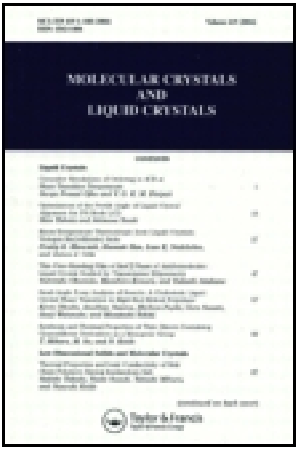

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Molecular Field Theory of Biaxial Order in Distorted Cholesteric Liquid Crystals

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Mean field theory in the form usually applied to homogeneous liquid crystals is shown to be applicable to biaxial cholesteric liquid crystals with spatially varying orientational order. The theory is applied to simple cholesteric textures.

INTRODUCTION

It has been noted that the biaxial order of cholesteric liquid crystals results primarily from the asymmetry of the orientational distribution of the long molecular axis rather than the cylindrical asymmetry of the molecules themselves.[1,2] Molecular field theories capable of treating undistorted cholesterics[2] and cholesterics distorted by magnetic field[3] have been developed and emphasize the role of the "phase-induced" biaxiality. Here we examine spatially varying biaxial order resulting from elastic distortions. The theory is relevant to cholesteric structures distorted by restricted geometries[4] or boundary conditions as well as current models of the blue phase.[5,6]

MOLECULAR FIELD THEORY

We develop the mean field theory starting from an approximate expression for the Helmholtz free energy, in terms of the one-particle

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distribution function $f(\vec{r},\hat{\Omega})$[7]

$$F[f(\vec{r},\hat{\Omega})|T,\rho] = F_0(T,\rho)$$

$$+ \frac{1}{2}\rho^2\int d\vec{r}_1 d\vec{r}_2 d\hat{\Omega}_1 d\hat{\Omega}_2\, f(\vec{r}_1,\hat{\Omega}_1) f(\vec{r}_2,\hat{\Omega}_2) V(1,2)$$

$$+ \rho kT\int d\vec{r} d\hat{\Omega}\, f(\vec{r},\hat{\Omega})\, \ell n 4\pi f(\vec{r},\hat{\Omega})$$

where $\rho = N/V$ is the average number density, $V(1,2)$ is the two particle potential, employed by Lin-Liu, Shih, Woo and Tan,[7] describing the interaction of two cylindrically symmetric chiral molecules.

$$V(1,2) = V_0(r_{12}) + V_N(r_{12})P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2)$$

$$+ V_\chi(r_{12})(\hat{\Omega}_1 \cdot \hat{\Omega}_2)(\hat{r}_{12} \cdot \hat{\Omega}_1 \times \hat{\Omega}_2).$$

This potential which depends on the molecular orientation vectors $\hat{\Omega}$, and the interpartical separation r_{12} in a simple fashion, has been shown to produce the biaxial character of cholesteric phases in earlier investigations.[1,2]

Minimizing the free energy with respect to the one particle distribution function $f(\vec{r},\ \hat{\Omega})$, yields the usual self consistent field equations. In carrying out the minimization it is customary to introduce the second rank order parameter tensor, $Q_{\alpha\beta}$,which in general is a function of position,

$$Q_{\alpha\beta}(\vec{r}) \equiv \left\langle \frac{3}{2}\,\Omega_\alpha\Omega_\beta - \frac{1}{2}\,\delta_{\alpha\beta} \right\rangle \equiv \int f(\vec{r},\,\hat{\Omega})\left(\frac{3}{2}\,\Omega_\alpha\Omega_\beta - \frac{1}{2}\,\delta_{\alpha\beta}\right) d\hat{\Omega}.$$

With these definitions, the potential energy takes the form of an orientation independent contribution, PE_0, plus terms involving $Q_{\alpha\beta}$.

$$PE = PE_0 + \frac{1}{3}\rho^2\int d\vec{r}_1 d\vec{r}_2\, V_N(\vec{r}_{12})\, Q_{\alpha\beta}(\vec{r}_1)\, Q_{\alpha\beta}(\vec{r}_2)$$

$$+ \frac{2}{9}\rho^2\int d\vec{r}_1 d\vec{r}_2\, \frac{V_\chi(r_{12})}{r_{12}}\, \epsilon_{\alpha\beta\gamma}\, r_{12_\alpha}\, Q_{\beta\delta}(\vec{r}_1)\, Q_{\gamma\delta}(\vec{r}_2).$$

The connection with elastic theory is readily made in the long wavelength limit. We assume the $Q_{\alpha\beta}$ does not change appreciably over the range of the potential and is locally well approximated by a Taylor series expansion.

$$Q_{\alpha\beta}(\vec{r} + \vec{x}) \cong Q_{\alpha\beta}(\vec{r}) + x_i \frac{\partial}{\partial r_i} Q_{\alpha\beta}(\vec{r}) + \frac{1}{2} x_i x_j \frac{\partial}{\partial r_i} \frac{\partial}{\partial r_j} Q_{\alpha\beta}(\vec{r})$$

This is consistent with and analogous to the argument in the standard elastic theory that the local free energy must be positive definite and quadratic in the distortion.

With this approximation the potential energy is

$$\begin{aligned} PE = PE_0 &- \frac{2}{3} A\rho \int d\vec{r}\, Q_{\alpha\beta}(\vec{r})\, Q_{\alpha\beta}(\vec{r}) \\ &- \frac{2}{9} B\rho \int d\vec{r}\, Q_{\alpha\beta}(\vec{r})\, \partial_\mu \partial_\mu Q_{\alpha\beta}(\vec{r}) \\ &- \frac{8}{9} C\rho \int d\vec{r}\, \epsilon_{\alpha\beta\gamma}\, Q_{\beta\delta}(\vec{r})\, \partial_\alpha Q_{\gamma\delta}(\vec{r}) \end{aligned}$$

where

$$A = -\frac{1}{2}\rho \int d\vec{r}\, V_N(\vec{r})$$

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

$$C = -\frac{1}{4}\rho \int d\vec{r}\, V_\chi(\vec{r}) \frac{x^2}{r}.$$

This expression is now in the form of the integral of a potential energy density. It is essentially identical to a Landau expansion for a cholesteric except that it lacks a term like $\partial_\mu Q_{\alpha\beta} \partial_\alpha Q_{\mu\beta}$. In this manner of arriving at the density however, the origin of the coefficients is given in terms of moments of the potential and thus have a well defined density dependence and temperature independence. The particular role that these constants play in determining the physical parameters of the material can be made clearer by considering particular textures.

In order to investigate a particular texture, it is useful to work with a local cartesian coordinate system constructed at each point in space such that the order parameter tensor is diagonal at that local coordinate system. The direction of the local coordinate axes is specified by three unit vectors, the director $\hat{n}(\vec{r})$, the pitch $\hat{\ell}(\vec{r})$ and the perpendicular vector $\hat{m}(\vec{r}) = \hat{n}(\vec{r}) \times \hat{\ell}(\vec{r})$, and define the local z, x, and y cartesian coordinates of a diagonal reference frame. The order parameter tensor is then

$$Q_{\alpha\beta}(\vec{r}) = S_{xx}(\vec{r})\, \ell_\alpha(\vec{r})\ell_\beta(\vec{r}) + S_{yy}(\vec{r})\, m_\alpha(\vec{r})\, m_\beta(\vec{r}) + S_{zz}(\vec{r}) n_\alpha(\vec{r}) n_\beta(\vec{r})$$

where $S_{zz} \equiv S$, the usual Maier-Saupe[8] uniaxial order parameter, and $S_{xx} - S_{yy} \equiv \Delta$, the biaxial order parameter.

For a uniform cholesteric with its pitch along the z-axis, the unit vectors are given by

$$\hat{\ell} = \hat{k}$$

$$\hat{n} = \hat{i} \cos qz + \hat{j} \sin qz$$

where $\psi = qz$ is the angle formed between the local director, or average of the long molecular axis, and the z-axis. The free energy takes on the simple form

$$\frac{F}{N} = \frac{kT}{L} \int_0^L dz d\Omega f(z,\Omega) \ln 4\pi f(z,\Omega) - A\left(s^2 + \frac{\Delta^2}{3}\right)$$
$$+ Bq^2(s + \Delta/3)^2 - 2qC(s + \Delta/3)^2.$$

For the equilibrium structure, the twist of the cholesteric is uniform, or the angle is linear in z, i.e. $\psi = q_0 z$, where $P = 2\pi/q_0$ is the pitch. The angular integration in the entropy term yields a result which is position independent, hence a function of the local values of the order parameters only. Minimizing F with respect to q to obtain q_0 yields

$$q_0 = C/B.$$

It is interesting to note that this result is order parameter independent, hence temperature independent,[7] as well as independent of whether the system is uniaxial or biaxial. The term in the free energy proportional to q^2 can be identified as a "bare" twist elastic constant

$$K_{22} = 2B\rho S^2$$

by comparing the expression for the potential energy to the standard distortion free energy of the cholesteric,[9]

$$F_d = \frac{1}{2}\int K_{22}(\hat{n} \cdot \vec{\nabla} x\hat{n} - q_0)^2 dV.$$

We refer to this as a bare elastic constant, because it only reflects changes in the potential energy and does not incorporate entropy changes.

This simple theory has been shown previously[2] to yield the biaxial order parameter for the cholesteric in qualitative agreement with experiment.[1] The predictions for the ratio Δ/S are shown in Figure 1. Qualitative features of the results worth noting include the obser-

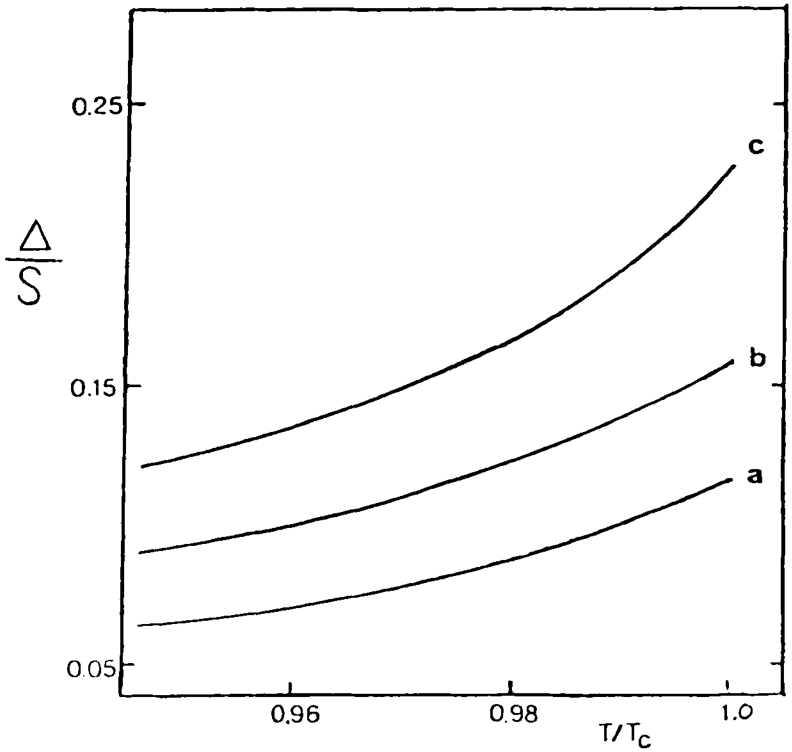

FIGURE 1 Temperature dependence of the ratio of the biaxial order parameter to the uniaxial order parameter for three values of the chiral strength. (a) $\epsilon = 0.2$; (b) $\epsilon = 0.3$; (c) $\epsilon = 0.4$.

vation that the biaxial order is a maximum at the transition temperature.

The simplest distortion of cholesteric is the imposition of a uniform twist $q \neq q_0$. The potential energy can then be written

$$PE = -A\left\{\left(s^2 + \frac{\Delta^2}{3}\right) + \epsilon\left[1 - \left(\frac{q - q_0}{q_0}\right)^2\right](s + \Delta/3)^2\right\}.$$

The effect is such as to decrease the effective strength of the chiral interaction. From Figure 1, we see that this results in a decrease in the degree of biaxial order.

The uniform cholesteric gives some insight into the molecular origins of the twist elastic constant. Arbitray distortions involve derivatives of both the directors $\hat{\ell}$, $\hat{m}$ and $\hat{n}$ and the order parameters S and Δ. The potential energy for arbitary distortions is given by

$$\begin{aligned} PE = -\rho\int d\vec{r}A[&S^2(\vec{r}) + 3\Delta^2(r) \\ &+ \frac{B}{9}[3(\vec{\nabla}S)^2 + (\vec{\nabla}\Delta)^2 + (9S^2 - \Delta^2)(\hat{n}\cdot\nabla^2\hat{n}) \\ &+ 2\Delta(3S - \Delta)(\hat{\ell}\cdot\nabla^2\hat{\ell}) - 2\Delta(3S + \Delta)(\hat{m}\cdot\vec{\nabla}^2\hat{m})] \\ &- \frac{2c}{9}[9S^2(\hat{n}\cdot\vec{\nabla}x\hat{n}) + 6S\Delta(\hat{m}\cdot\vec{\nabla}x\hat{m} - \hat{\ell}\cdot\vec{\nabla}x\hat{\ell}) \\ &+ \Delta^2(2\hat{m}\cdot\vec{\nabla}x\hat{m} + 2\hat{\ell}\cdot\vec{\nabla}x\hat{\ell} - \hat{n}\cdot\vec{\nabla}x\hat{n})]. \end{aligned}$$

The connection between this expression and uniaxial elastic theory can be made manifest when the order parameters are constant in magnitude and $\Delta = 0$. In that case the change in free energy is only due to the change in potential energy,[2] and becomes

$$\Delta F = -\frac{K}{2}\int d^3r\,(\hat{n}\cdot\nabla^2\hat{n}) + 2q_0\,\hat{n}\cdot\vec{\nabla}x\hat{n}$$

where we have identified $K = 2BS^2\rho$ as an elastic constant. It is easily shown, that except for surface terms, and an additive constant, this expression is identical to the usual Oseen-Frank distortion free energy of a cholesteric,[9]

$$F_d = \frac{1}{2}\int d\vec{r}\, K_1\,(\vec{\nabla}\cdot n)^2 + K_2(\hat{n}\cdot\vec{\nabla}x\hat{n} + q_0)^2 + K_3(\hat{n}x\vec{\nabla}x\hat{n})^2$$

when the equal constant approximation $K_1 = K_2 = K_3 = K$ is valid. One may raise the question of whether the equal constant prediction of mean field theory is primarily a consequence of the meanfield approximation or the simple two-body potential. This point remains to be investigated.

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