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Landau theory of twist-induced biaxiality in cholesteric liquid crystals

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The Landau theory of twist-induced biaxiality in cholesteric liquid crystals is presented. Results are given for the asymmetry parameter η_C as a function of temperature and chirality. These are compared with the experimental data of Yaniv *et al.* and the Maier-Saupe-type calculation of Lin-Liu and Lee. While the theoretical curves are qualitatively similar to those reported experimentally, the magnitude of the latter is as much as an order-of-magnitude greater than the theoretical prediction. Some possible reasons for this discrepancy are discussed.

It is well known[1,2] that cholesteric liquid crystals are, in principle, biaxial even if the chiral molecules composing the systems possess cylindrical symmetry. In other words, even when the liquid-crystal system is such that the nematic phase obtained, e.g., by applying a sufficiently strong magnetic field perpendicular to the cholesteric axis is necessarily uniaxial, there will exist biaxiality in the cholesteric phase as a consequence of its twist. Recently, Yaniv and co-workers[3,4] have reported the observation of rather strong biaxiality in cholesterics and have identified a dominant twist- or phase-induced contribution. Subsequently, Lin-Liu and Lee[5] carried out a molecular-field calculation of twist-induced biaxiality using a simple molecular model and the Maier-Saupe approach. Independently, we showed[6] that this biaxiality could be studied theoretically using Landau theory. Here, we further develop the Landau theory of twist-induced biaxiality and compare our results with those obtained experimentally and by the Maier-Saupe method.

An appropriate order parameter to describe a transition to an ordered phase in cholesteric liquid-crystal systems is the anisotropic part of the dielectric tensor,

$$\epsilon_{ij}(\vec{r})=\epsilon_{ij}^{d}(\vec{r})-\tfrac{1}{3}\mathrm{Tr}(\epsilon^{d})\delta_{ij}\ . \qquad (1)$$

In terms of ϵ_{ij} the average free energy density takes the form[7]

$$F=V^{-1}\int d\vec{r}\,\{\tfrac{1}{2}[a\epsilon_{ij}^2+c_1\epsilon_{ij,l}^2+c_2\epsilon_{ij,i}\epsilon_{lj,l}-2de_{ijl}\epsilon_{in}\epsilon_{jn,l}] -\beta\epsilon_{ij}\epsilon_{jl}\epsilon_{li}+\gamma(\epsilon_{ij}^2)^2\}\ , \qquad (2)$$

where a is proportional to a reduced temperature, c_1, c_2, d, β, and γ are temperature independent, $\epsilon_{ij,l}=\partial\epsilon_{ij}/\partial x_l$, and we sum on repeated indices. Thermodynamic stability requires that c_1, γ, and[6] $c_1+\frac{2}{3}c_2$ all be positive. Note that we could equally well formulate all our arguments in terms of, e.g., the anisotropic part of the magnetic susceptibility tensor. Within the framework of the Landau free energy given in (2) the choice of order parameter does not affect the results or conclusions.

The usual helicoidal cholesteric phase (C) is characterized by a single nonzero wave vector and has the form of a transverse spiral. For such a system the order parameter $[\epsilon^{(C)}(\vec{r})]$ takes the exact form[6]

$$[\epsilon^{C}(\vec{r})]=-\frac{1}{\sqrt{6}}\epsilon_0\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&2\end{pmatrix} +\frac{1}{2\sqrt{2}}\epsilon_2\left[e^{i(q_Cz+\psi)}\begin{pmatrix}1&i&0\\i&-1&0\\0&0&0\end{pmatrix}+\text{c.c.}\right]\ , \qquad (3)$$

where c.c. denotes the complex conjugate. Substituting (3) into (2) and minimizing F with respect to q_C, we obtain[6] $q_C=d/c_1$ and

$$F_C=\tfrac{1}{2}\left[a\epsilon_0^2+\left(a-\frac{d^2}{c_1}\right)\epsilon_2^2\right] +\frac{1}{\sqrt{6}}\beta(\epsilon_0^3-3\epsilon_0\epsilon_2^2)+\gamma(\epsilon_0^2+\epsilon_2^2)^2\ . \qquad (4)$$

Equation (4) is put into a more convenient form using the reduced quantities[6]

$$\begin{aligned}&\epsilon_i=s\mu_i,\quad s=\beta/\sqrt{6}\gamma,\quad f=F/(\beta^4/36\gamma^3)\ ,\\ &\tfrac{1}{4}t=(3\gamma/\beta^2)a,\quad \tfrac{1}{4}\xi_R^2=(3\gamma/\beta^2)c_1,\quad \kappa=q_C\xi_R\ .\end{aligned} \qquad (5)$$

Substituting (5) into (4) gives

$$f_C=\tfrac{1}{4}t\mu_0^2+\tfrac{1}{4}(t-\kappa^2)\mu_2^2+(\mu_0^3-3\mu_0\mu_2^2)+(\mu_0^2+\mu_2^2)^2\ . \qquad (6)$$

The meaning of t and ξ_R is easily understood by considering a racemic (R) mixture where $q_C=\kappa=0$. The quantity $f_R\equiv f_C(\kappa=0)$ is minimized when $\mu_2/\mu_0=\sqrt{3}$. Defining $\mu^2=\mu_0^2+\mu_2^2$ we then have $f_R=\frac{1}{4}t\mu^2-\mu^3+\mu^4$. From $f_R=\partial f_R/\partial\mu=0$, we find that the isotropic-racemic (I-R) phase boundary is at $t=t_R=1$. From (5) it then follows that ξ_R is the correlation length on the I-R phase boundary and our unit of reduced temperature is the difference between the $q_C=0$ thermodynamic and the extrapolated-from-the-disordered-phase transition temperatures.

A convenient measure of the biaxiality of a given system which is also accessible to experimental measurement is the asymmetry parameter $\eta=\eta(\vec{r})$ $(0\leq\eta\leq1)$. It is determined by diagonalizing the order-parameter matrix and rewriting it in the form

$$[\epsilon]=\bar{\epsilon}\begin{pmatrix}\frac{1}{2}(-1-\eta) & 0 & 0\\ 0 & \frac{1}{2}(-1+\eta) & 0\\ 0 & 0 & 1\end{pmatrix} . \tag{7}$$

In the C phase, $\eta=\eta_C$ is independent of $\vec{r}$. Setting

$$\mu_0=\mu\sin\theta,\ \mu_2=\mu\cos\theta\ , \tag{8}$$

we obtain from (3), (5), and (7)

$$\eta_C=1-4\tan\theta/(\sqrt{3}+\tan\theta)\ . \tag{9}$$

We thus need to determine $\tan\theta$ at a function of t and κ.

On the I-C phase boundary $(t-t_{IC})$, this is easily done. We substitute (8) into (6) and set $f_C=\partial f_C/\partial\mu=\partial f_C/\partial\theta=0$. After some algebra, we obtain

$$\tan[\theta(t_{IC},\kappa)]=\left[\frac{2-(1+\frac{1}{3}\kappa^2)^{1/2}}{2+(1+\frac{1}{3}\kappa^2)^{1/2}}\right]^{1/2} , \tag{10}$$

with

$$t_{IC}=\begin{cases}\frac{1}{2}[1+\kappa^2+(1+\frac{1}{3}\kappa^2)^{3/2}], & \kappa\leq3\\ \kappa^2, & \kappa>3\end{cases} . \tag{11}$$

For $t<t_{IC}$, $\tan\theta(t,\kappa)$ is determined by solving the pair of equations $\partial f_C/\partial\mu=\partial f_C/\partial\theta=0$. We obtain

$$\tan[\theta(t,\kappa)]=\left[\frac{36t-27\kappa^2-\kappa^4+\kappa^2[\kappa^4+54\kappa^2+9(9-8t)]^{1/2}}{108t-45\kappa^2+\kappa^4-\kappa^2[\kappa^4+54\kappa^2+9(9-8t)]^{1/2}}\right]^{1/2} . \tag{12}$$

This, of course, reduces to (10) for $t=t_{IC}$.

In Fig. 1, we show η_C as a function of κ for $t=t_{IC}$. For comparison with experiment, note that the C-phase Bragg reflection wavelength is $\lambda_C^{\mathrm{AIR}}=4\pi n/q_C=4\pi n\xi_R/\kappa$, where n is the index of refraction. Thus $\kappa=4\pi n\xi_R/\lambda_C^{\mathrm{AIR}}$. Typical values[8,9] of n and ξ_R are 1.6 and 25 nm, respectively, in which case $\kappa\simeq500/\lambda_C^{\mathrm{AIR}}$ (nm). We see from the figure that $\eta_C(t_{IC},\kappa)$ is a monotonically increasing function of κ. In other words, the twist- or phase-induced biaxiality of the cholesteric phase increases with decreasing pitch. However, it is now well known[10] that, as the C-phase pitch is decreased, an intermediate phase or phases appear between I and C [the so-called cholesteric blue (B) phases]. We therefore also show in Fig. 1 η_C as a function of κ for $t=t_{BC}$, the temperature at which the thermodynamic transition between the B and C phases occurs.[6] Since $\eta_C(t,\kappa)$ is a monotonically increasing function of t for fixed κ, experimentally attainable values of η_C are significantly smaller than those given by $\eta_C(t_{IC},\kappa)$ as κ is increased. That is, for those κ values at which blue phases exist between the disordered and C phases, $\eta_C(t_{IC},\kappa)$ is not physically attainable.

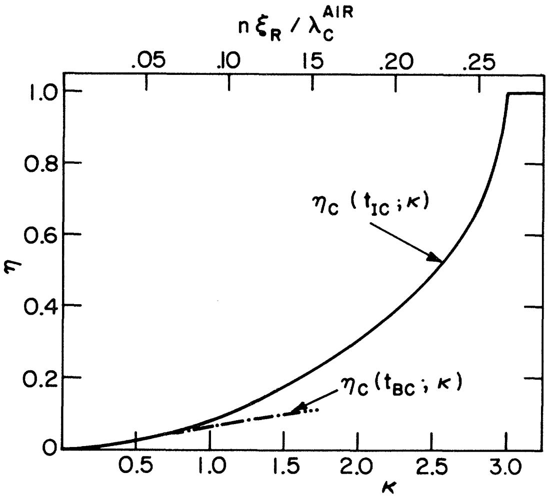

FIG. 1. The theoretical asymmetry parameter η_C in the cholesteric (C) phase as a function of the chirality parameter κ. Here λ_C^{AIR} is the C-phase Bragg backreflection wavelength in air, n is the index of refraction, and ξ_R is a racemic mixture correlation length at the phase transition. Results are given at t_{IC} and t_{BC}, the isotropic-cholesteric and blue-phase–cholesteric transition temperatures, respectively. The portion of the $\eta_C(t_{IC};\kappa)$ curve above $\eta_C(t_{BC};\kappa)$ is physically unattainable.

Experimental results for η_C are generally presented as a function of temperature with q_C (and, therefore, κ) regarded as essentially constant in the relatively small reduced temperature range in which measurements are made. We therefore present, in Fig. 2, the normalized asymmetry parameter ratios $\eta(t;\kappa)/\eta(t_{IC};\kappa)$ as a function of $t-t_{IC}$ for $\kappa=0.1$, 0.5, 1.0, 1.5, and 2.0. We find that the resulting curves, to an excellent approximation, are *universal*, i.e., they are essentially κ independent.

We now turn to the experimental results of Yaniv and co-workers[3,4] on mixtures for the asymmetry parameter. Their most striking feature is the high η_C values (up to 0.35 near T_{IC}) reported. These are considerably greater than those predicted by the Landau theory. As a specific example, Yaniv and co-workers[3,4] find, at T_{IC}, $\eta_C=0.13$ for a mixture of 4-methoxybenzylidene-4′-butylaniline (MBBA) and chiral 4-methoxybenzylidene-4′-[(+)-2-methylbutyl]-

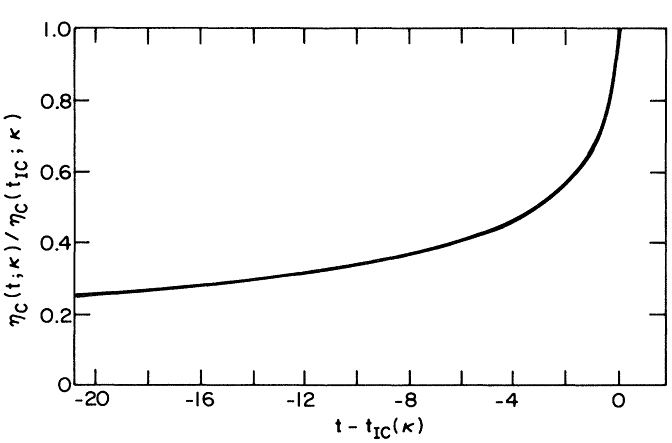

FIG. 2. The theoretical normalized asymmetry parameter $\eta_C(t)/\eta_C(t_{IC})$ as a function of temperature for $\kappa=0.1$, 0.5, 1.0, 1.5, 2.0. The five curves are essentially indistinguishable.

aniline (MBMBA). This mixture was found[3] to have a pitch of 1.4 μm which corresponds to a value (for $\xi_R = 25$ nm) of $\kappa = 0.22$. Using (9) and (10), we see that $\kappa = 0.22$ the Landau model yields a value for the asymmetry parameter which is an order of magnitude smaller than that found experimentally. Another discrepancy is provided by the observation of Yaniv and co-workers[3,4] that the cholesteric- to blue-phase transition occurs when $\eta_C \simeq 0.35$ in a wide range of materials. Theoretically (see Fig. 1), we find that η_C at this transition is considerably smaller ($\simeq 0.1$).

The reasons for these disagreements are not clear. Since real molecules are not cylindrical in shape, one possibility is that molecular as well as twist biaxiality contributes to the experimental asymmetry parameter. However, Yaniv and co-workers[3,4] argue that the molecular contribution is small in the systems which they studied. More serious, perhaps, is that all measurements were carried out on mixtures and η_C was measured at a specific site on one component of the system only. However, it is difficult to see this local η could differ considerably from that given here. Even if this were the case, we might still expect that the *temperature dependence* of the measured asymmetry parameter should be the same as that found theoretically. In order to examine this point we give, in Fig. 3, a portion of the theoretical curves of Fig. 2 together with normalized experimental results taken from Ref. 3. The theoretical and experimental temperature scales were matched by fitting the experimental point at $\eta_C(t)/\eta_C(t_{IC}) = \frac{1}{2}$ to the theoretical curve. We see that the experimental asymmetry parameter values are in reasonable agreement with the theoretical results, the main discrepancy being at lower temperatures where the data points lie significantly below the theoretical curves. This could possibly be a consequence of the technique used in obtaining the experimental values of η_C from the measurements; in particular, Yaniv *et al.*[3,4] assumed that the magnitude of the order-parameter (μ in our notation) could be taken as κ independent and used the values for the nonchiral compound.

Turning to the Maier-Saupe–type calculation of η_C carried out by Lin-Liu and Lee,[5] we find that their results are quite similar to ours. In particular (although they do not show this explicitly), their curves of η_C versus temperature, when suitably normalized, also show the quasiuniversality pointed out above. Their model also requires the introduction of a measure ϵ of the chiral interaction strength, which is analogous to our κ. However, Lin-Liu and Lee do not relate ϵ specifically to the two basic lengths—pitch and coherence length—as has been done here, but rather use ϵ as a free parameter in terms of which their model results are adjusted to fit the experimental data.

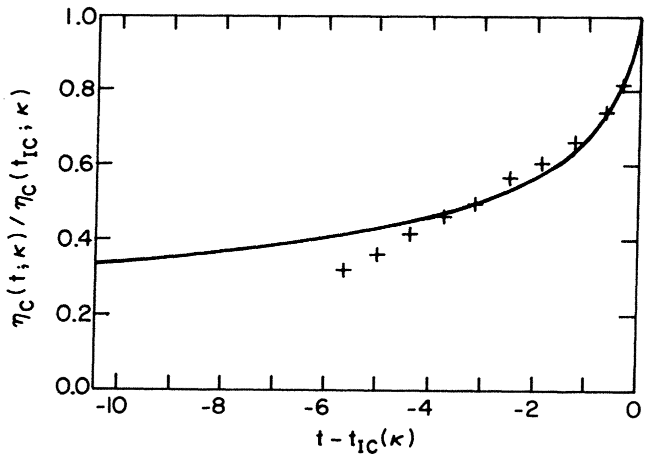

FIG. 3. Curves as in Fig. 2. Also shown are experimental results (+) taken from Yaniv, Vaz, Chidichimo, and Doane (Ref. 3).

In conclusion, it is clear that both Landau and Maier-Saupe models yield results for the temperature dependence of twist-induced biaxiality which are qualitatively similar to those reported experimentally. However, the magnitude of the measured results is significantly greater than our theoretical prediction. Additional experimental results, in particular on single component systems, could help to resolve this puzzle.

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