Long-Range Interlayer Interactions in Ferroelectric Liquid Crystals

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Some smectic liquid crystals exhibit a series of phases, including ferroelectric, antiferroelectric, and ferrielectric commensurate structures as well as an incommensurate phase. A long-standing problem has been to understand the origin of the long-range interaction responsible for this rich variety of phases. We study a model that incorporates thermal fluctuations in the flexing of layers and find that it supports commensurate and incommensurate structures. The vibrational entropy competes with an assumed helical interaction between nearest-neighbor layers. An increase in temperature then leads to an unwinding of the helix that proceeds at first through commensurate phases and then into an incommensurate phase. This result is consistent with the experimentally observed "distorted clock model."

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In smectic liquid crystals, rod-shaped molecules are arranged in layers, whose normal we take as defining the z axis. In the smectic-C phase the molecules are tilted from the layer normal. This tilt identifies a unique direction in the x-y plane, along which the c director is said to lie. If we denote the angle between the c director and the x axis in the lth smectic layer as ϕ_l, we may characterize the system in terms of how ϕ_l changes with increasing l. When ϕ_l remains constant we have a synclinic phase, while when it increases by π per layer the phase is anticlinic. In the chiral smectic-C^* phases the presence of a transverse permanent electric dipole moment leads to the alternative description of these phases as ferroelectric and antiferroelectric. In some materials there is an even richer structure, with ϕ_l increasing by 2π every three or four layers (the so-called ferrielectric or intermediate phases), or advancing in an incommensurate manner.

Experimental studies have found a wide variety of observed sequences of phases as the temperature is raised from the melting point through the various smectic phases [1,2]. Of the many interesting possibilities one example has the following sequence: Sm-C_A^* (antiferroelectric)–Sm-C_{FI1}^* (intermediate)–Sm-C_{FI2}^* (intermediate)–Sm-C^* (ferroelectric)–Sm-C_α^* (incommensurate)–Sm-A (smectic-A) [3]. In other materials, one or more of these phases may be missing, but the ordering generally follows in the same sequence. This suggests a common origin in the underlying mechanism responsible for the existence of the various phases.

Before recent experimental observations had clarified the nature of the variation of ϕ_l with l, two different models had been proposed to describe the molecular arrangement in these materials. In the Ising-like model [4–6] $\Delta\phi_l \equiv \phi_{l+1} - \phi_l$ is restricted to be either 0 or π, while in the clock model [7–9] $\Delta\phi_l = 2\pi/n$, where n is the number of the layers in the repeating unit cell, namely, one for ferroelectric, two for antiferroelectric, and three or four for the intermediate phases. Recent experiments [10–12] have ruled out both the Ising-like model and the pure clock model and have led to the introduction of the so-called distorted clock model [13–19]. As indicated in Fig. 1, in this model, for a system with three-layer periodicity we have $\Delta\phi_{3m+1} = \Delta\phi_{3m+3} = \mu$, and $\Delta\phi_{3m+2} = 2(\pi - \mu)$, while a system with four layers in a unit cell can be characterized by $\Delta\phi_{4m+1} = \Delta\phi_{4m+3} = \nu$, and $\Delta\phi_{4m+2} = \Delta\phi_{4m+4} = \pi - \nu$ with $m = 0, 1, 2, \ldots$.

The existence of these phases raises a fundamental question. If the interaction between layers is restricted to nearest neighbors, then there is no reason why $\Delta\phi_l$ should not be constant. In order for phases of period three or four to exist, there must be interlayer interactions beyond nearest neighboring layers. For commensurate structures to form, this interaction must be of long range. What, then, is the mechanism by which the orientation of the c director in one layer influences that of a distant layer? Bruinsma and Prost [20] have discussed an interaction between layers arising from the effective charge density produced by in-plane variation in $\delta\phi_l(x, y)$ and hence in the electric polarization and suggest that this may induce a tendency to anticlinic ordering in distant layers. They did not suggest any mechanism that could lead to more complex structures.

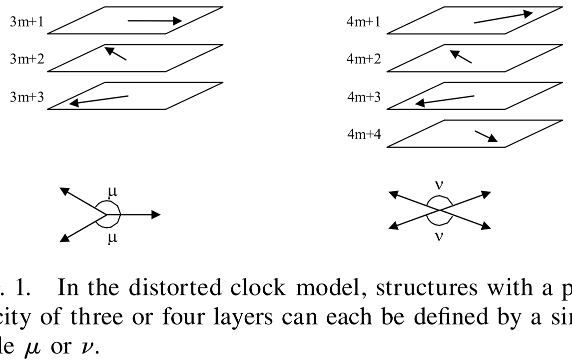

FIG. 1. In the distorted clock model, structures with a periodicity of three or four layers can each be defined by a single angle μ or ν.

Here we present a new model from which the distorted clock structure of the various phases can be derived. In order to be capable of supporting a variety of commensurate and incommensurate phases, a model must have two components. The first of these is a short-range interaction that typically favors a particular relationship between nearest neighbors. This is usually a tunable term whose nature varies with some control parameter, such as temperature or pressure. The second component is a longer-range interaction, which favors a structure different from that preferred by the short-range forces.

In our model of antiferroelectric liquid crystals, the short-range interaction $V_{\rm sr}$ will be taken to be a term favoring a particular value of $\Delta\phi$, the angle between c directors in successive layers. For layers of area L^2 we could choose the form

$$V_{\rm sr} = -vL^2\sum_l \cos(\phi_{l+1} - \phi_l - \alpha), \qquad (1)$$

with the parameter v being an energy of interaction per unit area. This term favors the formation of a helical ordering in which $\phi_l = \text{const} + l\alpha$. We assume that α varies with temperature T from a value near zero to a value near π as the temperature is lowered through the range in which the multiple smectic-C^* phases are found. There is no explicit microscopic model for this variation, but its existence can be argued as plausible. It becomes clear that it is not feasible to develop a microscopic model for the form of $\alpha(T)$ when one considers some recent measurements by Cady *et al.* [21] of the pitch of the helix in the incommensurate Sm-C^*_α phase. There it was found that the addition of one extra CH_2 group to the achiral alkyl chain of the large molecule 10-OHFBBB1M7 had a dramatic effect on the pitch of the helix. It not only changed the pitch by an order of magnitude but also changed the sign of its temperature dependence. In terms of our model, the sign of $d\alpha/dT$ was reversed.

The mechanism we propose for the longer-range interaction is the contribution to the free energy from the anisotropy in the force required for the physical bending of a layer in a smectic-C liquid crystal [22]. This anisotropy causes the energy of distortion of two neighboring layers to depend on the extent to which their c directors are aligned. The spontaneous thermal fluctuations in the shape of a layer give contributions to the entropy of the system that reflect the degree of alignment. This effective long-range elastic interaction is strong enough to induce commensurate ordering.

Our model consists of N layers of thickness d in a Sm-C^* liquid crystal of density ρ. In the absence of thermal fluctuations, each layer lies in the x-y plane, as shown in Fig. 2. The director in each layer is assumed to be tilted away from the layer normal by a tilt angle θ that is a constant throughout the sample. The angle ϕ_l between the c director of the lth layer and the x axis is uniform within each layer and so does not depend on x or y. Different layers, however, have different ϕ's. Thermal fluctuations then cause a spatially varying displacement $u_l(x, y)$ of the lth layer in the z direction. The dynamic variables in terms of which the system is defined are then the N angles ϕ_l and the N functions $u_l(x, y)$.

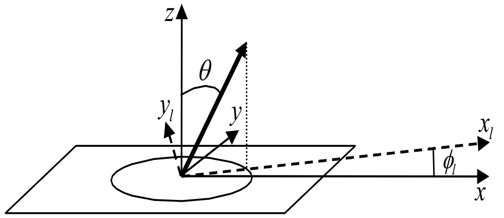

FIG. 2. In each smectic layer the c director lies in the x-y plane at an angle ϕ_l to the x axis. The ϕ_l in different layers are coupled by direct short-range interactions and indirect long-range interactions.

If x_l is an axis in the direction of the c director in the lth layer and y_l is the perpendicular axis in the x-y plane, one can write the elastic energy density of this layer (with neglect of an unimportant cross term) as

$$f_l = \frac{1}{2}\left(k_x\frac{\partial^2 u_l}{\partial x_l^2} + k_y\frac{\partial^2 u_l}{\partial y_l^2}\right)^2, \qquad (2)$$

where k_x and k_y are the elastic constants for bending the layer in the two principal directions. Transformed back to the original coordinates, this expression becomes

$$f_l = \frac{1}{2}\left[(k_+ + k_- \cos 2\phi_l)\frac{\partial^2 u_l}{\partial x^2} + 2k_- \sin 2\phi_l \frac{\partial^2 u_l}{\partial x \partial y} + (k_+ - k_- \cos 2\phi_l)\frac{\partial^2 u_l}{\partial y^2}\right]^2, \qquad (3)$$

with $k_+ = \frac{1}{2}(k_x + k_y)$, the average elastic constant, and with $k_- = \frac{1}{2}(k_x - k_y)$.

The total elastic energy of the system will also include a contribution due to the compression or expansion of the thickness of a layer when $u_l(x, y)$ varies with l. We associate an elastic constant k with this compression energy. The total effective Hamiltonian of the system is then of the form

$$\mathcal{H} = V_{\rm sr} + \iint \sum_{l=1}^{N}\left[f_l + \frac{1}{2}k\Delta u_l^2 + \frac{1}{2}\rho d\left(\frac{\partial u_l}{\partial t}\right)^2\right]dxdy, \qquad (4)$$

with $\Delta u_l = u_{l+1} - u_l$. Our approach now is to find the set of values of the macroscopic variables ϕ_l that minimize the free energy of the system. We do this by first finding the normal modes of excitation of the microscopic variables $u_l(x, y)$ for a given set of fixed values for the ϕ_l. We then add the contribution to the free energy from these thermal excitations to the short-range potential energy and minimize this total. Because the frequencies of the normal modes themselves depend on the ϕ_l, this is a self-consistent procedure.

The system is studied most easily for a given set of fixed values for the ϕ_l if we impose periodic boundary conditions in a sample of thickness Nd and layer area L^2 and write

$$u_l(x, y, t) = \sum_{\mathbf{q}} u_{\mathbf{q}} \exp i(q_x x + q_y y + q_z l d). \tag{5}$$

Here $q_x = 2\pi n_x/L$, $q_y = 2\pi n_y/L$, and $q_z = 2\pi n_z/Nd$. This transformation diagonalizes the energy for motion in the x-y plane but leaves interactions between modes of different q_z. Fortunately, it is a reasonable approximation to retain only the diagonal terms. The justification for this lies in the fact the entropy contributed by each normal mode varies as $\ln\omega_{\mathbf{q}}$, and so it is the low-frequency modes that make the dominant contribution. We put $q_x = q_\perp \cos\varphi$ and $q_y = q_\perp \sin\varphi$ and assume that the symmetry is broken in such a way that the distribution of the ϕ_l is symmetric about the x axis, causing sums like $\sum_l \sin 2\phi_l$ to vanish. The order parameter for the symmetry breaking is then

$$J \equiv N^{-1} \sum_l \cos 2\phi_l, \tag{6}$$

in terms of which

$$\mathcal{H} = V_{\rm sr} + \frac{1}{2} N L^2 \sum_{\mathbf{q}} \left\{ \rho d \frac{\partial u_{\mathbf{q}}}{\partial t} \frac{\partial u_{-\mathbf{q}}}{\partial t} + \left[2k(1 - \cos q_z d) + q_\perp^4 \left(k_+^2 + 2 J k_+ k_- \cos 2\varphi + \frac{1}{2} k_-^2 \right) \right] u_{\mathbf{q}} u_{-\mathbf{q}} \right\} \tag{7}$$

when terms in $\sum_l \cos 4\phi_l$ are neglected. The dispersion relation of the normal-mode frequencies is then

$$(\rho d/k)\omega_{\mathbf{q}}^2 = 4\sin^2\left(\frac{q_z d}{2}\right) + (q_\perp d)^4 (1/\pi)^2 g(\varphi)^2, \tag{8}$$

where $g(\varphi) = c\sqrt{1 + 2J\gamma\cos 2\varphi + \frac{1}{2}\gamma^2}$ with $\gamma = k_-/k_+$ and $c = k_+\pi/\sqrt{k}d^2$. Because the low-frequency modes are dominant, a Debye-like approximation can be made in which $\sin q_z d$ can be replaced by $q_z d$.

The contribution to the free energy from the normal modes will be

$$\mathcal{F}_\omega = k_B T \sum_{\mathbf{q}} \ln \omega_{\mathbf{q}} = \frac{N d L^2 k_B T}{8\pi^3} \int_0^{\pi/d} dq_z \int_0^{\pi/d} q_\perp dq_\perp \int_0^{2\pi} d\varphi \ln \omega_{\mathbf{q}}^2. \tag{9}$$

The upper limit for the integration over $q_\perp$ was chosen to be about the reciprocal of the layer thickness, since distinct modes will not exist when the wavelength approaches molecular dimensions. We drop unimportant constant terms and integrate over q_z and $q_\perp$ to find

$$\mathcal{F}_\omega = \frac{N L^2 k_B T}{16 d^2} \int_0^{2\pi} d\varphi \{ f(g(\varphi)) + \ln[1 + g(\varphi)^2] \}, \tag{10}$$

where $f(x) = (1/x)\arctan x + x\arctan(1/x)$.

Since the anisotropy parameter γ is small, $\mathcal{F}_\omega$ can be expanded as a power series in γ. To lowest order, the total free energy can be written as

$$\mathcal{F} = -\frac{v}{Nd} \sum_l [\cos(\phi_{l+1} - \phi_l - \alpha) + \eta J^2] \tag{11}$$

with $\eta = (\pi k_B T \gamma^2/32 d^2 v)[3 - (4/c)\arctan c + f(c)]$ and J as defined in Eq. (6).

For any given value of α, the controlling factor is thus the quantity η that describes the relative strengths of the long-range and short-range interactions between layers. There will be a critical value $\eta_c(\alpha)$, of order unity, below which the structure is always incommensurate and above which it will be commensurate.

The crucial question is whether the proposed long-range interaction is sufficiently strong to give rise to commensurate phases, which is equivalent to asking whether η can be of order unity. We return to the definition of η, and note that $c \sim 1$, since it is a ratio of elastic constants. We estimate the anisotropy parameter γ by noting that if the tilt angle θ could approach $\pi/2$, then k_y would vanish, and we would have $\gamma = 1$. If we suppose γ to vary as $\sin^2\theta$, then for a typical tilt angle of 18° we would have $\gamma \sim 0.1$. We can estimate the magnitude of the energy $d^2 v$ by considering the electric field strength E_0 necessary to switch a material of dipole moment per unit volume P_0 between phases. At this transition, the electrostatic energy per unit volume, $P_0 E_0$, will be of the order of v/d. The switching field is of the order of 0.3×10^6 V/m [23], and the dipole moment per unit volume is probably around 7×10^{-4} C/m^2 [24]. We then deduce that for a layer thickness d of 3 nm, the energy $d^2 v$ will be around $P_0 E_0 d^3$, or about 5×10^{-24} J, making $k_B T/d^2 v$ about 1000 and $\eta \sim 1$. The magnitudes thus appear to be in the appropriate range for the proposed mechanism to be important.

A combination of analytical and numerical methods was used to find solutions for the system defined by Eq. (11) for all α and η. These results are shown in Fig. 3(a). One sees that only a few commensurate phases exist in this model, and there are no stable phases of order of commensurability higher than six. The six-layer periodicity, also predicted by Dolganov *et al.* [18], has not yet been observed experimentally.

To convert the phase diagram into a prediction of the sequence in which the different phases appear as the temperature is raised, we require knowledge of the function $\alpha(\eta)$, which can be obtained from $\alpha(T)$ and $\eta(T)$ if these are available. The main dependence of long-range-interaction parameter η on T will come from its proportionality to γ^2, since the anisotropy parameter γ will vanish at the temperature of the transition to the Sm-A

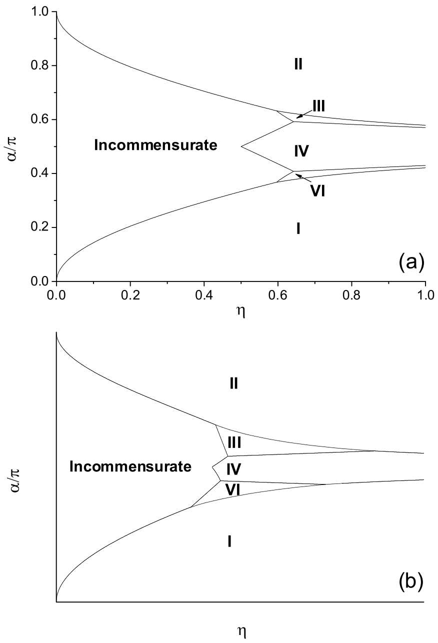

FIG. 3. (a) Stable phases as a function of α (helix angle favored by nearest-layer interactions) and η (strength of mean-field long-range interaction) in the case of a simple symmetric short-range interaction. Roman numerals indicate number of layers per repeat in the commensurate phases. (b) Schematic phase diagram corresponding to an arbitrary asymmetric short-range interaction.

phase. As discussed previously, the dependence of α on T appears to be very sensitive to the small details of the molecular structure and so cannot be predicted. We expect the most common behavior to be a steady reduction from a value near π to a value near zero as the temperature is raised. The most common form of $\alpha(\eta)$ would then be a curve connecting the lower left part of Fig. 3(a) to the upper right part. The particular path followed then determines the phase sequence.

The unrealistically simple form of the short-range interaction V_{sr} results in the phase diagram in Fig. 3(a) being symmetric in α about $\pi/2$. As a consequence, there is a phase with a six-layer repeat in addition to the expected three-layer and four-layer-repeat structures. When the short-range interaction is modified from the oversimplified form given in Eqs. (1) and (11) the phase diagram is altered. For example, strengthening V_{sr} for large α distorts the diagram while maintaining its topology, while adding to V_{sr} a term of the form $\cos[3(\phi_{l+1} - \phi_l - \alpha)]$ changes the topology. The combined effect is shown schematically in Fig. 3(b), which accommodates many of the observed phase sequences. More elaborate modifications of V_{sr} can produce phases having five-, seven-, and eight-layer repeats.

In this study we have explored the consequences of including in the free energy of a Sm-C^* liquid crystal the entropy due to thermal fluctuations in the shape of the smectic layers. We find that this term translates into an effective long-range interaction between c directors in distant layers. The magnitude of this contribution appears sufficient to induce a variety of commensurate phases.

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