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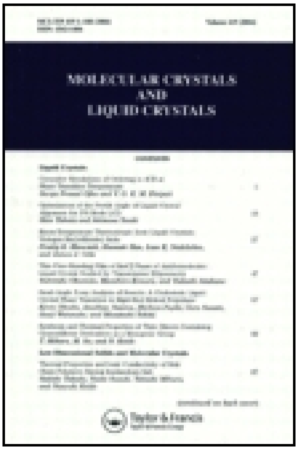

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Theory of the Change in Cholesteric Pitch Near Cholesteric–Smectic Phase Transitions†‡

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Abstract—The large change in pitch of cholesterics in the vicinity of a transition to a smectic phase is argued to be governed entirely by the behavior of the twist elastic constant, K_{22}. The twist constant increases rapidly near a smectic phase transition because of the coupling of the director $\mathbf{n}(\mathbf{r})$ with local smectic-like positional correlations. This coupling gives a rapidly increasing term in the energy of the form $(\mathbf{n}\cdot\nabla\times\mathbf{n})^2$. The other important energy term is of the form $\mathbf{n}\cdot\nabla\times\mathbf{n}$ and comes from chiral intermolecular interactions. We derive a mean field theory of a typical such interaction and obtain a contribution to the energy which is relatively insensitive to smectic-like order. We thus predict that, although both K_{22} and the pitch increase rapidly, the ratio of K_{22} to pitch should be constant near the transition to the smectic phase.

1. Introduction

The thermally induced color change of cholesterics is one of the most striking of liquid crystal effects⁽¹⁾; for many materials, the color changes from a bright blue to a deep red in a temperature range of less than one degree. It now seems apparent⁽²,³⁾ that this rapid change in color is really a " pretransition effect "; it occurs as the cholesteric helix unwinds with decreasing temperature just before a transition from the cholesteric to a smectic phase. Away from smectic transitions, the wave number of cholesterics typically changes with temperature at less than one-thirtieth the rate as for the pretransition effect.⁽⁴,⁵⁾

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Keating⁽⁶⁾ has proposed a theory of cholesterics in which anharmonic librations are responsible for changes in pitch. However, recent light-scattering experiments⁽⁷,⁸⁾ indicate that, at least for nematics, the librations are of a different character than in the oscillator model used by Keating. Goossens⁽⁹⁾ considered the forces between cholesteric molecules and found that the interactions are quite complicated with no obvious effects near smectic phase transitions.

In this paper, we propose a theory for the pretransitional color change of cholesterics in which the coupling of the director with incipient smectic-like order plays the central role. In Sec. 2, we argue that the elastic energy associated with cholesteric helix formation is most naturally considered as a sum of a stiffness and a rotary term. In Sec. 3, we examine the effect of smectic-like order on the stiffness term and find a contribution which increases rapidly with both the magnitude and the range of local smectic-like positional correlations. In Sec. 4, we examine the rotary term for a specific microscopic model treated in a mean field approximation. Our main result, which should transcend the specific approximate model, is that the positional correlations should not significantly affect the rotary term. In Sec. 5, we examine the implications of these results and suggest an experiment to test them.

2. Elastic Energy

The spiral structure of a cholesteric is associated with a term in the volume elastic energy usually written as⁽¹⁰⁾

$$E = \frac{1}{2}\int \mathrm{d}^3r\, K_{22}(T)\left[\mathbf{n}\cdot\nabla\times\mathbf{n} + \frac{2\pi}{p(T)}\right]^2, \tag{1}$$

where the director $\mathbf{n}(\mathbf{r})$ is a unit vector along the local average direction of the longest axes of the molecules and K_{22} and p are material parameters which may vary with temperature T. The energy is a minimum if the director describes a helix. With Z taken as the helix axis, the equilibrium director field is given by

$$\begin{aligned} n_x &= \cos 2\pi Z/p \\ n_y &= \sin 2\pi Z/p \\ n_z &= 0, \end{aligned} \tag{2}$$

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which leads to the interpretation of p as the pitch of the equilibrium helix of the material.

To understand the variation of p and K_{22} with T, it is useful to rewrite Eq. (1) as the sum of a constant and two terms which are respectively even and odd under improper rotations. Omitting the constant, we have

$$E = \frac{1}{2}\int d^3r\left[K_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2 + 4\pi\frac{K_{22}}{p}(\mathbf{n}\cdot\nabla\times\mathbf{n})\right]. \qquad (3)$$

The K_{22} or stiffness term has the same form as the twist energy of a nematic. The K_{22}/p or rotary term occurs only in cholesterics and originates in intermolecular interactions associated with the rotary sense of the cholesteric molecules. With E written as in Eq. (3), the pitch p may be interpreted as proportional to the ratio of the stiffness-term coefficient to that of the rotary term. We have now to examine the effect of incipient smectic-like order on each of these coefficients.

3. Local Layer Order—Contribution to Stiffness

What is the nature of incipient smectic-like order in the cholesteric phase? In an ideal smectic, the molecules occur in layers and the positions of the centers of mass have long-range correlations in the direction perpendicular to the layers. This long-range layer order can be described by a parameter s⁽¹¹⁾ which measures the degree to which the centers of mass are concentrated in layers, a phase⁽¹²⁾ which gives the position of the layers, and a vector $\mathbf{q}$ which is perpendicular to the layer planes and whose magnitude is inversely proportional to the inter-layer spacing. The long-range layer order disappears above the smectic–cholesteric transition. However, anomalies have been observed in several different properties of cholesterics near the transition which suggests that even in the cholesteric phase there is some tendency of molecules to form a local layer structure.⁽¹³⁻¹⁵⁾ Local layer order can be described by parameters $s'(\mathbf{r})$ and $\mathbf{q}'(\mathbf{r})$, which are like s and q defined for small volumes centered at different points $\mathbf{r}$ in the sample.

Having defined local layer order, we may ask how this positional order affects the orientational order described by the director $\mathbf{n}$. In smectic phases of the usual type (smectic-A), $\mathbf{n}$ is perpendicular to

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the layer structure. Thus we surmise that in cholesterics the layer order couples to **n** with an energy of the form:

$$E' = -\frac{1}{2}A\int d^3r(s'\mathbf{q}'\cdot\mathbf{n})^2, \tag{4}$$

where A is a constant. By analogy with smectics, we may surmise that the local layers tend to be flat planes implying a constant $\mathbf{q}'$. The reason that $\mathbf{q}'$ tends to be constant, while **n** tends to be helical, is that $\mathbf{q}'$ is a more restricted type of vector field: its direction is given by the normals to a family of surfaces. Such a vector field may always be written as a scalar $f_1(\mathbf{r})$ times the gradient of another scalar $f_2(\mathbf{r})$. Therefore, we have

$$\mathbf{q}'\cdot\nabla\times\mathbf{q}' = (f_1\nabla f_2)\cdot\nabla\times(f_1\nabla f_2) \equiv 0, \tag{5}$$

and thus $\mathbf{q}'$ cannot follow a helix. If **n** varies in direction, and especially if it varies as in a helix, the energy from (4) will increase. If we assume that $\mathbf{q}'$ cannot significantly change direction in a distance shorter than the persistence range l of the local layer correlations, then the energy cost for a helix is of the form

$$E'' = B\int d^3r s'^2 l^2(\mathbf{n}\cdot\nabla\times\mathbf{n})^2, \tag{6}$$

where B is constant and it is assumed that $l \ll (\mathbf{n}\cdot\nabla\times\mathbf{n})^{-1}$. The energy E'' gives an addition to the stiffness coefficient in Eq. (3) which increases with both the magnitude and the range of smectic-like correlations. There is no contribution from (4) to the rotary term.

4. The Rotary Term

It remains to examine the pretransitional behavior of the rotary term. This term arises from a complicated combination of intermolecular steric and multipolar interactions.$^{(16,17)}$ However, the main features of the pretransitional behavior can be illustrated by the simple interaction term described in Fig. 1. Two cholesteric molecules freely rotating about their long axes **k** are shown in an equilibrium configuration in which they are turned with respect to one another by an angle θ_e about the center-of-mass separation

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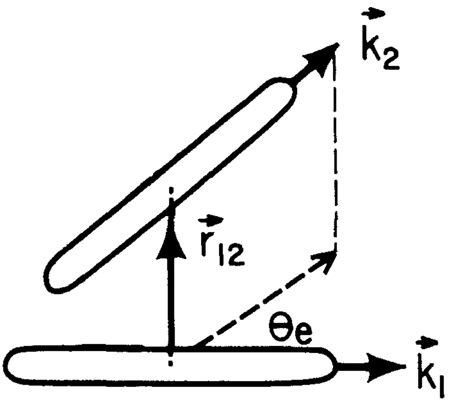

Figure 1. Illustration of a simple interaction between cholesteric molecules which contributes to the rotary term in Eq. (3). The energy, averaged over rotations about the long axes, is lowest if these axes are turned with respect to one another by an angle θ_e about the center-of-mass separation vector.

vector $\mathbf{r}_{12}$. The corresponding interaction energy is

$$E_{12} = -f(r_{12})\left\{\left[\frac{\mathbf{k}_1\cdot\mathbf{r}_{12}\mathbf{k}_2\cdot\mathbf{r}_{12}}{r_{12}^2}(1-\cos\theta_e)+\mathbf{k}_1\cdot\mathbf{k}_2\cos\theta_e + \mathbf{k}_1\cdot\left(\mathbf{k}_2\times\frac{\mathbf{r}_{12}}{r_{12}}\right)\sin\theta_e\right]^2-\frac{1}{3}\right\}, \qquad (7)$$

where f is some function of the absolute value of the center-of-mass separation $\mathbf{r}_{12}$. Equation (7) is invariant under all of the symmetries usually assumed for the average molecular distribution in cholesterics, and thus its effect must be present except for special cases where contributions of opposite chirality accidentally cancel.

The interaction (7) contributes to both stiffness and rotary terms, but only the rotary contribution is of interest here. This may be most easily estimated with a mean field approximation where the molecular axes are assumed to follow the average director. We let

$$\begin{aligned}\mathbf{k}_1 &= \mathbf{n}(\mathbf{r}_1)\\ \mathbf{k}_2 &= \mathbf{n}(\mathbf{r}_1)+(\mathbf{r}_{12}\cdot\nabla)\mathbf{n}(\mathbf{r}_1)\end{aligned} \qquad (8)$$

in Eq. (7) and obtain the following contribution to the rotary term:

$$E''' = \frac{1}{2}C\int d^3r\left\langle r_{12}f(r_{12})\left(\frac{\mathbf{r}_{12}}{r_{12}}\times\mathbf{n}\right)^2\right\rangle\mathbf{n}\cdot\nabla\times\mathbf{n}, \qquad (9)$$

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where $\langle\ \rangle$ denotes an average over the positions of pairs of molecules and C is a constant which depends on the degree of orientational order. If strong smectic-like positional correlations develop, the positional average in (9) will of course be affected. For this example, the rotary term would be somewhat enhanced. However, the effect is not large and furthermore it is governed by correlations over molecular dimensions. These short-range correlations do not change nearly as rapidly near a transition as do the longer range correlations responsible for the stiffness term. Although we have considered here only a limited approximate model, the conclusion that the rotary term varies relatively weakly with smectic order should be valid for a wide class of interactions.

5. Discussion

Given the results of Secs. 3 and 4, what can we predict about the pretransition color change? We have found that a local smectic-like layer structure should define a direction of low energy for the director which resists deformation and makes the stiffness term increase rapidly near the transition. However, there is no corresponding contribution to the rotary term. Thus K_{22} and p should increase rapidly while K_{22}/p varies comparatively little.

In order to test these ideas, it is necessary to measure both p and K_{22} independently as functions of temperature near the transition. It is relatively easy to measure p from optical properties. Determining K_{22} is more difficult. One way is to observe the deformation of the cholesteric helix by an applied field.(18–20) For either positive(10) or negative(18) anisotropy materials, the electric field $\mathscr{E}$ necessary to unwind the helix entirely is given by a formula of the form

$$\mathscr{E} = D\frac{\surd K_{22}}{p}, \tag{10}$$

where D is a constant which depends on the dielectric anisotropy. In past work(5,18–20) on mixtures of right- and left-handed materials, K_{22} could be regarded as constant so that $\mathscr{E}$ varied as p^{-1}. Near the smectic transition, however, it is K_{22}/p which should be constant, so $\mathscr{E}$ should vary as $p^{-1/2}$. Empirically(2,4) we find that the pretransitional behavior of p is fairly well given by

$$p = p_0 + \frac{a}{(T - T^*)^{\nu}}, \tag{11}$$

where p_0 and a are constants, the exponent ν appears to be about 2, and T^* is a temperature about 0.5 K below the transition temperature. If indeed K_{22}/p is approximately constant, then the pretransitional behavior of $\mathscr{E}$ should be fitted by

$$\mathscr{E} = b \frac{(T - T^*)^{\nu/2}}{[p_0(T - T^*)^{\nu} + a]^{1/2}}, \tag{12}$$

where b is a constant independent of T. Especially near the transition, $\mathscr{E}$ should be low enough so that reasonably accurate measurements should be possible for some materials.

In summary, we have proposed that the pretransitional color change of cholesterics is due to the coupling of a local smectic layer structure with the director field. If this supposition is correct, then the rapid increase in p should be governed by a corresponding increase in K_{22}, and measurements of the variation of the latter would provide a good test of the theory.

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