (16)$$

whence, by the same argument as before (omitting the redundant information),

$$k_2 = 0 \text{ and } k_{12} = 0. \quad (17)$$

Hence, while (15) with (11) and (12) expresses the most general dependence of free energy density on curvature in molecularly uniaxial liquid crystals,  $k_1$  vanishes in the absence of polarity,  $k_2$  vanishes in the absence of enantiomorphy, and  $k_{12}$  vanishes unless both polarity and enantiomorphy occur together.

The general expression for energy density in terms of the notation of eqn. (1) is

$$g = k_1(s_1 + s_2) + k_2(t_1 + t_2) + \frac{1}{2}k_{11}(s_1 + s_2)^2 + \frac{1}{2}k_{22}(t_1 + t_2)^2 + \frac{1}{2}k_{33}(b_1^2 + b_2^2) + k_{12}(s_1 + s_2)(t_1 + t_2) - (k_{22} + k_{24})(s_1s_2 + t_1t_2). \quad (18)$$

By introducing

$$s_0 = -k_1/k_{11}, \quad t_0 = -k_2/k_{22}, \quad (19)$$

and

$$g' = g + \frac{1}{2}k_{11}s_0^2 + \frac{1}{2}k_{22}t_0^2, \quad (20)$$

i.e. by adopting a new and (in the general case) lower zero for the free-energy density, corresponding not to the state of uniform orientation but to that with the optimum degree of splay and twist, we obtain the more compact expression

$$g' = \frac{1}{2}k_{11}(s_1 + s_2 - s_0)^2 + \frac{1}{2}k_{22}(t_1 + t_2 - t_0)^2 + \frac{1}{2}k_{33}(b_1^2 + b_2^2) + k_{12}(s_1 + s_2)(t_1 + t_2) - (k_{22} + k_{24})(s_1s_2 + t_1t_2). \quad (21)$$

An alternative form of this expression is given as eqn. (25) below.

## 2.2 COMPARISON WITH OSEEN'S THEORY

According to Oseen, the energy is expressed by

$$\begin{aligned} & \frac{1}{2m^2} \iint \rho_1 \rho_2 Q(\xi_1, \xi_2) d\tau_1 d\tau_2 \\ & + \frac{1}{2m^2} \int \rho_2 \{ K_1 \mathbf{L} \cdot \nabla \times \mathbf{L} + K_{11} (\mathbf{L} \cdot \nabla \times \mathbf{L})^2 + K_{22} (\nabla \cdot \mathbf{L})^2 \\ & \quad + K_{33} (\mathbf{L} \cdot \nabla) \mathbf{L}^2 + 2K_{12} (\nabla \cdot \mathbf{L})(\mathbf{L} \cdot \nabla \times \mathbf{L}) \} d\tau. \end{aligned} \quad (22)$$

We are not concerned with the first integral, which is not related to the dependence of energy on curvature (and which plays only a minor role in Oseen's theory). It is the integrand of the second integral which should be compared with our free-energy density  $g$ . Noting that

$$\begin{aligned} \mathbf{L} \cdot \nabla \times \mathbf{L} &= \partial L_y / \partial x - \partial L_x / \partial y = -(t_1 + t_2), \\ \nabla \cdot \mathbf{L} &= \partial L_x / \partial x + \partial L_y / \partial y = (s_1 + s_2), \\ ((\mathbf{L} \cdot \nabla) \mathbf{L})^2 &= (\partial L_x / \partial z)^2 + (\partial L_y / \partial z)^2 = (b_1^2 + b_2^2), \end{aligned} \quad (23)$$

we see that with

$$\begin{aligned} -(\rho^2/2m^2)K_1 &= k_2, \quad (\rho^2/m^2)K_{11} = k_{22}, \quad (\rho^2/m^2)K_{22} = k_{11}, \\ -(\rho^2/m^2)K_{12} &= k_{12}, \quad (\rho^2/m^2)K_{33} = k_{33}, \end{aligned} \quad (24)$$

Oseen's expression is equivalent to (18), except that the latter contains the additional terms,

$$k_1(s_1 + s_2) - (k_{22} + k_{24})(s_1s_2 + t_1t_2).$$

This accords with the anticipation that Oseen was in danger of missing terms by adopting a Cauchy-like approach to the problem.

The first omission is not very important, since it is virtually certain that there is no physical polarity along the direction  $\mathbf{L}$  in any of the normal liquid crystal substances which were discussed by Oseen; and  $k_1$  is then zero. The second omission is of more general significance: but  $(s_1 s_2 + t_1 t_2)$  relates to an essentially three-dimensional kind of curvature. It occurs in pure form (with  $(s_1 + s_2)$  and  $(t_1 + t_2)$  equal to zero) in what we may call "saddle-splay", when the preferred directions  $\mathbf{L}$  are normal to a saddle-surface; and then contributes a positive term to the energy if  $(k_{22} + k_{24})$  is positive. It is zero if  $\mathbf{L}$  is either constant in a plane or parallel to a plane. It may be disregarded in all the simpler configurations which would be employed for the determination of moduli other than  $k_{24}$ , provided only that  $(k_{22} + k_{24})$  is non-negative.

The most gratifying result of the comparison is to notice that there is one term in Oseen's expression which can be omitted, namely the last, since  $K_{12}$  is always zero under the conditions which justify omitting the term  $k_1(s_1 + s_2)$ . For many purposes we actually have a simpler result than Oseen's. In detailed application, he in fact assumed  $K_{12} = 0$ , supposing this to be an approximation.

We may conveniently use relations (23) to cast eqn. (21) into co-ordinate-free notation:

$$g' = \frac{1}{2}k_{11}(\nabla \cdot \mathbf{L} - s_0)^2 + \frac{1}{2}k_{22}(\mathbf{L} \cdot \nabla \times \mathbf{L} + t_0)^2 + \frac{1}{2}k_{33}((\mathbf{L} \cdot \nabla)\mathbf{L})^2 \\ - k_{12}(\nabla \cdot \mathbf{L})(\mathbf{L} \cdot \nabla \times \mathbf{L}) - \frac{1}{2}(k_{22} + k_{24})((\nabla \cdot \mathbf{L})^2 \\ + (\nabla \times \mathbf{L})^2 - \nabla \mathbf{L} : \nabla \mathbf{L}), \quad (25)$$

where

$$\nabla \mathbf{L} : \Delta \mathbf{L} = \left(\frac{\partial L_x}{\partial x}\right)^2 + \left(\frac{\partial L_y}{\partial y}\right)^2 + \left(\frac{\partial L_z}{\partial z}\right)^2 + \left(\frac{\partial L_y}{\partial x}\right)^2 + \left(\frac{\partial L_x}{\partial y}\right)^2 + \left(\frac{\partial L_z}{\partial x}\right)^2 \\ + \left(\frac{\partial L_z}{\partial y}\right)^2 + \left(\frac{\partial L_x}{\partial z}\right)^2 + \left(\frac{\partial L_y}{\partial z}\right)^2,$$

$$\text{or} \quad (\nabla \cdot \mathbf{L})^2 + (\nabla \times \mathbf{L})^2 - (\nabla \mathbf{L} : \Delta \mathbf{L}) \\ = 2 \left\{ \frac{\partial L_x}{\partial x} \frac{\partial L_y}{\partial y} + \frac{\partial L_y}{\partial y} \frac{\partial L_z}{\partial z} + \frac{\partial L_z}{\partial z} \frac{\partial L_x}{\partial x} - \frac{\partial L_y}{\partial x} \frac{\partial L_x}{\partial y} - \frac{\partial L_z}{\partial y} \frac{\partial L_y}{\partial z} - \frac{\partial L_z}{\partial z} \frac{\partial L_x}{\partial x} \right\},$$

in a fully arbitrary system of co-ordinates.

### 3. PARTICULAR CASES

#### 3.1. THE SMECTIC STATE

According to Oseen, the smectic state corresponds to the vanishing of all the moduli except  $k_{22}$  and  $k_{33}$  (our notation). The (free) energy is then minimized when

$$\mathbf{L} \cdot \nabla \times \mathbf{L} = 0, (\mathbf{L} \cdot \nabla)\mathbf{L} = 0. \quad (26)$$

The second of these equations states that a line following the preferred direction of molecular axes is straight: the first, that the family of such straight lines is normal to a family of parallel surfaces (defining the surface parallel to a given curved surface as the envelope of spheres of uniform radius centred at all points on the given surface). Hence he formally predicts the geometry explicable by molecular layering without apparently appealing to the existence of layers: their real existence he explains separately by use of his  $Q$  integral. The present writer considers this a perverse approach. We need to explain why  $k_{22}$  and  $k_{33}$  are so large that the other moduli are negligible, and can do so from the existence of the layering. There is no real need to employ the theory of curvature strains

to interpret smectic structures, until one requires to deal with small departures from the geometrically interpretable structures, which will be permitted if the other moduli are merely small, instead of vanishing, compared with  $k_{22}$  and  $k_{33}$ .

Before leaving the subject of the smectic state, we may remark that to explain deformations in which the area of individual molecular layers does not remain constant, it is necessary to invoke dislocations of these layers. It is likely that these dislocations are usually combined with the focal conic singularity lines, being then essentially screw dislocations.

### 3.2. THE NEMATIC STATE

The nematic state is characterized by  $s_0 = 0$ ,  $t_0 = 0$ ,  $k_{12} = 0$ , corresponding to the absence both of polarity and enantiomorphy. There are four non-vanishing moduli,  $k_{11}$ ,  $k_{22}$ ,  $k_{33}$  and  $k_{24}$ . The last has no effect in "planar" structures. Hence Zocher's<sup>3</sup> three-constant theory is justified (his  $k_1$ ,  $k_2$ ,  $k_t$  are the same as  $k_{11}$ ,  $k_{33}$ ,  $k_{22}$ ). Formerly, this appeared to be only an approximate theory, neglecting  $k_{12}$  which appeared in the theory of Oseen. The simplest way to measure the moduli is to impose body torques by imposing magnetic fields.  $k_{22}$  can be determined straightforwardly;  $k_{11}$  and  $k_{33}$  are more difficult to separate from each other. There is evidence that they are about equal. Using the experimental data of Fréederickz and of Foëx and Royer, Zocher shows that if they are equal the value for *p*-azoxyanisole is  $1.0 \times 10^{-6}$  dynes. Information about the relative magnitude of these moduli is obtainable from the detailed geometry of the "disinclination" structures described in § 4. The fact that there is not another unknown in  $k_{12}$  ought to encourage a complete experimental determination of the moduli for some nematic substances.

### 3.3. THE CHOLESTERIC STATE

Enantiomorphy, either in the molecules of the liquid-crystal-forming substance, or in added solutes, converts the nematic into the cholesteric state.  $k_2 \neq 0$ , and the state of lowest free energy has a finite twist,  $t_0 = k_2/k_{22}$ . In the absence of other curvature components, there is only one structure of uniform twist, in which **L** is uniform in each of a family of parallel planes, and twists uniformly about the normal to these planes. The torsion has a full pitch of  $2\pi/t_0$ : but since **L** and  $-\mathbf{L}$  are physically indistinguishable, the physical period of repetition is  $\pi/t_0$ . When, as is usually the case, this is of the order of magnitude of a wavelength of light or greater, it can be measured with precision by optical methods. Some additional information should be obtainable by perturbing this structure with a magnetic field. Uniform twist can also exist throughout a volume when the repetition surfaces are not planes, but curved surfaces: for example, spheres, though in this case there has to be at least one singular radius on which the uniformity breaks down. Since the cholesteric substances, like the smectic substances (though for entirely different reasons) give rise to structures containing families of equidistant curved surfaces, their structures show considerable geometric similarity to those of the smectic substances. This was appreciated by Friedel, who also realized that it was misleading, and that the cholesteric phases are in reality thermodynamically equivalent to nematic phases.

### 3.4. THE CASE $k_1 \neq 0$

If  $k_1 \neq 0$ , the state of lowest free-energy density has a finite splay,  $s_0 = k_1/k_{11}$ . This can only exist when the molecules are distinguishable end from end, and there is polarity along **L** in their preferred orientation. Then, almost inevitably, the molecules have an electric dipole moment, and therefore, unless the material is an electric conductor, the condition  $\nabla \cdot \mathbf{L} \neq 0$  implies  $\nabla \cdot \mathbf{P} \neq 0$  (where **P** is the electric polarization), so that finite splay produces a space-charge. As a second consideration, it is not geometrically possible to have uniform splay in a three-dimensionally extended region. The simple cases of uniform splay are those in



which  $\mathbf{L}$  is radial in a thin spherical shell of radius  $2/s_0$ , or a thin cylindrical shell of radius  $1/s_0$ . These considerations relate this hypothetical polar class of liquid crystals to the substances which produce "myelin figures": but since the only allowed structures for this class have a high surface-to-volume ratio, a theory of their configurations which does not pay explicit attention to interfacial tensions will be seriously incomplete.

#### 4. "DISINCLINATIONS"

The nematic state is named for the apparent threads seen within the fluid under the microscope. Their nature was appreciated by Lehmann and by Friedel. In thin films they may be seen end on, crossing the specimen from slide to cover-slip, and their nature deduced from observation in polarized light. In this position they were named *Kerne* and *Konvergenzpunkte* by Lehmann, positive and negative nuclei (*noyaux*) by Friedel. They are line singularities such that the cardinal direction of the preferred axis changes by a multiple of  $\pi$  on a circuit taken round one of the lines. They thus provide examples of the configurations excluded (under the name of "Möbius crystals") from consideration in the establishment of a general definition of crystal dislocations.<sup>4</sup> In analogy with dislocations, they might be named "disinclinations". It is the motion of these disinclination lines which provides one of the mechanisms for change of configuration of a nematic specimen under an orienting influence, in the same way as motion of a domain boundary performs this function for a ferromagnetic substance. It is the lack of a crystal lattice which allows the discontinuities of orientation to have a line topology, instead of a topology of surfaces dividing the material into domains, in the present case. Disinclination lines occur in cholesteric as well as in nematic liquid crystals.

The actual configuration around disinclination lines was calculated by Oseen for the case  $k_{11} = k_{33}$ ,  $k_{12} = 0$ , the latter assumption actually being exact. Then if  $\mathbf{L}$  is parallel to a plane and  $\phi$  is the azimuth of  $\mathbf{L}$  in this plane, in which  $x_1, x_2$  are Cartesian co-ordinates, the free energy is minimized in the absence of body torques when

$$\partial^2 \phi / \partial x^2 + \partial^2 \phi / \partial y^2 = 0. \quad (27)$$

The solutions of this equation representing disinclinations are

$$\phi = \frac{1}{2} n \psi + \phi_0, \tan \psi = x_2/x_1, \quad (28)$$

$n$  being an integer. These configurations are sketched in fig. 2. Changing  $\phi_0$ , merely rotates the figure in all cases except  $n = +2$ , for which three examples are shown. Of these, the first or the third will be stable, for a nematic substance according as  $k_{33}$  or  $k_{11}$  is the larger. In the other cases, non-equality of  $k_{11}$  and  $k_{33}$  should not make drastic changes, but only changes of curvature in patterns of the same topology. Thus, for  $n = -2$  or  $-1$ , if  $k_{33}$  is larger than  $k_{11}$  the bends will be sharpened, and conversely. This would be observed as a non-uniform rotation of the extinction arms with uniform rotation of polarizer and analyzer. The ratio of  $k_{11}$  and  $k_{33}$  can thus be determined from a simple optical experiment.

In cholesteric substances  $\phi_0$  is not constant, but a linear function of the co-ordinate  $x_3$ , normal to the  $x_1, x_2$  plane: except for the case  $n = 2$ , with  $k_{11} \neq k_{33}$ , which should show a periodic departure from linearity near the core, from which the relative magnitudes of  $k_{22}$  and  $(k_{11} - k_{33})$  could be deduced, though the observations would not be simple.

Oseen was puzzled at the non-occurrence of configurations corresponding to

$$\phi = c \ln r + \text{const.}, \quad r = (x_1^2 + x_2^2)^{\frac{1}{2}}. \quad (29)$$

The reason is obvious: unlike  $n$  in (28),  $c$  is not restricted to integral values, and can relax continuously to zero. Alternatively stated, this configuration requires an impressed torque at the core for its maintenance.



At the time Friedel and Oseen wrote their papers, the values of the disinclination strength  $n$  which had been observed were  $-2, -1, 1, 2$ . Since then the case  $n = 4$  has been observed by Robinson<sup>5</sup> in the radial singularity of a cholesteric "spherulite". The non-occurrence of high values of  $|n|$  is explained by the fact that the energy is proportional to  $n^2$ . The fact that higher values than one occur indicates a relatively high energy in the disorderly core of the disinclination line, which must be as large as its field energy so that it becomes profitable for a pair of disinclinations to share the same core.

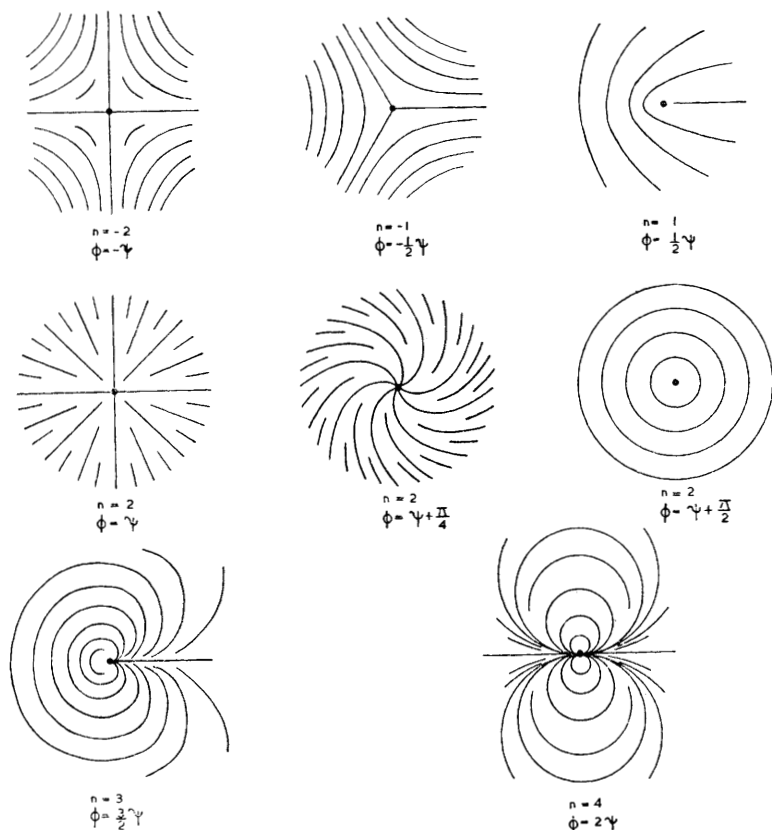


FIG. 2.

5.  $k_{24}$ 

Let us leave aside the question of how to determine  $k_{24}$ , necessarily involving the observation of three-dimensional curvatures, until we have better information about the moduli of plane curvature,  $k_{11}$ ,  $k_{22}$  and  $k_{33}$ .

## 6. RELATIONSHIP TO THE ORDINARY ELASTIC CONSTANTS

Let us take note that the molecular interactions giving rise to liquid crystal properties must also be present in solids. This indicates that conventional elastic theory is incomplete: the direct curvature-strain moduli should also be included. This is true, but does not seriously invalidate the accepted theory of elasticity. Consider the bending of a beam, of thickness  $2a$ , to a radius  $R$ . Then the stored free energy according to ordinary elasticity theory is  $g_E = Ea^2/24R^2$ , where  $E$

is Young's modulus. The stored free energy arising from a curvature modulus  $k$  (corresponding to  $k_{11}$  or  $k_{33}$  according to the molecular orientation in the beam) would be  $g_k = k/2R^2$ . Their ratio is

$$g_k/g_E = 12k/Ea^2.$$

Taking  $k$  as  $10^{-6}$  dyne, and  $E$  as  $10^{10}$  dyne/cm<sup>2</sup>, this ratio is unity when  $a$  is about  $3.5 \times 10^{-8}$  cm, and negligible for beams of thickness as large as a micron. Thus, on the visible scale, the curvature-elastic constants are always negligible compared with the ordinary elastic constants, unless the latter are zero.

<sup>1</sup> Oseen, *Trans. Faraday Soc.*, 1933, **29**, 883.

<sup>2</sup> Friedel, *Annales Physique*, 1922, **18**, 273.

<sup>3</sup> Zocher, *Trans. Faraday Soc.*, 1933, **29**, 945.

<sup>4</sup> Frank, *Phil. Mag.*, 1951, **42**, 809.

<sup>5</sup> Robinson, this Discussion.