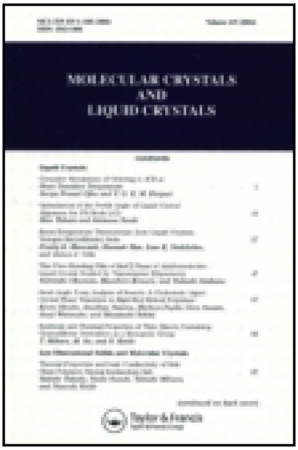

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THEORY OF MAGNETIC FIELD EFFECTS AND BIAXIAL ORDER IN CHOLESTERIC LIQUID CRYSTALS

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A molecular field theory capable of treating cholesterics with spatially varying order is developed. Results for the biaxial order of a cholesteric distorted by a magnetic field are presented.

1. INTRODUCTION

It has been understood for some time[1,2] that a cholesteric liquid crystal should be biaxial because of the symmetry of the phase. The presence of the pitch axis defines a direction in space perpendicular to the local director and breaks the cylindrical symmetry of the environment of a cholesteric molecule. The actual mechanism causing the biaxiality could result from the fact that the molecules themselves are not cylindrically symmetric[1] or could result from an asymmetry of the orientation distribution of the long molecular axis. This latter biaxiality is a result of the phase symmetry rather than molecular shape and we will refer to it as phase-induced biaxiality. Lin-Liu and Lee[3] have recently discussed the role of phase-induced biaxiality in undistorted cholesterics. The experiments of Yaniv et. al.[4] are in general agreement with the theoretical results and support the contention that phase-induced biaxial orientational order rather than molecular shape plays the dominant role.

2. MOLECULAR FIELD THEORY

It is convenient to develop the mean field theory starting from an approximate expression for the Helmhotz free energy in terms of the one particle distribution function $f(\vec{r},\Omega)$.

$$\begin{aligned} F(f(\vec{r},\Omega)\,|\,T,\rho) &= F_o(T,\rho) \\ &+ \frac{1}{2}\rho^2 \int f(\vec{r}_1,\hat{\Omega}_1)\, f(\vec{r}_2,\hat{\Omega}_2)\, V(1,2)\, d\vec{r}_1 d\vec{r}_2\, d\hat{\Omega}_1 d\hat{\Omega}_2 \\ &+ \rho kT \int f(\vec{r},\hat{\Omega}) \ln 4\pi f(\vec{r},\hat{\Omega})\, d\vec{r}\, d\hat{\Omega} \end{aligned} \tag{1}$$

Here V(1,2) is the pair potential and any external field. Minimizing this functional with respect to f, subject to the normalization condition, yields the self-consistent mean field equations. If $V(1,2) = -A\,P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)$ then the well-known Maier-Saupe equation[5] for the nematic phase results. We will consider the two particle potential introduced by Lin-Liu, Shih, Woo and Tan,[6] which describes the interaction of two cylindrically symmetric chiral molecules.

$$\begin{aligned} V(1,2) &= V_o(r_{12}) + V_N(r_{12})\, P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2) \\ &+ V_X(r_{12})\, P_1(\hat{\Omega}_1\cdot\hat{\Omega}_2)\, (\vec{r}_{12}\cdot\hat{\Omega}_1 X \hat{\Omega}_2) \end{aligned} \tag{2}$$

The molecular interaction with an external field is incorporated by adding a potential

$$V_{ex}(\hat{\Omega}) = -\gamma(\hat{\Omega}\cdot\vec{H})^2, \tag{3}$$

γ being a measure of the anisotropy of the molecular polarizability.

3. ORDER PARAMETERS

The degree of orientational order at a position $\vec{r}$ in the cholesteric phase may be characterized in terms of the uniaxial order parameter S and the biaxial order parameter Δ, as

$$\begin{aligned} S(\vec{r}) &= Szz(\vec{r}) = \int f(\vec{r},\hat{\Omega})\, P_2(\cos\theta)\, d\Omega \\ \Delta(\vec{r}) &= Sxx(\vec{r}) - Syy(\vec{r}) = \int f(\vec{r},\hat{\Omega})\, \frac{3}{2} \sin^2\theta \cos 2\phi\, d\Omega \end{aligned} \qquad (4)$$

We will later employ the quantity $\eta = \Delta/S$ as a measure of biaxiality since this is more easily accessable experimentally.[4] The details of the determination of these order parameters for an undistorted cholesteric within the context of mean field theory are given in reference 3.

4. ELASTIC THEORY

The structure of a cholesteric distorted by a magnetic field has been considered previously by de Gennes[7] and Meyer[8] within the framework of elastic theory. The elastic free energy per unit volume contains only the twist contribution.

$$\frac{F}{V} = \frac{1}{L}\frac{1}{2}\int dx\, [K_{22}(\frac{d\psi}{dx} - q_o)^2 - \chi_a H^2 \sin^2\psi(x)] \qquad (5)$$

Here K_{22} is the twist elastic constant, χ_a is the anisotropic contribution to the susceptibility, q_o is the equilibrium pitch, and the magnetic field $\vec{H}$ is the Y-direction. This free energy expression assumes that the degree of local orientational order is unaffected by the local twist $q(x) \equiv d\psi/dx$ and the field H. These effects will be taken into account by the molecular field theory.

The solution for $\psi(x)$ is described by de Gennes.[7] An extension incorporating biaxiality has been discussed by Lin-Liu[9] in the case when the order parameters can be considered to be independent of position.

5. MEAN FIELD RESULTS

We will proceed with the minimization of the free energy in three stages. First, we will obtain the order parameters and pitch in the absence of the field. Secondly, the free energy will be minimized with respect to $\psi(x)$ while the order parameters Δ and S are held constant. The final step will be to let S and Δ relax due to the local pitch distortions. This procedure could be numerically iterated to convergence but it should become evident that this approximate minimization manifests the important behavior of the system.

In the absence of a magnetic field the free energy can be shown to reduce to[3]

$$\frac{F}{N} = kT \langle \ln 4\pi f \rangle - A\left(S^2 + \frac{\Delta^2}{3}\right) + Bq^2\left(S + \frac{\Delta}{3}\right)^2 - 2qC\left(S + \frac{\Delta}{3}\right)^2 \qquad (6)$$

where we have defined

$$A = -\frac{\rho}{2} \int V_N(r) d\vec{r}$$

$$B = -\frac{3}{4} \rho \int V_N(r) x^2 \, d\vec{r}$$

$$C = -\frac{\rho}{4} \int V_\chi(r) \frac{x^2}{r} \, d\vec{r}$$

Since S and Δ are position independent, we may minimize the potential energy with respect to q to obtain the equilibrium pitch $q_o = C/B$. Subsequent minimization to obtain the order parameters S_o and Δ_o of the undistorted cholesteric yields

$$f(\Omega) = \frac{e^{g(\theta,\phi)/\tau}}{\int d\Omega e^{g(\theta,\phi)/\tau}}$$

where

$$\begin{aligned} g(\theta,\phi) &= P_2(\cos\theta)\ (2\,S_o + 2\varepsilon_o\ (S_o + \Delta_o/3)) \\ &+ \frac{3}{2}\sin^2\theta\ \cos 2\phi\ (\frac{2}{3}\Delta_o + \frac{2}{3}\varepsilon_o\ (S_o + \Delta_o/3)) \end{aligned} \tag{7}$$

and

$$\varepsilon_o = C^2/BA, \quad \tau = kT/A.$$

The solutions for S_o and Δ_o as a function of reduced temperature τ and chiral strength ε_o are given in reference 3.

Keeping S_o and Δ_o fixed, the free energy of the distorted cholesteric becomes,

$$\begin{aligned} \frac{F}{N} &= kT\ \langle \ln 4\pi f\rangle - \frac{A}{L}\ (S_o^2 + \frac{\Delta_o^2}{3}) \\ &+ \frac{B}{L}\ (S_o + \frac{\Delta_o}{3})^2 \int_0^L [\psi'(x)^2 - 2q_o\ \psi'(x)]\ dx \\ &- \frac{B}{L}\,\frac{3}{2}\,(\frac{\gamma H^2}{B})\ (S_o + \frac{\Delta_o}{3}) \int_0^L \sin^2\psi(x)\ dx + \frac{\gamma^2 H^2}{2}\ (S_o + \Delta_o) \end{aligned} \tag{8}$$

Comparing this to the expression for the elastic free energy, Eq. 6, we identify

$$K_{22} = 2\rho\ \ B(S_o + \frac{\Delta_o}{3})^2 \text{ and } \chi_a = 3\rho\gamma(S_o + \frac{\Delta_o}{3}) \tag{9}$$

The $\psi(x)$ which minimizes F is then simply the de Gennes solution with the appropriate substitutions for K_{22} and χ_a.

Finally, the full free energy with spatially varying order parameters can be written in the form

$$\begin{aligned} \frac{F}{N} &= -\frac{A}{L}\int dx\ (S^2(x) + \frac{\Delta^2(x)}{3}) + \varepsilon(x)\ \ (S(x) + \frac{\Delta(x)}{3})^2 \\ &+ \frac{\gamma H^2}{L}\int dx\ (\frac{S(x) + \Delta(x)}{2}) - \frac{3}{2}\sin^2\psi(x)\ \ (S(x) + \frac{\Delta(x)}{3}) \\ &+ \frac{kT}{L}\int f(x,\Omega)\ \ln 4\pi\ f(x,\Omega)\ dx\ d\Omega \end{aligned} \tag{10}$$

where $\varepsilon(x) = \varepsilon_o\ (2q_o(x)/q_o - q^2(x)/q_o^2)$. When this functional is minimized to obtain the distribution function $f(x,\Omega)$. The result is

$$f(x,\Omega) \sim e^{g(x,\theta,\phi)/\tau}$$

where $g(x,\theta,\phi) =$

$$P_2(\cos\theta)[2S(x) + 2\varepsilon(x)\ (S(x) + \frac{\Delta(x)}{3}) - h^2(1-3\sin^2\psi(x))]$$
$$+ \frac{3}{2}\sin^2\theta\ \cos 2\phi[\frac{2}{3}\Delta(x) + \frac{2}{3}\varepsilon(x)\ (S(x) + \frac{\Delta(x)}{3}) - h^2\ (1-\sin^2\psi(x))] \quad (11)$$

and $h^2 = \varepsilon_o/(q_o\xi_o)^2$, $\xi_o = B/A$.

Comparing the mean field represented by $g(x,\theta,\phi)$ to the unperturbed mean field of Eq. 8, one sees that the effect of the distortion lowers the local chiral strength $\varepsilon(x)$ and the effect of the field is to make $\Delta(x)$ smaller. This reasoning suggests a global decrease in the biaxiality due to both effects. This is in agreement with the global prediction of Landau theory by Lin-Liu.[9] When the chiral strength ε_o is not small, the biaxial order parameter $\Delta(x)$ can vary significantly with position and even be enhanced over the unperturbed value. Figure 1 shows the behavior of the biaxiality parameter $\eta(x) = \Delta(x)/S(x)$ as a function of position along the pitch axis in several representative cases. The spatial variation is clearly significant in some circumstances.

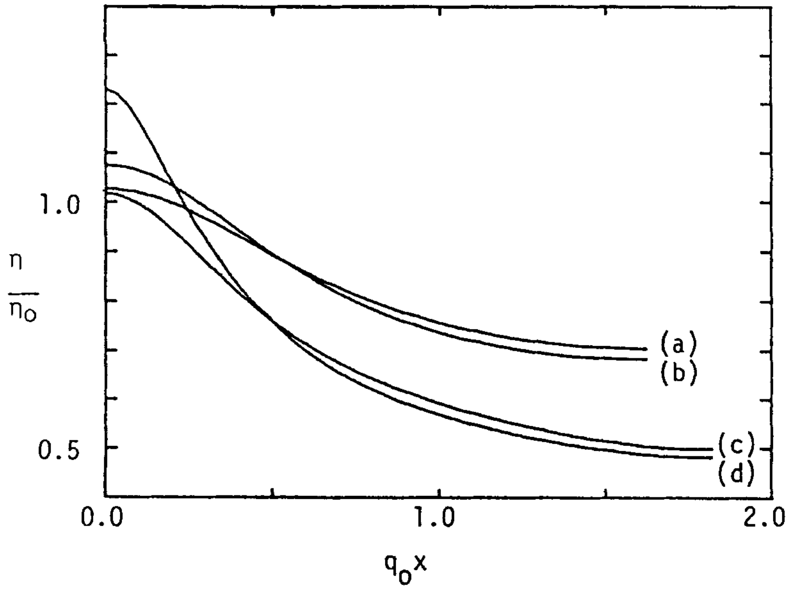

FIGURE 1. Biaxiality as a function of position for $\varepsilon_0 = 0.5$ and (a) $\tau=.45$, $h^2=.26$, (b) $\tau=0.5$, $h^2=.24$, (c) $\tau= .45$, $h^2=.49$, (d) $\tau=0.5$, $h^2=.46$. The reduced field h^2 and temperature τ are defined in the text.

6. CONCLUSION

Qualitatively, the effect of distorting the pitch causes the local biaxiality to be larger when the local pitch is short. The effect of the magnetic field is to decrease the anisotropy of the orientational distribution and is dominant unless the local pitch is significantly shorter than the equilibrium value.

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