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Molecular field theory of phase-induced biaxiality in cholesteric liquid crystals

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The anisotropy of orientational order in cholesteric liquid crystals is investigated within a mean-field model of the cholesteric phase. It is shown that this biaxiality emerges as a direct consequence of the helical structure of the phase and the chiral character of the intermolecular interactions. The dependence of the biaxiality on temperature and pitch is compared with recent NMR measurements.

In the canonical uniaxial nematic- and smectic-*A* phases of liquid crystals, there is one direction in space along which the molecules preferentially orient. It is also theoretically possible[1,2] that molecules which are not axially symmetric will exhibit a biaxial nematic phase where the "flat faces" of the molecules align along a second preferred direction perpendicular to the first. No biaxial thermotropic nematics have been observed, but Saupe[3] has demonstrated the existence of biaxial lyotropic liquid crystals.

It has been known for some time that cholesteric liquid crystals could also exhibit biaxiality,[4,5] but only recently has this been observed in NMR experiments.[6] The experimental observation suggests that this biaxiality is not due to the noncylindrical nature of the molecule, but is almost entirely a consequence of the anisotropy of the orientational distribution parallel and perpendicular to the pitch axis. This phase-induced biaxiality prompts us to consider a molecular-field model of the Maier-Saupe[7] type for molecules with uniaxial symmetry and a chiral interaction only.

We shall build upon a simple molecular model of the cholesteric phase introduced by Shih, Woo, Tan, and one of us.[8] The model begins with prototype nematogenic rigid molecules which are structurally cylindrically symmetric. Superimposed on this symmetry is a chirality that gives a sense of "handedness" to the molecules. Such a picture is equivalent to one presented by Van der Meer.[9] The lowest-order contributions to the intermolecular potential which are sufficient to induce the cholesteric phase are[8,9]

$$V(1,2) \cong V_0(r_{12}) + V_N(r_{12}) P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2) + V_X(r_{12}) P_1(\hat{\Omega}_1 \cdot \hat{\Omega}_2)(\hat{r}_{12} \cdot \hat{\Omega}_1 \times \hat{\Omega}_2) \ . \tag{1}$$

Here $\hat{\Omega}$ is a unit vector, indicating the orientation of the molecule. Terms depending on $\hat{\Omega}_1 \cdot \hat{r}_{12}$ have not been included in this lowest-order expansion, because they are not required by the symmetry of the cholesteric phase, but are probably more important in the smectic phases.

With this "minimal symmetry" potential, we are now in a position to write down the standard mean-field approximation for the Helmholtz free energy,

$$\mathcal{F}[f(\vec{r}, \hat{\Omega}) \,|\, T, \rho] = \mathcal{F}_0(T, \rho) + \tfrac{1}{2}\rho^2 \int f(\vec{r}_1, \hat{\Omega}_1) f(\vec{r}_2, \hat{\Omega}_2) V(1,2)\, d\vec{r}_1\, d\hat{\Omega}_1\, d\vec{r}_2\, d\hat{\Omega}_2 + \rho k T \int f(\vec{r}, \hat{\Omega}) \ln 4\pi f(\vec{r}, \hat{\Omega})\, d\vec{r}\, d\hat{\Omega} \ , \tag{2}$$

where $\rho = N/V$ is the average number density, and the one-particle distribution function is $f(\vec{r}, \hat{\Omega})$. The minimization of $\mathcal{F}$ will give the usual mean-field self-consistency condition.

The degree of local orientational order for a given $f(\vec{r}, \hat{\Omega})$ can be specified by the traceless symmetric tensor $Q_{\alpha\beta}(\vec{r})$,

$$Q_{\alpha\beta}(\vec{r}) \equiv \int d\Omega\, f(\vec{r}, \hat{\Omega}) (\tfrac{3}{2}\Omega_\alpha \Omega_\beta - \tfrac{1}{2}\delta_{\alpha\beta}) \equiv \langle \tfrac{3}{2}\Omega_\alpha \Omega_\beta - \tfrac{1}{2}\delta_{\alpha\beta} \rangle_\Omega \ . \tag{3}$$

Here Ω_α is the Cartesian component of the molecular orientation vector $\hat{\Omega} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ at position $\vec{r}$.

In the cholesteric phase, the *magnitude* of the orientational order is uniform, but the twist causes the local director to change as a function of position. To describe this variation, we will establish at each point in the phase a local Cartesian coordinate system defined by three mutually orthogonal unit vectors $\hat{l}(\vec{r})$, $\hat{m}(\vec{r})$, $\hat{n}(\vec{r})$. These are to be chosen so that the local order-parameter tensor is diagonal. Let S_{xx}, S_{yy}, and S_{zz} be these diagonal elements (constants independent of position); then globally the order-parameter tensor is

$$Q_{\alpha\beta}(\vec{r}) = S_{xx} l_\alpha(\vec{r}) l_\beta(\vec{r}) + S_{yy} m_\alpha(\vec{r}) m_\beta(\vec{r}) + S_{zz} n_\alpha(\vec{r}) n_\beta(\vec{r}) \ . \tag{4}$$

The "local nematic" order parameters are now $S = S_{zz}$ and $\Delta = S_{xx} - S_{yy}$ and a nonzero Δ indicates a biaxial phase.

We now proceed to write the free-energy as an explicit function of the order parameters. Using the definition of

$Q_{\alpha\beta}(\vec{r})$ given in Eq. (3), the average over Ω_1 and Ω_2 of the last two terms of the potential given in Eq. (1) is easily carried out to yield

$$\tfrac{9}{4}\langle \hat{r}_{12}\cdot(\hat{\Omega}_1\times\hat{\Omega}_2)(\hat{\Omega}_1\cdot\hat{\Omega}_2)\rangle_{\Omega}=\epsilon_{\alpha\beta\gamma}\hat{r}_{12\alpha}Q_{\beta\delta}(\vec{r}_1)Q_{\gamma\delta}(\vec{r}_2),$$
$$\tfrac{3}{2}\langle P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)\rangle_{\Omega}=Q_{\alpha\beta}(\vec{r}_1)Q_{\alpha\beta}(\vec{r}_2)\quad . \tag{5}$$

Using Eq. (4), the magnitude of the orientational order may explicitly be separated from the position dependence. We may now choose any texture by specifying the spatial dependence of $\hat{l}$, $\hat{m}$, $\hat{n}$, and then minimize the free energy only with respect to the orientational order parameters.

For the special case of a helical texture with the pitch along the x axis, $\hat{l}$ is constant and

$$\hat{m}(\vec{r})=(0,\cos qx,\sin qx)\quad ,$$
$$\hat{n}(\vec{r})=(0,-\sin qx,\cos qx)\quad . \tag{6}$$

The following expression for the orientational contribution to the free energy per molecule in the cholesteric phase it obtained:

$$\frac{F}{N}=\frac{\rho}{3}\int d\vec{r}\,V_N(r)[S_{xx}^2+(S_{yy}^2+S_{zz}^2)\cos^2 qx+2S_{yy}S_{zz}\sin^2 qx]+\frac{\rho}{9}\int d\vec{r}\,\frac{V_\chi(r)}{r}(S_{zz}-S_{yy})^2 x\sin 2qx+kT\langle \ln 4\pi f\rangle_{\Omega}\quad . \tag{7}$$

The pitch of a cholesteric is much greater than the molecular dimensions, and hence it is possible to treat the expression for the free energy in the long-wavelength limit when $qR \gg 1$ with R being a characteristic range of the potential. Then

$$\frac{F}{N}=kT\langle \ln 4\pi f\rangle - A\left[S^2+\frac{\Delta^2}{3}\right]+Bq^2\left[S+\frac{\Delta}{3}\right]^2-2qC\left[S+\frac{\Delta}{3}\right]^2\quad , \tag{8}$$

where we have defined

$$A=-\frac{\rho}{2}\int V_N(\vec{r})\,d\vec{r}\quad ,$$
$$B=-\frac{3}{4}\rho\int V_N(\vec{r})x^2\,d\vec{r}\quad , \tag{9}$$
$$C=-\frac{\rho}{4}\int dr\,V_\chi(\vec{r})\frac{x^2}{r}\,d\vec{r}\quad .$$

Within the mean-field approximation, the entropy $\langle \ln 4\pi f\rangle_{\Omega}$ depends only on the local order and is independent of pitch.[4] The optimum pitch q_0 can be obtained by minimizing the potential energy with respect to q,

$$q_0=\frac{C}{B}=\frac{2\pi}{P}\quad . \tag{10}$$

The pitch is as expected, inversely proportional to the strength of the chiral potential, and proportional to the twist elastic term of the nematic (P_2) part of the interaction.

Using the equilibrium value of the pitch, the free energy becomes

$$\frac{F}{N}=kT\langle \ln 4\pi f\rangle - A(S^2+\tfrac{1}{3}\Delta^2)-\frac{C^2}{B}(S+\tfrac{1}{3}\Delta)^2\quad . \tag{11}$$

The free energy may be minimized with respect to f in the usual fashion,

$$\frac{\delta}{\delta f}\left[\frac{F}{N}-\lambda\int f(\Omega)\,d\Omega\right]=0\quad , \tag{12}$$

to yield

$$f(\theta,\phi)=\frac{e^{g(\theta,\phi)}}{\int d\Omega\, e^{g(\theta,\phi)}}\quad , \tag{13}$$

where

$$g(\theta,\phi)=\frac{P_2(\cos\theta)}{kT}\left[2AS+\frac{2C^2}{B}(S+\tfrac{1}{3}\Delta)\right]+\frac{3}{2}\frac{\sin^2\theta\cos 2\phi}{kT}\left[\frac{2}{3}A\Delta+\frac{2}{3}\frac{C^2}{B}(S+\tfrac{1}{3}\Delta)\right]. \tag{14}$$

This result, with the definition of S and Δ,

$$S=\int f(\theta,\phi)P_2(\cos\theta)\,d\Omega\quad ,$$
$$\Delta=\int f(\theta,\phi)\tfrac{3}{2}\sin^2\theta\cos 2\phi\,d\Omega\quad , \tag{15}$$

yields a set of self-consistent equations which can be solved for S and Δ given a reduced temperature $\tau=kT/A$, and a measure of the chiral interaction strength $\epsilon=C^2/BA$.

Figures 1 and 2 show experimental[6,10] and theoretical results for the biaxial parameter[11] $\eta=\Delta/S$, as a function of temperature in systems of different chiral strength. We note that the two sets of results share several qualitative features.

(i) The biaxiality is positive. If a nematic ($C=0$) is twisted mechanically, then minimizing Eq. (8) with fixed q yields an identical mean-field potential except that ϵ becomes $-B/A$. The resulting biaxiality is negative.

(ii) The biaxiality is a monotonically increasing function of temperature, with a noticeably larger rate of increase just below T_c (due to part to the opposite behavior of S). This is to be distinguished from the behavior of other order parameters as calculated by Straley,[2] which exhibit a maximum below T_c.

(iii) The biaxiality increases with increasing chiral strength, i.e., tighter pitches.

(iv) The Maier-Saupe order parameter S does not change much when biaxiality is included. This feature is consistent with optical data.[12] We observed that the shape of S vs T changed very little, but its value at the transition did decrease from the usual nematic mean-field result of $S_c \approx 0.44$ to the mean-field maximum supercooled result of $S_{sc} \approx 0.33$ when ϵ increased to 0.3–0.4.

Although the experimental agreement is encouraging, one cannot say that this is a rigorous test of the theoretical approach presented here. Firstly, the real molecules are not cylindrical in shape, so that in general two more order parameters, one biaxial and one uniaxial, should be includ-

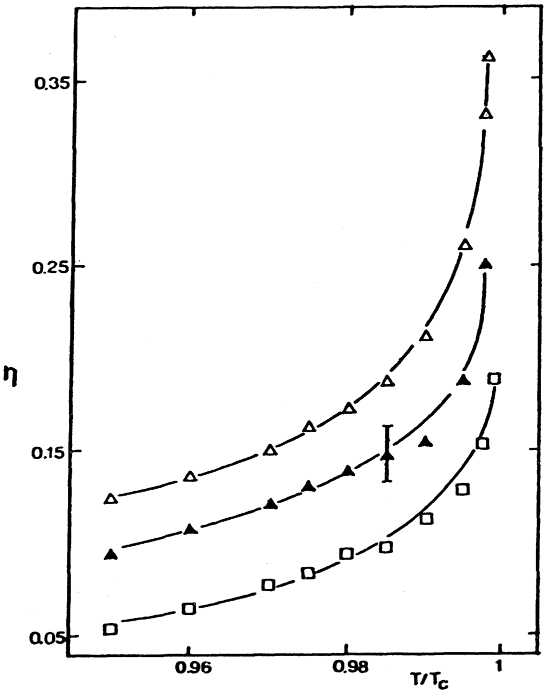

FIG. 1. Experimental results for the temperature dependence of the biaxiality parameter $(S_{xx}-S_{yy})/S_{zz}=\eta$ for mixtures of 4-methoxybenzylidene-4′-butylaniline (MBBA) and 4-methoxybenzylidene-4′-[(+)-2-methylbutyl]aniline (MBMBA) from Refs. 6 and 10: (□) 21.8 wt.% MBMBA; (Δ) 30 wt.% MBMBA; (Δ) 40 wt.% MBMBA.

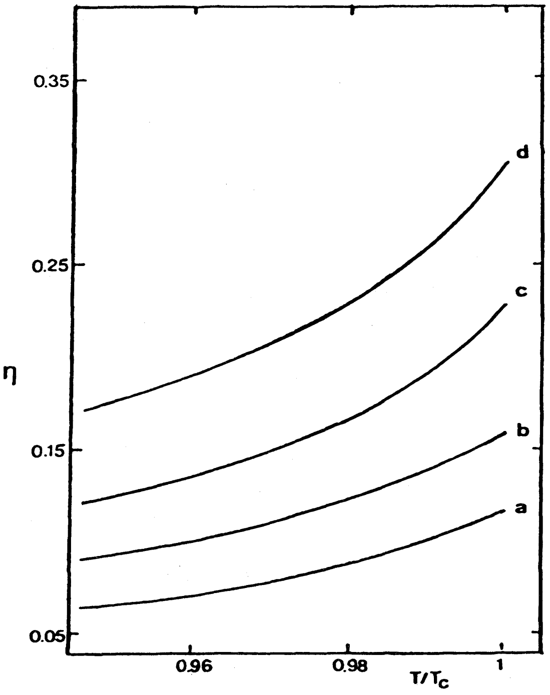

FIG. 2. Temperature dependence of the calculated biaxiality parameter at various values of the chiral strength parameter ϵ: (a) $\epsilon=0.2$; (b) $\epsilon=0.3$; (c) $\epsilon=0.4$; and (d) $\epsilon=0.7$.

ed.[2] For the particular experimental system considered, the order parameter which reflects the noncylindrical character of the molecule was negligibly small,[10] thus encouraging the application of our model. Secondly, and possibly more importantly, the experimental results are for a mixture of chiral and nonchiral molecules, the biaxiality being measured only for the nonchiral constituent. Here we have only conjectured that ϵ must increase as the concentration of the chiral component increases.

Finally, the simplicity of mean-field theory and our minimum symmetry potential are unable to reconcile macrosocpic observables such as elastic constants with microscopic order parameters. Attempts to estimate $\epsilon=C^2/BA=q_0^2(B/A)$ from knowledge of the pitch $(3\times10^{-7}\text{ m})$, twist elastic constants $[B=K_{22}(V/N)S^2\cong2\times10^{-38}\text{ J m}^2]$, and the transition temperature $(\tau_c=0.22,\ A=10^{-20}\text{ J})$ yield values of ϵ far too small $(\epsilon\approx10^{-3})$. One may, of course, argue that the fluctuations are collective as in swarm theory and ϵ should be scaled by the number of correlated molecules. In the absence of a theoretical treatment incorporating such correlations, we suggest that mean-field theory has demonstrated a mechanism for phase-induced biaxiality in cholesterics and yields the correct qualitative behavior of the order as a function of temperature and pitch.

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