PHYSICAL REVIEW A VOLUME 9, NUMBER 2 FEBRUARY 1974

Biaxial model of cholesteric liquid crystals

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(Received 18 May 1973; revised manuscript received 28 September 1973)

A model for cholesteric liquid crystals with biaxial molecules is introduced. It is found that the biaxial order parameter for such systems is of order $(q_0 a)^2$ where a is a molecular length and $q_0 = 2\pi/p$ where p is the helical pitch. The generalized susceptibility is calculated and is found to predict a fluctuation instability as in uniaxial cholesterics.

Molecules which condense into the various liquid-crystalline states are typically composed of a central core of two or more benzene rings lying in a single plane with hydrocarbon tails of varying length extending from the core in the plane of the core.[1] On a gross scale, these molecules can be viewed as flat plates with three inequivalent directions specified by the unit vectors $\vec{\nu}^1$, $\vec{\nu}^2$, and $\vec{\nu}^3$ (Fig. 1). In other words, the molecules are biaxial. In usual treatments of the nematic state, one assumes that molecular rotation about the long axis is uninhibited so that the molecules can be treated as uniaxial and characterized by a single unit vector $\vec{\nu}^1$ along the long body axis. The planar character of molecules forming the cholesteric state is more pronounced than that of molecules forming the nematic state. Furthermore, it seems reasonable to expect that the molecular planes will want to align perpendicular to the cholesteric pitch axis (Fig. 2). In this paper, we will investigate some properties of the cholesteric phase formed by biaxial molecules.

In Sec. I, we introduce the tensors needed to describe biaxial molecules and the simplest Hamiltonian which produces a helical state with molecular planes perpendicular to the pitch axis. We also introduce the parameters defining the biaxiality of the cholesteric phase. This phase biaxiality is to be distinguished from molecular biaxiality. In Sec. II, we show that the usual cholesteric state corresponds to a minimum of the mean-field free energy derived from our model Hamiltonian. In Sec. III, we calculate the phase biaxialities within the mean field. Finally in Sec. IV, we calculate the fluctuations about the ground state of a biaxial cholesteric.

The principal results of this paper are as follows. (a) All cholesterics which are composed of molecules which tend to align with their flat planes perpendicular to the axis of rotation (we believe this to include virtually all cholesterics) have phase biaxialities proportional to $(qa)^2$ when cooperative biaxial effects are unimportant, where q is the helical wave number (2π/pitch) and a is a molecular length. (b) Biaxial cholesterics exhibit the same fluctuation instability exhibited by uniaxial cholesterics and smectic liquid crystals. The first result has also been obtained by Wulf[2] using a phenomenological free energy. The second result corroborates work on somewhat less general models[3] and is consistent with the view that no cholesteric can support a uniform shear.[4]

I. TENSORS AND MICROSCOPIC INTERACTION

As discussed by de Gennes,[5] properties of liquid-crystal systems can be discussed in terms of second-rank Cartesian tensors. In particular, we consider

$$Q^{\alpha}_{ij}(\vec{r}) = \nu^{\alpha}_i(\vec{r})\,\nu^{\alpha}_j(\vec{r}) - \tfrac{1}{3}\delta_{ij}, \quad \alpha = 1, 2, 3. \tag{1}$$

The object $\nu^{\alpha}_i(\vec{r})$ is the ith Cartesian component of a unit vector $\vec{\nu}^{\alpha}$, parallel to the body α axis of

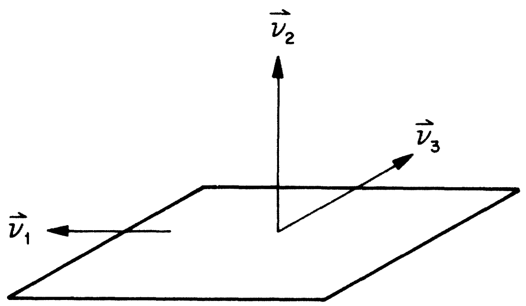

FIG. 1. Schematic representation of a biaxial molecule indicating the three orthogonal directions $\vec{\nu}^1, \vec{\nu}^2$, and $\vec{\nu}^3$.

the molecule at the point $\vec{r}$. We define the parity through $\vec{\nu}^3 = \vec{\nu}^1 \times \vec{\nu}^2$. It will be convenient to have an explicit representation for the $\vec{\nu}$'s in terms of Euler angles relative to a space-fixed axis. Let $\vec{x}_1$, $\vec{x}_2$, and $\vec{x}_3$ be space-fixed orthogonal unit vectors and let $\vec{x}_1$ be along the helical pitch axis of the cholesteric. Anticipating that $\vec{\nu}^2$ will on the average be parallel to $\vec{x}_1$ and $\vec{\nu}^1$ and $\vec{\nu}^3$ will on the average be in $\vec{x}_2 - \vec{x}_3$ plane, we write

$$\nu^1 = \begin{pmatrix} \sin\theta\cos\varphi \\ \cos\theta \\ \sin\theta\sin\varphi \end{pmatrix},$$

$$\nu^2 = \begin{pmatrix} \cos\varphi\cos\theta\cos\psi - \sin\varphi\sin\psi \\ -\sin\theta\cos\psi \\ \sin\varphi\cos\theta\cos\psi + \cos\varphi\sin\psi \end{pmatrix}, \tag{2}$$

$$\nu^3 = \begin{pmatrix} \cos\varphi\cos\theta\sin\psi + \sin\varphi\cos\psi \\ -\sin\theta\sin\psi \\ \sin\varphi\cos\theta\sin\psi - \cos\varphi\cos\psi \end{pmatrix}.$$

The intermolecular interactions may be constructed from scalar combinations of the Q tensors. A simple form of the orientational potential energy of the liquid is

$$H = H_{n1} + H_{n2} + H_c,$$

$$H_{n1} = -\tfrac{1}{2}\sum_{rr'} A(|\vec{r}' - \vec{r}|)Q^1_{jl}(\vec{r})Q^1_{jl}(\vec{r}'),$$

$$H_{n2} = -\tfrac{1}{2}\sum_{rr'} A_2(|\vec{r}' - \vec{r}|)Q^2_{jl}(\vec{r})Q^2_{jl}(\vec{r}'), \tag{3}$$

$$H_c = \sum_{rr'} B(|\vec{r}' - \vec{r}|)\epsilon_{ijk}(r'_i - r_i)Q^1_{jl}(\vec{r})Q^3_{kl}(\vec{r}').$$

The repeated index sum convention is used here and below. This form of H is general enough to illustrate the features of biaxial cholesterics. The term H_c is actually a pseudoscalar. This implies that it cannot be present in systems composed of molecules which transform into themselves under the operation of coordinate inversion. On the other hand it should, in general, be present in systems composed of molecules which are either right or left handed. All known cholesterics belong to the second class. Note that H_c is minimized when adjacent molecules are rotated relative to each other with the axis of rotation along $\vec{\nu}^2(\vec{r})// \vec{\nu}^2(\vec{r}')$. This is most easily seen by reexpressing H_c in terms of the $\vec{\nu}$'s,

$$H_c = \sum_{rr'} B(|\vec{r} - \vec{r}'|)(\vec{r} - \vec{r}')\cdot\vec{\nu}^2(\vec{r})[\vec{\nu}^1(\vec{r})\cdot\vec{\nu}^3(\vec{r}')]. \tag{4}$$

This is minimized when $\vec{r} - \vec{r}'$ is parallel to $\vec{\nu}^2(\vec{r})$, and $\vec{\nu}^1(\vec{r})$ is parallel or antiparallel to $\vec{\nu}^3(\vec{r}')$, depending on the sign of B. The second condition causes a rotation of adjacent molecules and the first puts the axis of rotation parallel to $\vec{\nu}^2$. The competition between H_{n1} and H_{n2} which tend to keep adjacent molecules parallel and H_c produces cholesteric ordering.

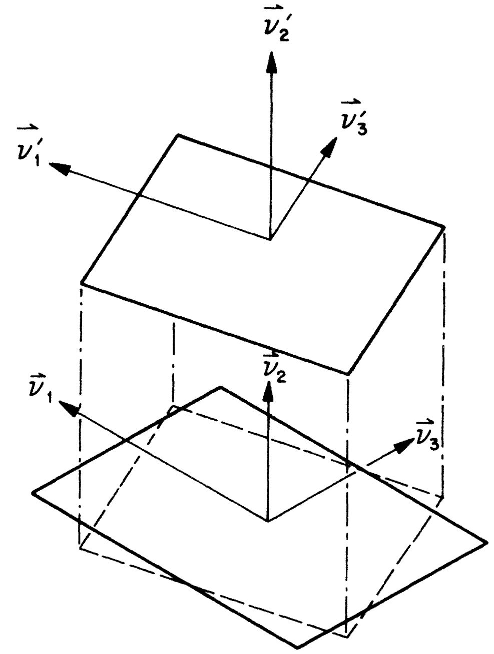

FIG. 2. Schematic representation of configuration of two biaxial cholesteric molecules which minimizes their potential energy. Note that the planes of the two molecules are parallel and that the long axis of one is rotated relative to the other.

To analyze the biaxial model it is necessary to calculate the thermodynamic averages of the Q tensors, $\langle Q\rangle$. Since there are no external fields, every point in space in equivalent. This implies that the principal values of the $\langle Q\rangle$ tensors are independent of position. The orientations of the principal axes of the $\langle Q\rangle$ tensors can be specified by the unit vectors, called the directors, $\vec{n}^\alpha(\vec{r})$. The vector $\vec{n}^\alpha(\vec{r})$ is parallel to the preferred orientations of the body α axis at the point $\vec{r}$. We have $\vec{n}^3 = \vec{n}^1 \times \vec{n}^2$. In terms of the directors and their principal values the $\langle Q\rangle$ tensors can be written as

$$\langle Q^1_{ij}(\vec{r})\rangle = S(n^1_i n^1_j - \tfrac{1}{3}\delta_{ij}) + \tfrac{1}{2}\Delta(n^2_i n^2_j - n^3_i n^3_j),$$

$$\begin{aligned}\langle Q^2_{ij}(\vec{r})\rangle = {}& -\tfrac{1}{2}(S - \eta')(n^1_i n^1_j - \tfrac{1}{3}\delta_{ij}) \\ & + (\eta - \tfrac{1}{4}\Delta)(n^2_i n^2_j - n^3_i n^3_j),\end{aligned} \tag{5}$$

$$\begin{aligned}\langle Q^3_{ij}(\vec{r})\rangle = {}& -\tfrac{1}{2}(S + \eta')(n^1_i n^1_j - \tfrac{1}{3}\delta_{ij}) \\ & + (-\eta - \tfrac{1}{4}\Delta)(n^2_i n^2_j - n^3_i n^3_j).\end{aligned}$$

The dependence of $\vec{n}^\alpha(\vec{r})$ on $\vec{r}$ is suppressed here for ease of notation. The principal values of these tensors are the indicated combinations of S, η, Δ, and η'. In a space-fixed local coordinate system with axes which coincide with the principal axes we have

$$\begin{aligned} &S = \langle \tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}\rangle, \quad \Delta = \langle \sin^2\theta \cos 2\varphi\rangle, \\ &\eta' = \tfrac{3}{2}\langle \sin^2\theta \cos 2\psi\rangle, \\ &\eta = \langle \tfrac{1}{4}(1+\cos^2\theta)\cos 2\varphi \cos 2\psi\rangle, \end{aligned} \tag{6}$$

where φ, θ, and ψ are the Euler angles introduced in Eq. (2). In systems composed of uniaxial molecules, only S is nonzero. If Δ or η is nonzero the local environment is biaxial (i.e., there are three inequivalent directions). We will, therefore. call Δ and η the phase biaxialities to emphasize that they are properties of a given phase and not of molecular structure. If Δ and η are zero but η' is nonzero, the local environment remains uniaxial. We will, therefore, not refer to η' as a biaxiality even though it can be nonzero only in systems composed of biaxial molecules.

II. GROUND-STATE CONFIGURATION

In this section, we will show that the helical state with pitch axis along $\vec{n}_2$ corresponds to a minimum of the mean-field free energy, and we will determine the equilibrium-pitch wave number q in terms of moments of the fundamental interaction potentials $A(\vec{r})$, $A_2(\vec{r})$, and $B(\vec{r})$. To find the spatial dependence of the equilibrium directors, we need only consider the internal energy since spatial variations of the director do not change the entropy in the mean-field approximation. The internal energy density at the point $\vec{r}$ is given in the mean-field approximation by

$$\begin{aligned} E(\vec{r}) = &-\tfrac{1}{2}\sum_{r'} A(|\vec{r}'-\vec{r}|)\langle Q^1_{jl}(\vec{r}'+\vec{r})\rangle\langle Q^1_{jl}(\vec{r})\rangle - \tfrac{1}{2}\sum_{r'} A_2(|\vec{r}'-\vec{r}|)\langle Q^2_{jl}(\vec{r}'+\vec{r})\rangle\langle Q^2_{jl}(\vec{r})\rangle \\ &+\sum_{r'} B(|\vec{r}'-\vec{r}|)(r'_i - r_i)\epsilon_{ijk}\langle Q^1_{jl}(\vec{r})\rangle\langle Q^3_{kl}(\vec{r}'+\vec{r})\rangle \end{aligned} \tag{7}$$

If we assume that spatial variations are slow on the scale of the range of the interparticle potentials, we can perform a gradient expansion of Eq. (7) and arrive at a local Frank free energy[6] for a biaxial cholesteric. To perform this expansion, we express $n_i^\alpha(\vec{r}')$ ($\alpha = 1, 2, 3$) in terms of gradients of $n_i^\alpha(\vec{r})$,

$$\begin{aligned} n_i^\alpha(\vec{r}') = n_i^\alpha(\vec{r}) + (r'_j - r_j)\nabla_j n_i^\alpha(\vec{r}) + \tfrac{1}{2}(r'_j - r_j) \\ \times (r'_k - r_k)\nabla_j \nabla_k n_i^\alpha(\vec{r}). \end{aligned} \tag{8}$$

Continuation of the above Taylor series is unnecessary because of the short range of $A(\vec{r})$, $A_2(\vec{r})$, and $B(\vec{r})$. Application of Eq. (6) to Eq. (5) yields a local expression for the internal-energy density in terms of spatial derivatives of the directors with coefficients depending on the moments of the potentials. A and A_2 have units of energy and B has units of energy over a length. If we let a be the length of the long molecular axis, we can define three constants which have units of energy,

$$\begin{aligned} K_4 &= \frac{1}{3a^2}\sum_r A(\vec{r})r^2, \\ K_5 &= \frac{1}{3a^2}\sum_r A_2(\vec{r})r^2, \\ K_6 &= \frac{1}{3a}\sum_r B(\vec{r})r^2. \end{aligned} \tag{9}$$

The internal-energy density, which results from Eqs. (7)–(9) after a fair amount of algebra and judicious integration by parts, is

$$\begin{aligned} E(\vec{r}) = &(\text{const}) + \tfrac{1}{2}f_1\nabla_l n_i^1 \nabla_l n_i^1 + f_2\vec{n}^1\cdot\vec{\nabla}\times\vec{n}^1 + \tfrac{1}{2}g_1\nabla_l n_i^1\nabla_l n_j^1(n_i^2 n_j^2 - n_i^3 n_j^3) + g_2(n_i^3 n_l^2 \nabla_i n_l^1 + n_i^2 n_l^3 \nabla_i n_l^1) \\ &+\tfrac{1}{2}h_1(\nabla_l n_i^2\nabla_l n_i^2 + \nabla_l n_i^3 \nabla_l n_i^3 - 2n_i^2 n_j^3 \nabla_l n_i^3 \nabla_l n_j^2) + h_2(\vec{n}^2\cdot\vec{\nabla}\times\vec{n}^2 + \vec{n}^3\cdot\vec{\nabla}\times\vec{n}^3 - 2n_l^1 n_i^3 \nabla_l n_i^2), \end{aligned} \tag{10}$$

where

$$\begin{aligned} f_1 &= S^2K_4a^2 + \tfrac{1}{4}(S-\eta')^2K_5a^2, \\ f_2 &= \tfrac{1}{2}S(S+\eta')K_6a, \\ g_1 &= -S\Delta K_4a^2 + (S-\eta')(\eta - \tfrac{1}{4}\Delta)K_5a^2, \\ g_2 &= [S(\eta + \tfrac{1}{2}\Delta) + \tfrac{1}{4}\eta'\Delta]K_6a, \\ h_1 &= \tfrac{1}{4}\Delta^2K_4a^2 + (\eta - \tfrac{1}{4}\Delta)^2K_5a^2, \\ h_2 &= \tfrac{1}{2}\Delta(\eta + \tfrac{1}{4}\Delta)K_6a. \end{aligned} \tag{11}$$

Here f_1 and f_2 are zeroth order, g_1 and g_2 are first order, and h_1 and h_2 second order in the biaxialities η and Δ. f_1, g_1, and h_1 have units of (energy)× (length)^2 whereas f_2, g_2, and h_2 have units of (energy)× (length).

We now verify that $E(\vec{r})$ is a minimum for the usual cholesteric state. That is

$$\begin{aligned} &\vec{n}^1(\vec{r}) = \vec{x}_2\cos(q\vec{r}\cdot\vec{x}_1) + \vec{x}_3\sin(q\vec{r}\cdot\vec{x}_1), \\ &\vec{n}^2(\vec{r}) = \vec{x}_1, \quad \vec{n}^3(\vec{r}) = \vec{n}^1\times\vec{n}^2, \end{aligned} \tag{12}$$

corresponds to a local minimum of $E(\vec{r})$. To do this, we introduce three Euler angles α, β, and γ which give the orientation of the principal coordinate system at the point $\vec{r}$. In terms of these angles, the directors are

$$n^1 = \begin{pmatrix} \sin\beta \\ \cos\beta\cos\alpha \\ \cos\beta\sin\alpha \end{pmatrix},$$

$$n^2 = \begin{pmatrix} \cos\beta\cos\gamma \\ -\sin\gamma\sin\alpha - \cos\gamma\cos\alpha\sin\beta \\ \sin\gamma\cos\alpha - \sin\alpha\sin\beta\cos\gamma \end{pmatrix}, \qquad (13)$$

$$n^3 = \begin{pmatrix} \cos\beta\sin\gamma \\ \sin\alpha\cos\gamma - \cos\alpha\sin\beta\sin\gamma \\ -\cos\alpha\cos\gamma - \sin\alpha\sin\beta\sin\gamma \end{pmatrix},$$

where $\alpha = \alpha' + q\vec{r}\cdot\vec{x}_1$. Equation (12) is retrieved if $\alpha' = \beta = \gamma = 0$. We now express $E(\vec{r})$ of Eq. (10) in terms of the variables α', β, and γ. In order for Eq. (10) to represent a minimum of $E(\vec{r})$, there must be no terms linear in α', β, γ or their spatial derivatives. Tedious calculation yields

$$\sum_r E(\vec{r}) = (\text{const}) + \sum_r \nabla_1\alpha'[q(f_1 - g_1 + h_1) - (f_2 + g_2 + h_2)] + (\text{second-order terms}). \qquad (14)$$

We will consider the second-order terms in Sec. IV. The coefficient of $\nabla_1\alpha'$ must be zero in equilibrium. Hence, the equilibrium value of q is given by

$$q = \frac{f_2 + g_2 + h_2}{f_1 - g_1 + h_1} \qquad (15)$$

or

$$qa = \frac{1}{2}\,\frac{[S^2 + S(\eta' + \Delta + 2\eta) + \frac{1}{4}\Delta(2\eta' + 4\eta + \Delta)]}{(S + \frac{1}{2}\Delta)^2 K_4 + [\frac{1}{2}(S - \eta') - (\eta - \frac{1}{4}\Delta)]^2 K_5}\,K_6. \qquad (16)$$

If the phase biaxialities are zero, this reduces to

$$qa = \frac{1}{2}\,\frac{S(S + \eta')K_6}{S^2 K_4 + \frac{1}{4}(S - \eta')^2 K_5}\,. \qquad (17)$$

Hence, the helical state minimizes the internal energy, Eq. (10), even if the phase biaxialities are zero.

III. COMPUTATION OF BIAXIALITIES

In this section, we will calculate the phase biaxialities Δ and η within the mean-field approximation to lowest order in qa. To keep algebra at a minimum, we will consider in detail the case with $A_2 = 0$. If $A_2 = 0$, the coefficient η' is zero. If A_2 and hence η' is nonzero and $A_2 \ll A$, the equations to be derived for η and Δ will be somewhat modified but their functional dependence on qa will not change.

In the mean-field approximation, we have

$$\Delta = \int d\Omega\,\sin^2\theta\cos 2\varphi\, e^{-V_{\text{mf}}(\Omega)/k_BT} \times\left(\int d\Omega\, e^{-V_{\text{mf}}(\Omega)/k_BT}\right)^{-1},$$

$$\eta = \int d\Omega\,\tfrac{1}{4}(1 + \cos^2\theta)\cos^2\varphi\cos 2\psi\, e^{-V_{\text{mf}}(\Omega)/k_BT} \times\left(\int d\Omega\, e^{-V_{\text{mf}}(\Omega)/k_BT}\right)^{-1}, \qquad (18)$$

$$V_{\text{mf}} = -\sum_r A(r)\langle Q^1_{jl}(\vec{r})\rangle Q^1_{jl}(0) + \sum_r B(r)[\epsilon_{ijk}r_i\langle Q^3_{kl}(\vec{r})\rangle Q^1_{jl}(0) - \epsilon_{ijk}r_i\langle Q^1_{jl}(\vec{r})\rangle Q^3_{kl}(0)]\,.$$

The integration is over all orientations $\Omega = (\varphi, \theta, \psi)$ as measured in the local coordinate system. The tensors $Q^\alpha_{jl}(0)$ depend on Ω [see Eq. (1)]. Spatial variations in $\langle Q^\alpha_{jl}(\vec{r})\rangle$ are determined by q^{-1} and those of A and B by a. Since $qa \ll 1$, we can obtain an expansion of V_{mf} in powers of qa by expanding $\langle Q^\alpha_{ij}(\vec{r})\rangle$ about the origin

$$\langle Q^\alpha_{ij}(\vec{r})\rangle = \langle Q^\alpha_{ij}(0)\rangle + (\vec{r}\cdot\vec{x}_1)[\nabla_1\langle Q^\alpha_{ij}(\vec{r})\rangle]_{r=0} + \tfrac{1}{2}(\vec{r}\cdot\vec{x}_1)^2[\nabla_1^2\langle Q^\alpha_{ij}(\vec{r})\rangle]_{r=0} + \cdots. \qquad (19)$$

This yields

$$V_{\text{mf}} = V^0_{\text{mf}} + V^1_{\text{mf}} + V^2_{\text{mf}}\,,$$

$$V^0_{\text{mf}} = -\left(\sum_r A(r)\right)[\langle Q^1_{jl}(0)\rangle]Q^1_{jl}(0),$$

$$V^1_{\text{mf}} = (qa)\;K_6\epsilon_{1jk}\left[\frac{1}{q}\nabla_1\langle Q^3_{kl}(\vec{r})\rangle\right]_{r=0} Q^1_{jl}(0) - (qa)\;K_6\epsilon_{1jk}\left[\frac{1}{q}\nabla_1\langle Q^1_{jl}(\vec{r})\rangle\right]_{r=0} Q^3_{kl}(0), \qquad (20)$$

$$V^2_{\text{mf}} = -\tfrac{1}{2}K_4(qa)^2\left[\frac{1}{q^2}\nabla_1^2\langle Q^1_{jl}(\vec{r})\rangle\right]_{r=0} Q^1_{jl}(0).$$

The quantities in the square brackets are second-rank tensors. They can be calculated from Eqs. (12) and (5). For the purposes of a lowest-order calculation of the biaxialities, the explicit biaxialities in these expressions are set equal to zero. This leads to

$$
\begin{aligned}
V_{\mathrm{mf}}^{0} &= -\sum_{r} A(r) S\left[\tfrac{2}{3}Q_{22}^{1}(0) - \tfrac{1}{3}Q_{33}^{1}(0) - \tfrac{1}{3}Q_{11}^{1}(0)\right], \\
V_{\mathrm{mf}}^{1} &= -SK_6(qa)\,\left[\tfrac{1}{2}Q_{22}^{1}(0) - \tfrac{1}{2}Q_{33}^{1}(0) + Q_{33}^{3}(0) - Q_{22}^{3}(0)\right], \\
V_{\mathrm{mf}}^{2} &= -SK_4(qa)^2\left[-Q_{22}^{1}(0) + Q_{33}^{1}(0)\right].
\end{aligned}
\tag{21}
$$

The form of $Q_{ii}^{\alpha}(0)$ may be found from Eqs. (1) and (2). Note that V_{mf}^{0} depends only on θ. Hence the integrals over φ and ψ are unweighted and may be carried out directly. The results are

$$
\begin{aligned}
\Delta &= (qa)^2 \frac{1}{k_B T} S \tfrac{1}{4} K_4 \langle \sin^4\theta \rangle, \\
\eta &= (qa)^2 \frac{1}{k_B T} S \tfrac{1}{32} K_4 \langle (1+\cos^2\theta)^2 \rangle.
\end{aligned}
\tag{22}
$$

Here the averages are with respect to the uniaxial weight $e^{-V_{\mathrm{mf}}/k_B T}$. They may be approximated as

$$
\begin{aligned}
\langle \sin^4\theta \rangle &\sim (\tfrac{2}{3} - \tfrac{2}{3}S)^2, \\
\langle (1+\cos^2\theta)^2 \rangle &\sim (\tfrac{4}{3} + \tfrac{2}{3}S)^2.
\end{aligned}
\tag{23}
$$

When $A_2(\vec{r})$ is nonzero, V_{mf}^{0} becomes

$$
V_{\mathrm{mf}}^{0} = -S\left(\sum_{r} A(\vec{r})\right)(\cos^2\theta - \tfrac{1}{3}) + \tfrac{1}{4}(S - \eta') \times \sum_{r} A_2(\vec{r}) \sin^2\theta\,(1 + \cos 2\psi). \tag{24}
$$

η' to lowest order in qa is then

$$
\eta' = \int d\Omega\, \sin^2\theta \cos 2\psi\, e^{-V_{\mathrm{mf}}^{0}/k_B T}\left(\int d\Omega\, e^{-V_{\mathrm{mf}}^{0}/k_B T}\right)^{-1} \tag{25}
$$

Hence η' is nonzero whenever $A_2(\vec{r})$ is nonzero even if $q = 0$. In other words, η' is nonzero in a nematic liquid crystal composed of biaxial molecules. Note, however, that a nonzero η' does not change the uniaxial symmetry of the nematic state. There is still only one preferred direction in space. The phase biaxialities Δ and η are zero in the nematic state. Hence, within the mean-field theory for the Hamiltonian, Eq. (3), the nematic state cannot be biaxial. We believe this property to be quite general. It is in agreement with experiment since to date there has been no report of a biaxial nematic.

IV. FLUCTUATIONS

Fluctuations about the cholesteric ground state are of some interest. It is already well known that the uniaxial cholesteric is unstable with respect to fluctuations[7] in much the same way that a two-dimensional Heisenberg ferromagnet[8] or superconductor[9] is unstable with respect to fluctuations. This instability also exists in smectic liquid crystals.[10] Landau and Peierls have argued that such an instability is a result of broken translational invariance along a single spatial direction.[11] One can also show that the absence of such an instability would imply that the system in question could support a uniform shear.[4,7,12] In this section, we will investigate the fluctuations of a biaxial cholesteric and show that one of the inverse director susceptibilities is proportional to $k_z^2 + O(k_\perp^4)$ where z is along the 2 direction. This leads to the expected instability of the low-temperature phase.

Fluctuations about the cholesteric state are governed by the quadratic terms in the expansion of the internal energy, Eqs. (10) and (14). Choosing q so that the coefficient of $\nabla_1 \alpha'$ is zero, we obtain after very tedious application of the steps outlined in Sec. II:

$$
\sum_{r} E(\vec{r}) = (\mathrm{const}) + \tfrac{1}{2}\sum_{rr'} X_i(\vec{r})\,\chi_{ij}{}^{-1}(\vec{r}\vec{r}')\,X_j(\vec{r}'), \tag{26}
$$

with $X_1 = \alpha'$, $X_2 = \beta$, $X_3 = \gamma$, and

$$
\chi^{-1} = \begin{bmatrix}
-A\dfrac{1}{q^2}\nabla^2 & -B\dfrac{1}{q}\vec{n}^{1}\cdot\vec{\nabla} & C\dfrac{1}{q}\vec{n}^{3}\cdot\vec{\nabla} \\
B\dfrac{1}{q}\vec{n}^{1}\circ\vec{\nabla} & -D - E\dfrac{1}{q^2}\nabla^2 & F\dfrac{1}{q}\nabla_1 \\
-C\dfrac{1}{q}\vec{n}^{3}\cdot\vec{\nabla} & -F\dfrac{1}{q}\nabla_1 & G + H\dfrac{1}{q^2}\nabla^2
\end{bmatrix} \delta_{rr'}, \tag{27}
$$

where

$$
\begin{aligned}
A &= q^2(f_1 - g_1 + h_1), \\
B &= 2q(f_2 - h_2), \\
C &= -2q(g_2 + 2h_2), \\
D &= q^2(f_1 - g_1 - 3h_1) - q(2f_2 + 2g_2 + 3h_2), \\
E &= q^2(f_1 + g_1 + h_1), \\
F &= -q^2(2g_1 + 4h_1) - q(2g_2 - 4h_2), \\
G &= 2q^2 g_1 + 4q g_2, \\
H &= -4q^2 h_1.
\end{aligned}
\tag{28}
$$

The long-wavelength fluctuations away from the ground state described by the variables α', β, and γ are static distortions of the ground state. Since there is no entropy associated with static distortions, $E(\vec{r})$ is equivalent to the free-energy density associated with static deformations. This implies that the reciprocal of χ^{-1}, χ, is just the zero-frequency generalized susceptibility of the system. The susceptibility is related to the equal-time-correlation function through the equipartition theorem:

$$\langle X_i X_j \rangle = k_B T \chi_{ij} . \tag{29}$$

The susceptibility is related to the eigenvalues λ^α and the eigenfunctions ζ^α of χ^{-1} through the relation:

$$\chi_{ij}(rr') = \sum_\alpha \frac{\zeta_i^\alpha(r)\zeta_j^\alpha(r')}{\lambda_\alpha} . \tag{30}$$

Therefore, by finding the eigenvalues of χ^{-1}, information is obtained about χ and the equal-time-correlation function. This information allows us to determine if the biaxial cholesteric has a fluctuation instability as does the uniaxial cholesteric.

The quantity χ^{-1} is translationally invariant with respect to translations perpendicular to $\vec{x}_1$. It therefore may be Fourier transformed with respect to $(\vec{r}' - \vec{r}) - [(\vec{r}' - \vec{r}) \cdot \vec{x}_1]\vec{x}_1 = (\vec{r}' - \vec{r})_\perp$. The Fourier transform $\chi_{ij}^{-1}(k_\perp, z', z)$, with z along the 1 axis, can be obtained from Eq. (27) by replacing $\vec{\nabla}$ with $i\vec{k} + \nabla_1 \vec{x}_1$ and $\delta_{rr'}$ with $\delta_{zz'}$. The eigenvalue equation for $\chi_{ij}^{-1}(k_\perp, z', z)$ is

$$\sum_{z'} \chi_{ij}{}^{-1}(k_\perp, z', z)\,\zeta_1^\alpha(z', k_\perp) = \lambda^\alpha \zeta_j^\alpha(k_\perp, z). \tag{31}$$

This equation can be solved by an extension of the method used by Lubensky[7] to solve this equation for the uniaxial case. We note the following symmetry property of χ^{-1}:

$$\left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} T^0 \right]^N \chi^{-1} \left[\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} T^0 \right]^{-N} = \chi^{-1}, \tag{32}$$

where T^0 is the translation operator for a half-twist length π/q and N is any integer. This implies that the eigenfunctions of χ^{-1} can be expressed as

$$\zeta^\alpha(k_\perp, z) = \zeta^\alpha(k_\perp, k_1, z) = \begin{bmatrix} \sum_m A_m(k_\perp)\, e^{i2mqz} \\ \sum_m B_m(k_\perp)\, e^{i(2m+1)qz} \\ \sum_m C_m(k_\perp)\, e^{i(2m+1)qz} \end{bmatrix} e^{ik_1 z} . \tag{33}$$

The index α is now interpreted as a "band" index and k_1 as a "band" momentum. Equation (32) may be substituted into Eq. (31) to find $\lambda^\alpha(k_\perp, k_1)$. The lowest band of eigenvalues is given to order k^2 by

$$\lambda^0(k_1, k_\perp) = A\frac{k_1^2}{q^2} + (A + J)\frac{k_\perp^2}{q^2} ,$$

$$J = [(D - E)(G - H) + F^2]^{-1}$$

$$\times [\tfrac{1}{2}(G - H)B^2 + FBC + \tfrac{1}{2}(E - D)C^2] . \tag{34}$$

Substitution of Eq. (28) into (34) gives $A + J = 0$. This ensures that the susceptibility diverges as $[k^2 + O(k_\perp^4)]^{-1}$. The integral $\int d^3k\,\chi$ diverges, which means[6,10] that the biaxial cholesteric, like the uniaxial cholesteric, has an orientational fluctuation instability.

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[*] Work supported in part by the Center for Theoretical Physics.

[†] Work supported in part by grants from the National Science Foundation and the Office of Naval Research.

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