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Theory of piezoelectricity in nematic liquid crystals, and of the cholesteric ordering

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A statistical-mechanical theory of the elastic constants of a liquid crystal based on the Onsager expansion is reexamined, with emphasis on the terms linear in the gradients of the director. This gives a microscopic theory of the piezoelectric effect in nematic liquid crystals, and of the spontaneous twisting of a cholesteric. Model cases of tapered rods, bent rods, and threaded rods are considered.

I. INTRODUCTION

Nematic liquid crystals have uniaxial symmetry: there is locally a single preferred axis, whose orientation is conventionally represented by a vector $\hat{n}$ (the "director"). Since these materials actually have quadrupole (rather than dipolar) ordering, the directions $\hat{n}$ and $-\hat{n}$ are not physically distinguishable. This implies that the probability that a given molecule has a chosen orientation is a function of the direction cosines $\{\hat{n}\cdot\hat{m}_i\}$ of the director relative to some body-fixed axes $\{\hat{m}_i\}$ of the molecule, but is invariant under rotations of the molecule about the director and is even in $\hat{n}$.

The molecules themselves are much less symmetric. The molecules forming a cholesteric liquid crystal need have no symmetry at all, and nematogens are expected only to have chiral symmetry (i.e., to be nonenantiomorphic[1]). The relatively low symmetry of the molecules comprising a liquid crystal does manifest itself in certain ways. Meyer[2] first noted that bent or tapered molecules can exhibit a piezoelectric effect under the conditions of orientational strain. This suggestion has received subsequent discussion by Helfrich[3] and Gruler.[4] A microscopic statistical-mechanical theory of this effect will be given here.

This paper will also give a microscopic theory of cholesteric liquid crystals. In the usual elastic theory of cholesterics, the pitch length appears as a ratio of two elastic constants, one of which is Frank's twist constant K_{22}, and the other of which is the coefficient in the free-energy density of terms linear in the gradients of the director.[5] This latter coefficient will be calculated here. The method may be regarded as an extension of Goossens's calculation[6] in which it is no longer necessary to assign molecules to planes.

The common feature of these two problems (piezoelectricity and cholesteric ordering) is that both involve the linear order response to gradients in the director field.

The published discussion of these aspects of liquid crystals have been somewhat qualitative: the relationships between molecular asymmetry and orientational order have been sought without reference to the microscopic theories which have been used to discuss the liquid-crystalline ordering.[7-12] This paper will extend the Onsager[7] theory to a calculation of the piezoelectric coefficients of a model nematic, and of the pitch of a cholesteric liquid crystal.

The extended theory is already in existence; it has been used previously[13,14] to calculate the Frank elastic constants for nematic liquid crystals; however, in these previous discussions the piezoelectric terms were ignored. A more careful rederivation of that theory will be given here (Sec. II). The theory will then be applied to some simple model systems, namely tapered rods (Sec. III), bent rods (Sec. IV), and enantiomorphic particles (Sec. V).

II. THEORY OF THE DISTRIBUTION FUNCTION

Consider a rigid molecule of arbitrary shape, and let its orientation be specified by the quantity $\vec{\omega}$, which may be represented as a triplet of Euler angles, or as the collection of direction cosines of a body-fixed axis system with respect to a laboratory frame. Following Onsager[7] we shall define an orientational distribution $f(\vec{\omega})$ which gives the relative probability that a molecule has orientation in the differential element $d\vec{\omega}$ near $\vec{\omega}$: if $dN(\vec{\omega})$ is the number of such particles in a volume dV, then

$$dN(\vec{\omega}) = \rho f(\vec{\omega})\, d\vec{\omega}\, dV. \tag{1}$$

Since all particles have some orientation, this distribution function is normalized

$$\int f(\vec{\omega})\, d\vec{\omega} = 1, \tag{2}$$

where the integral ranges over all orientations. In a distorted liquid crystal or in a cholesteric, $f(\vec{\omega})$ is also a function of position; for simplicity (and without great loss of generality) we will assume that the density remains uniform in these cases, so that Eq. (2) holds at each point in space.

The interparticle potential $V(\vec{\omega}, \vec{\tau}; \vec{r} - \vec{s})$, which describes the interaction of a particle at $\vec{r}$ of orientation $\vec{\omega}$ with a particle at $\vec{s}$ of orientation $\vec{\tau}$, is a general function of its arguments, except that it is invariant under arbitrary simultaneous rotations of $\vec{\omega}$, $\vec{\tau}$, and $\vec{r} - \vec{s}$. We will also define the function $U(\vec{\omega}, \vec{\tau}, \vec{r} - \vec{s}) = e^{-V/kT} - 1$, which vanishes for large $|\vec{r} - \vec{s}|$ and takes on the value -1 for configurations in which V is strongly repulsive (i.e., overlapping molecules). As Onsager has shown, the Meyer cluster expansion can be used to express the Helmholtz free energy in terms of $f(\vec{\omega}, \vec{r})$ and U as

$$\frac{F}{kT} = N \ln\rho + \rho \int f(\vec{\omega}, \vec{r}) \ln f(\vec{\omega}, \vec{r}) d\vec{\omega}\, d\vec{r} - \tfrac{1}{2}\rho^2 \int f(\vec{\omega}, \vec{r}) U(\vec{\omega}, \vec{\tau}, \vec{r} - \vec{s}) \times f(\vec{\tau}, \vec{s}) d\vec{\omega}\, d\vec{\tau}\, d\vec{r}\, d\vec{s}. \tag{3}$$

This expression is actually just the first few terms of an infinite series; truncating the series in this way gives a form of mean-field theory similar to the Maier-Saupe theory.[8]

The first two terms of Eq. (3) are local: the integrands involve the distribution function for a single point only. It is the last term which couples the distributions at neighboring points, and the dependence of the Helmholtz free energy on the spatial variation of the ordering will be found by expanding this term in the gradients of f. Writing $\vec{\xi} = \vec{r} - \vec{s}$, and substituting the Taylor expansion of $f(\vec{s} + \vec{\xi})$ into Eq. (3), there results $F = \int \mathfrak{F}(\vec{s}) d(\vec{s})$, where the free-energy density $\mathfrak{F}$ is given by[14]

$$\frac{\mathfrak{F}(\vec{s})}{kT} = \rho \ln\rho + \rho \int f(\vec{\omega}) \ln f(\vec{\omega})\, d\vec{\omega} + \tfrac{1}{2}\rho^2 \int f(\vec{\omega}) B(\vec{\omega}, \vec{\tau}) f(\vec{\tau}) d\vec{\omega}\, d\vec{\tau} + \tfrac{1}{2}\rho^2 \int f(\vec{\omega}) \vec{C}(\vec{\omega}, \vec{\tau}) \cdot \vec{\nabla}_s f(\vec{\tau}) d\vec{\omega}\, d\vec{\tau} - \tfrac{1}{2}\rho^2 \int \vec{\nabla}_s f(\vec{\omega}) \cdot \vec{\vec{D}}(\vec{\omega}, \vec{\tau}) \cdot \vec{\nabla}_s f(\vec{\tau}) d\vec{\omega}\, d\vec{\tau} + \cdots . \tag{4}$$

In this equation,

$$B(\vec{\omega}, \vec{\tau}) = -\int U(\vec{\omega}, \vec{\tau}, \vec{\xi})\, d\vec{\xi} \tag{5}$$

is the second virial coefficient defined and discussed by Onsager[7] and others[12]; the first-moment vector is

$$\vec{C}(\vec{\omega}, \vec{\tau}) = -\int \vec{\xi} U(\vec{\omega}, \vec{\tau}, \vec{\xi})\, d\vec{\xi}\,; \tag{6}$$

and the second-moment tensor

$$D_{ij} = -\int \xi_i \xi_j U(\vec{\omega}, \vec{\tau}, \vec{\xi})\, d\vec{\xi} \tag{7}$$

has previously appeared in discussions of the Frank elastic constants.[13,14] All terms in Eq. (4) are local; the integrands depend only on $\vec{s}$. The following symmetries should be noted: under exchange of labels $U(\vec{\omega}, \vec{\tau}, \vec{\xi}) = U(\vec{\tau}, \vec{\omega}, -\vec{\xi})$; consequently $B(\vec{\omega}, \vec{\tau}) = B(\vec{\tau}, \vec{\omega})$, $C(\vec{\omega}, \vec{\tau}) = -C(\vec{\tau}, \vec{\omega})$, and $D_{ij}(\vec{\omega}, \vec{\tau}) = D_{ij}(\vec{\tau}, \vec{\omega})$.

The expansion in Eq. (4) has been carried through terms quadratic in the gradients of $f(\omega, s)$, and it is desired to evaluate the free energy to this accuracy. We must first determine the local distribution of orientations which minimizes the free energy (4). The first three terms are the Onsager equation of state appropriate to a liquid of asymmetric particles; their sum is minimized by a uniaxial distribution function $f_0(\vec{\omega}, \vec{s})$ whose axis defines the director $\hat{n}(\vec{s})$. This function is appropriate to the undistorted liquid crystal; it has been studied for particles having C_{3m} symmetry,[15] and electrostatic quadrupolar coupling,[16] and a rank-2 spherical harmonic model.[17]

Distortion of the liquid crystal alters the equilibrium orientational distribution function through the later terms of Eq. (4); this causes the second and third terms to change to the same order. However, it proves not to be too difficult to take these effects into account. We may certainly assume that the distortions will take place over distances which are very large compared to the molecular scale; then the last two terms of Eq. (4) are small [the integrals of Eqs. (6) and (7) range over molecular dimensions]. Now let us write $f(\vec{\omega}, \vec{s}) = f_0(\vec{\omega}, \vec{s}) + g(\vec{\omega}, \vec{s}) f_0(\vec{\omega}, \vec{s})$, where we hope that g is small. This representation is motivated by the idea that the principal effect of orientational stress will be to cause the director to vary spatially, but that at each point in space the distribution function f will have the same uniaxial form with only the axis varying. The term in g represents the stress-induced changes in the distribution function.

Because f_0 minimizes the sum of the first three terms of Eq. (4), that sum will be stationary with respect to small changes in f: the corrections of order g to the second and third terms cancel, and only corrections of order g^2 actually arise. Therefore in order to calculate the free energy to second order in the gradients of the director it is sufficient to calculate the orientational distribution function to linear order only. Calculation of g to this order proceeds as follows. A Lagrange multiplier term $(\lambda_0 + \lambda_1) f(\vec{\omega}, \vec{s}) d\vec{\omega}$ is added to Eq. (4) (to ensure normalization), and a variational derivative is taken with respect to f to find the Onsager equation

$$-\ln f(\vec{\omega}) = \lambda_0 + \lambda_1 + \rho \int B(\vec{\omega}, \vec{\tau}) f(\vec{\tau})\, d\vec{\tau} + \rho^2 \int \vec{C}(\vec{\omega}, \vec{\tau}) \cdot \nabla_s f(\vec{\tau})\, d\vec{\tau}, \qquad (8)$$

where the term involving $\vec{D}$ has been dropped because it is quadratic in $\vec{\nabla}_s f$. Substitution of $f = f_0(1+g)$ gives

$$\left[-\ln f_0(\vec{\omega})\right] - g(\vec{\omega}) = \left[\lambda_0\right] + \lambda_1 + \left[\rho \int B(\vec{\omega}, \vec{\tau}) f_0(\vec{\tau})\, d\vec{\tau}\right] + \rho \int B(\vec{\omega}, \vec{\tau}) g(\vec{\tau}) f_0(\vec{\tau})\, d\vec{\tau} + \rho \int \vec{C}(\vec{\omega}, \vec{\tau}) \cdot \vec{\nabla}_s f_0(\vec{\tau})\, d\vec{\tau}, \qquad (9)$$

where terms of order higher than linear in the gradients of f have been deleted; the bracketed terms are the Onsager equation for f_0, which cancel. The remaining terms give an inhomogeneous linear integral equation for $g(\vec{\omega})$. Because both f and f_0 are normalized, g is orthogonal to $f_0[\int f_0(\vec{\omega}, \vec{s}) g(\vec{\omega}, \vec{s})\, d\vec{\omega} = 0]$. The parameter λ_1 in Eq. (9) is to be chosen so that this relationship holds.

The strain of the liquid crystal enters Eq. (9) only through the term $\vec{\nabla}_s f_0(\hat{m}, \vec{s})$, but f_0 depends on position only through the spatial dependence of $\hat{n}(\vec{s})$ itself: f_0 is the equilibrium distribution function with axis along $\hat{n}$. Thus Eq. (9) will eventually be written in terms of the gradients of the director. It is appropriate to note at this point that it is always possible to choose a coordinate system such that at any given point $\vec{r}$ in space, $\hat{n}(\vec{r}) = \hat{x}$ and

$$\vec{\nabla}_r(\hat{n}(\vec{r}) \cdot \hat{m}) = (b\hat{x} + s\hat{y} + t\hat{z})(m \cdot \hat{y}), \qquad (10)$$

where b, s, and t are, respectively, the amplitudes of bend, splay, and twist. Equation (9) thus relates these strains to g, which is the microscopic response to the strain. In particular, if the molecules carry a dipole moment, then the degree of alignment of these dipole moments is described by a moment of g. Thus we are finally led to a theory of the piezoelectric effect.

In order to see clearly the effects of distortion on the free-energy density of the liquid, let us also substitute $f = f_0(1+g)$ into Eq. (4), eliminating terms where possible through substitution of (9). There results

$$\mathcal{F}(\vec{s}) = \mathcal{F}_0 + \mathcal{F}_1(\vec{s}) + \mathcal{F}_2(\vec{s}). \qquad (11)$$

Here

$$\frac{\mathcal{F}_0}{kT} = \rho \ln\rho + \rho \int f_0(\vec{\omega}) \ln f_0(\vec{\omega})\, d\vec{\omega} + \tfrac{1}{2}\rho^2 \int\!\!\int f_0(\vec{\omega}) B(\vec{\omega}, \vec{\tau}) f_0(\vec{\tau})\, d\vec{\omega}\, d\vec{\tau}, \qquad (12)$$

which is the free-energy density of the unstrained nematic;

$$\mathcal{F}_1(\vec{s}) = \tfrac{1}{2}\rho^2 kT \int f_0(\omega) \vec{C}(\vec{\omega}, \vec{\tau}) \cdot \vec{\nabla}_s f_0(\vec{\tau})\, d\vec{\omega}\, d\vec{\tau}, \qquad (13)$$

which is linear in the gradients of f_0; and

$$\mathcal{F}_2(\vec{s}) = -\tfrac{1}{2}\rho^2 kT \int \nabla_i f_0(\vec{\omega}) D_{ij}(\vec{\omega}, \vec{\tau}) \nabla_j f_0(\vec{\tau})\, d\omega\, d\vec{\tau} + \tfrac{1}{2}\rho^2 kT \int f_0(\vec{\omega}) g(\vec{\omega}) \vec{C}(\vec{\omega}, \vec{\tau}) \cdot \vec{\nabla}_s f_0(\vec{\tau})\, d\vec{\omega}\, d\vec{\tau} \qquad (14)$$

which contains the elastic constants.

If $\mathcal{F}_1$ does not vanish, the liquid crystal will spontaneously distort. Thus it is expected to be nonzero only for cholesteric[18] materials (see Sec. V). The first term of $\mathcal{F}_2$ represents the "clamped" elastic constants (no alteration of f allowed) and is a positive term, despite its apparent sign, and the second term is the effect of relaxation of the distribution function and is expected to be negative.

In principle the definitions and equations of this section permit a calculation of the elastic constants for an arbitrary system. Owing to the neglect of the higher-order virial terms, the resulting values cannot be expected to be very accurate; and in any case the interparticle potential is poorly known. The chief value of the theory is to give a better understanding of how the elastic constants arise and depends on the molecular symmetry.

In the ensuing sections some model cases will be considered. Consistent with the understanding of the role of theory outlined here, the models will be chosen more for their tractability than for their accurate description of liquid crystals.

III. TAPERED RODS

Consider a hard rodlike particle of length L, whose diameter tapers smoothly from $D + \Delta$ to $D - \Delta$. The position of one such particle is specified by the position $\vec{r}$ of its midpoint, and the orientation $\hat{m}$ of its symmetry axis. The condition that two such particles be overlapping [so that $U(\vec{r}_1, \vec{r}_2; \hat{m}_1, \hat{m}_2) = -1$] is approximately that $\vec{\xi} = \vec{r}_1 - \vec{r}_2$ can be written as

$$\xi = x\hat{m}_1 - y\hat{m}_2 + z\hat{m}_3, \qquad (15)$$

where $|z| < D + \delta(x+y)$, $|x| < \tfrac{1}{2}L$, $|y| < \tfrac{1}{2}L$, $\delta = \Delta/L$, and $\hat{m}_3 = (\hat{m}_1 \times \hat{m}_2)/|m_1 \times m_2|$ (if $\hat{m}_1$ and $\hat{m}_2$ are not parallel; $\hat{m}_3$ is an arbitrary vector perpendicular to $\hat{m}_1$ otherwise), as illustrated in Fig. 1. This form is not a rigorously accurate representation of the geometry of tapered rods, but corresponds to it in the sense that if one rod is moved parallel to its axis (thus increasing x or y), the distance between their axes at which first contact occurs (the upper limit on z) increases. The integrals for the moments of U are readily done to give

$$B(\hat{m}_1, \hat{m}_2) = 2DL^2 |\hat{m}_1 \times \hat{m}_2|, \tag{16}$$

$$\vec{\mathrm{C}}(\hat{m}_1, \hat{m}_2) = \tfrac{1}{6}\Delta L^2 (\hat{m}_1 - \hat{m}_2) |\hat{m}_1 \times \hat{m}_2|, \tag{17}$$

$$\overleftrightarrow{\mathrm{D}}(\hat{m}_1, \hat{m}_2) = \tfrac{1}{6} DL^4 (\hat{m}_1\hat{m}_1 + \hat{m}_2\hat{m}_2) + (\tfrac{2}{3}D^3L^2 + \tfrac{1}{8}D\Delta^2L^2)\hat{m}_3\hat{m}_3, \tag{18}$$

where $\hat{m}_1\hat{m}_1$ is the tensor product of $\hat{m}_1$ with itself.[19] Study of the expressions for B and D shows that they are not significantly different from what would be obtained for untapered rods (which are the same expressions with $\Delta = 0$). In contrast, $\vec{\mathrm{C}}$ is nonvanishing only in the presence of taper.

Equation (9) determines $g(\hat{m})$:

$$-g(\hat{m}) = \lambda_1 + \rho \int B(\hat{m}, \hat{h}) f_0(\hat{n} \cdot \hat{h}) g(\hat{h})\, d\hat{h} + \rho \int \vec{\mathrm{C}}(\hat{m}, \hat{h}) \cdot \vec{\nabla}_s f_0(\hat{n} \cdot \hat{h})\, d\hat{h}; \tag{19}$$

where $\hat{n}(\vec{\mathrm{s}})$ is the director. However, since $f_0(\hat{n} \cdot \hat{h})$ is even in $\hat{h}$,

$$\int \vec{\mathrm{C}}(\hat{m}, \hat{h}) \cdot \vec{\nabla}_s f_0(\hat{h})\, d\hat{h} = \tfrac{1}{6}\Delta L^2 \hat{m} \cdot \vec{\nabla}_s \int |\hat{m} \times \hat{h}| f_0(\hat{h} \cdot \hat{n})\, d\hat{h}, \tag{20}$$

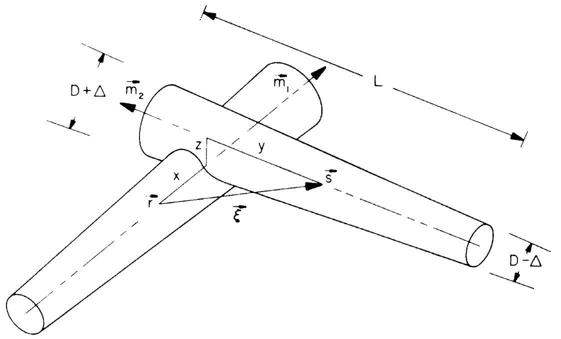

FIG. 1. Geometry of two interacting tapered rods. The separation of the centers of the rods can be expressed as $\vec{\xi} = x\hat{m}_1 - y\hat{m}_2 + z\hat{m}_3$, where z is the distance between the rods' axes. The condition that the two rods intersect can be approximately stated in terms of inequalities which x, y, and z satisfy.

which is explicitly odd in $\hat{m}$ (the other term in $\vec{\mathrm{C}}$ vanishes in the integration). The other two terms on the right-hand side of Eq. (19) are even in $\hat{m}$. We may break $g(\hat{m})$ into two parts, even and odd in $\hat{m}$, and show that they are not coupled in Eq. (19). The equation for g_e (the even part of g) depends only on B, so that $f = f_0(1 + g_e)$ is a solution to the same equation as f_0 itself [the bracketed parts of Eq. (9)]. There indeed are such alternate solutions to the Onsager equation, but they are of no physical interest. Hence we may take $g_e = 0$, and conclude that

$$g(\vec{\mathrm{m}}) = -\tfrac{1}{6}\Delta L^2 \rho (\hat{m} \cdot \vec{\nabla}_s) \times \hat{n}(s) \cdot \int \hat{h} |\hat{m} \times \hat{h}| f_0'(\hat{h} \cdot \hat{n})\, d\hat{h}, \tag{21}$$

where f_0' is the derivative of f_0 with respect to its argument.

Assuming the tapered rods carry a dipole moment along their axis ($\vec{\mathrm{p}} = p\hat{m}$), the stress-induced polarization of the liquid crystal is given by

$$\vec{\mathrm{P}} = \rho p \int f(\hat{m}) \hat{m}\, d\hat{m} = \rho p \int f_0(\hat{m}) g(\hat{m}) \hat{m}\, d\hat{m}. \tag{22}$$

Now substitute (21) and introduce the representation $\hat{n} = \hat{x}$ and $\vec{\nabla}_r(\hat{n}(\vec{\mathrm{r}}) \cdot \hat{m}) = (b\hat{x} + s\hat{y} + t\hat{z})(\hat{m} \cdot \hat{y})$. Several terms can be deleted from the integrand on the basis of symmetry; the survivors can be written

$$\vec{\mathrm{P}} = -\tfrac{1}{6}\Delta L^2 \rho^2 p (s\hat{x} + b\hat{y}) \times \int\int f_0'(h_x) h_y |\hat{m} \times \hat{h}| m_x m_y f_0(m_x)\, d\hat{m}\, d\hat{h}. \tag{23}$$

The double integral now involves only the equilibrium distribution function; it is a number of order unity which is approximately equal to $-\frac{1}{2}S$, where S is the usual order parameter. The interesting consequence of this result is that the coefficients of s and b (i.e., the piezoelectric coefficients e_{1z} and e_3) are the same. This has not been anticipated in the qualitative discussions of tapered rods but is not in conflict with them. Finally we note that in the Onsager theory $DL^2\rho \sim 5$ near the phase transition, and write (now *very* approximately) $e \sim \rho p \Delta / 60D$.

Symmetry arguments also imply that $\mathfrak{F}_1$ vanishes identically: then strains enter only quadratically into the free-energy density, so that the unstrained liquid crystal is the equilibrium configuration.[20]

IV. BENT RODS

Bent rods are intrinsically biaxial: it is not sufficient to specify the orientation of just one principal axis. Figure 2 shows a model bent rod, and suggests that its position and orientation can

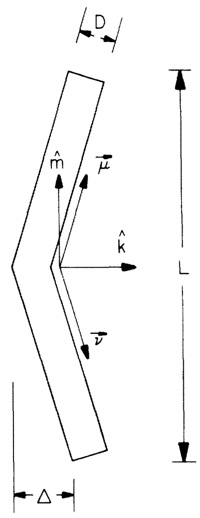

FIG. 2. Geometry of a bent rod.

be specified by three vectors $\vec{r}$, $\hat{m}$, and $\hat{k}$, where $\vec{r}$ specifies the position of the center of mass, $\hat{m}$ is the principal axis with smallest moment of inertia, and $\hat{k}$ is the twofold symmetry axis of the object. To the extent that Δ (which measures the amount of bend) is small compared with $\sqrt{LD}$, the second virial coefficient and the second-moment tensor are little different from those for a long rod (although there is a biaxiality effect as discussed elsewhere[15]). The first-moment vector is more interesting. In the usual approximation where the segments of the bent rod are taken to be long and thin and end corrections are neglected, $\vec{C}$ can be written in terms of $\vec{\mu}=\hat{m}+(2\Delta/L)\hat{k}$ and $\vec{\nu}=-\hat{m}+(2\Delta/L)\hat{k}$ as

$$\vec{C}(\hat{m}_1,\hat{k}_1;\hat{m}_2,\hat{k}_2)$$
$$=\tfrac{1}{16}DL^4(\hat{m}_1-\hat{m}_2)\{|\vec{\mu}_1\times\vec{\mu}_2|-|\vec{\nu}_1\times\vec{\nu}_2|\}$$
$$+\tfrac{1}{16}DL^4(\hat{m}_1+\hat{m}_2)\{|\vec{\mu}_1\times\vec{\nu}_2|-|\vec{\nu}_1\times\vec{\mu}_2|\}. \quad (24)$$

This form is symmetric under reversal of $\hat{m}_1$ or $\hat{m}_2$, antisymmetric under simultaneous reversal of $\hat{k}_1$ and $\hat{k}_2$, and antisymmetric under interchange of $(\hat{m}_1,\hat{k}_1)$ and $(\hat{m}_2,\hat{k}_2)$; these symmetries are implicit in the symmetry of the particles under consideration. By a similar argument to that preceding Eq. (21), $g(\hat{m},\hat{k})$ is given by

$$-g(\hat{m}_1,\hat{k}_1)$$
$$=\rho\int\vec{C}(\hat{m}_1,\hat{k}_1;\hat{m}_2,\hat{k}_2)\cdot\vec{\nabla}_s f_0(\hat{m}_2,\hat{k}_2)\,d(\hat{m}_2,\hat{k}_2) \quad (25)$$

(where the integration is over all orientations of $\hat{m}_2$ and $\hat{k}_2$ such that $\hat{k}_2$ is perpendicular to $\hat{m}_2$), because it is odd in $\hat{k}_1$ and the other terms in Eq. (9) are even; and likewise $\mathfrak{F}_1(\vec{s})$ vanishes.

We may again calculate the strain-induced polarization from (25). In the present case it is appropriate to assume the dipole moment points along $\hat{k}$ ($\vec{p}=p\hat{k}$), so that

$$\vec{P}=\rho p\int\hat{k}g(\hat{m},\hat{k})f_0(\hat{m},\hat{k})\,d(\hat{m},\hat{k}). \quad (26)$$

Upon substitution of (25) and (24) and deleting terms excluded by considerations of symmetry, there results

$$\vec{P}=\tfrac{1}{2}\rho^2 pDL^4\int f_0(\hat{m}_1,\hat{k}_1)\hat{k}_1\{|\vec{\mu}_1\times\vec{\mu}_2|-|\vec{\nu}_1\times\vec{\nu}_2|\}\hat{m}_1\cdot\nabla_s f_0(\hat{m}_2,\hat{k}_2)d(\hat{m}_1,\hat{k}_1)d(\hat{m}_2,\hat{k}_2). \quad (27)$$

This result may be further simplified if we neglect the weak biaxial ordering[15] (which leads to a $\hat{k}$ dependence of f_0) and put $f_0=f_0(\hat{m}\cdot\hat{n})$. Then

$$\vec{P}=\tfrac{1}{8}\rho^2 pDL^4\int f_0(m_{1x})\{|\vec{\mu}_1\times\vec{\mu}_2|-|\vec{\nu}_1\times\vec{\nu}_2|\}(k_{1x}m_{1y}s\hat{x}+k_{1y}m_{1x}b\hat{y})m_{2y}f_0'(m_{2x})\,d\hat{m}_1\,d\hat{m}_2\,. \quad (28)$$

The terms involving bend and splay are not equivalent, and in fact the term in splay is small.

V. CHOLESTERIC LIQUID CRYSTALS

In the arguments of the previous sections, the reflection symmetry properties of $\vec{C}$ played an important role. One way to study the phenomenology of liquid crystals would be to construct various simple model functions for $\vec{C}$, and observe the implications of each. From the definition (6), it is evident that $\vec{C}$ is antisymmetric under exchange of its two arguments; furthermore, $\vec{C}(\vec{\omega},\vec{\tau})$ should not be purely odd in $\vec{\tau}$, or else $\mathfrak{F}(\vec{s})$ and the last term of Eq. (9) will vanish identically, giving no physical consequences. If we restrict our attention to the case of molecules whose orientation is specified by a single vector $\hat{m}$, some possible forms for $C(\hat{m}_1,\hat{m}_2)$ are

$$(\hat{m}_1-\hat{m}_2)c,\ (\hat{m}_1-\hat{m}_2)(\hat{m}_1\cdot\hat{m}_2)c,$$
$$(\hat{m}_1\times\hat{m}_2)(\hat{m}_1\cdot\hat{m}_2)c,\ \ldots\,, \quad (29)$$

where c is an arbitrary function of $(\hat{m}_1 - \hat{m}_2)^2$. The first two examples are equivalent to the tapered-rod geometry, and lead to the same consequences. The third case is new and more interesting: since $\vec{C}$ is an even function of $\hat{m}_1$ and $\hat{m}_2$, reasons of symmetry no longer force $\mathfrak{F}_1$ to vanish. Thus we must consider

$$\mathfrak{F}_1(\vec{s}) = \tfrac{1}{2}\rho^2 \int f_0(\hat{n}\cdot\hat{m}_1)c(\hat{m}_1\cdot\hat{m}_2)(\hat{m}_1\cdot\hat{m}_2) \times (\hat{m}_1\times\hat{m}_2)\cdot\vec{\nabla}_s f_0(\hat{n}\cdot\hat{m}_2)\, d\hat{m}_1\, d\hat{m}_2. \quad (30)$$

In order to proceed further, we again use the representation (10). The terms in b and s vanish, but the term in t does not. Then since the free-energy density contains terms linear in the twist strain, its minimum occurs for a twisted geometry such that $t = -K_2/K_{22}$, where

$$\begin{aligned} K_2 &= \frac{\mathfrak{F}_1}{t} \\ &= \tfrac{1}{2}\rho^2 kT \int f_0(\hat{m}_{1x})c(\hat{m}_1\cdot\hat{m}_2) \\ &\qquad \times (\hat{m}_1\cdot\hat{m}_2)[(\hat{m}_1\times\hat{m}_2)\cdot\hat{z}] \\ &\qquad \times \hat{m}_{2y} f_0'(\hat{m}_{2x})\, d\hat{m}_1\, d\hat{m}_2. \qquad (31) \end{aligned}$$

This equation determines the equilibrium pitch length $p_0 = 2\pi/t$. If $c(\hat{m}_1\cdot\hat{m}_2)$ is just a constant, the integral may be performed to give $t = \frac{1}{2}\rho^2 ckTS^2/K_{22}$, where S is the usual order parameter. Reference to previous theory[14] shows that $K_{22} \sim \rho^2 kT$, but is relatively insensitive to variations in S; thus this theory predicts that as the phase transition is approached, p_0 increases just because S is decreasing.

Although this conclusion is in qualitative agreement with experiment, there is in this case a quantitative test available: Dupre and Duke[21] have measured K_{22} and p_0 as a function of temperature and concentration for the solutions of poly(γ-benzyl L-glutamate) in dioxane. If this system reasonably approximates a gas of long rods, this and previous theory[14] should give a good description. Experimentally, however, K_{22} is only slightly dependent on concentration (quite distinct from the theoretical $K_{22} \sim \rho^2$), and the cholesteric pitch rather accurately obeys a power-law dependence on concentration ($p_0 \sim \rho^{-1.8}$). These data can be combined to give $K_2 \sim \rho^2$, which is consistent with (31); but since the prediction for K_{22} comes from much the same sort of theory, the discrepancy forces us to conclude that the interparticle interactions are not as simple as have been assumed heretofore.

The theory is readily extended to mixtures of liquid crystals, with the conclusion that the elastic constants K_2 and K_{22} are each quadratic forms in the particle densities. Then the pitch length is the ratio of two such quadratic forms, as has already been suggested by Stegemeyer.[22] Bak and Labes[23] have shown that putting K_2 a quadratic form in the mole fraction (and ignoring any concentration dependence of K_{22}) already gives excellent account of the dependence of pitch on concentration in mixed-liquid-crystal systems.

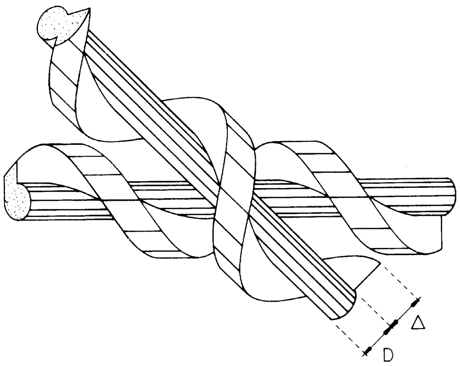

FIG. 3. Geometry of two threaded rods. The upper rod may approach the lower most closely if its principal axis is rotated clockwise with respect to the axis of the lower.

In order to complete this theory of the cholesteric phase, it is desirable to give physical interpretation to the form assumed for $\vec{C}(\hat{m}_1, \hat{m}_2)$. One method would be to postulate that $U(\hat{m}_1, \hat{m}_2, \xi)$ contains terms like $(\hat{m}_1\cdot\hat{m}_2)(\hat{m}_1\times\hat{m}_2)\cdot\vec{\xi} f(\xi)$, which gives $c(\hat{m}_1, \hat{m}_2) = \frac{4}{3}\pi \int_0^\infty f(\xi)\xi^4\, d\xi$ (independent of $\hat{m}_1\cdot\hat{m}_2$). Alternatively, we can try to give a geometric interpretation, as was done in the case of tapered and bent particles. Consider, for example, a threaded rod (Fig. 3). Technically this is a biaxial object, but we will assume that these particles rotate freely about their longitudinal axis, so that most of the consequences of the biaxiality average out. However, one consequence that remains is that $\vec{C}(\hat{m}_1, \hat{m}_2)$ does not vanish, and indeed has structure somewhat like that assumed above. Figure 3 demonstrates that the minimum approach distance of a pair of threaded rods depends on the sign of $\hat{m}_1\times\hat{m}_2$, and we may estimate $\vec{C}(\hat{m}_1, \hat{m}_2) \sim \frac{1}{2}L^2 D\Delta(\hat{m}_1\times\hat{m}_2)(\hat{m}_1\cdot\hat{m}_2)$.

VI. CONCLUSION

The unifying theme of this paper has been the attempt to exploit the information contained in the first moment vector C. This is a particularly interesting average of the interparticle potential because it is sensitive only to the asymmetry of the interaction. It has then been shown how the first-moment vector is implicated in piezoelectricity and the cholesteric ordering in the context of the Onsager theory. The emphasis has been on the symmetry of the functions under discussion; to the extent possible, integrands have been simplified by deletion of explicitly vanishing terms and averaging about known axes of symmetry.

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