Modulated Phases in Thin Ferroelectric Liquid-Crystal Films

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We discuss modulated phases that can occur in thin liquid-crystal films composed of tilted, chiral molecules. While the phase diagram depends on all orders of a Landau expansion we find that either a striped phase of parallel defect walls or a lattice of hexagonal unit cells containing disclinations and bounded by intersecting walls can occur. The striped phase can occur with either a positive or negative bend elastic constant depending on the underlying microscopic parameters. The transition into the modulated phases is, in general, continuous with infinite defect separation at the transition.

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Considerable experimental effort in the area of liquid crystals has focused on freely suspended smectic films, which can be drawn into stable films only a few molecular layers in thickness.[1] These systems provide an experimental realization of many two-dimensional models of critical phenomena,[2] and an opportunity to study the crossover from two-dimensional to bulk behavior by drawing films of increasing thickness.[3]

Many of these films are composed of chiral molecules which form ferroelectric phases[4] when the molecules are tilted as in the smectic C phase. Because chiral molecules have no inversion symmetry, the only symmetry of these phases is a twofold rotation axis perpendicular to the average tilt. As discussed by de Gennes[5] and in greater detail by Langer and Sethna,[6] this reduced symmetry gives rise to new terms in the free energy, which decrease the energy of certain defects in the molecular ordering field so that for sufficiently large chirality the defects have lower free energy than the uniform state. It is of interest then to consider the formation of modulated phases composed of regular arrays of defects. Langer and Sethna, using a fixed-length director model, studied one such phase, termed a striped phase, which is composed of parallel, infinitely long defect walls[2b] (Fig. 1).

Utilizing a nonfixed-length director model we study the possible modulated phases in greater detail within mean-field theory. We demonstrate that the bend elastic constant decreases and may become *negative* as the chirality increases, a phenomena which could not be anticipated in a fixed-length model. A modulated phase can form when the bend elastic constant is positive but defects have negative energy. However, defects whose

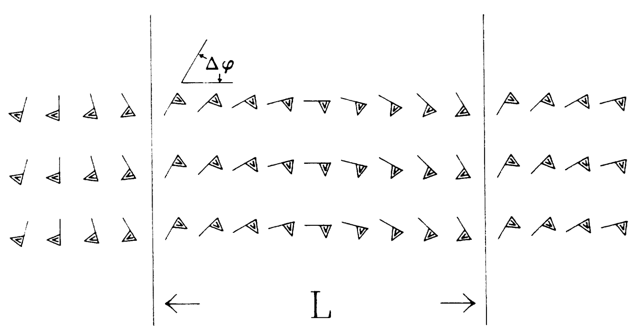

FIG. 1. A striped phase with $K_b > 0$ composed of parallel, infinitely long defect walls. The projection of the molecules onto the plane of the film is denoted by the flaglike object, where the pennant represents the bulge of the chiral molecule. The vector **c** lies along the staff of the flag, with its head fixed relative to the pennant. Within the walls, symbolized by solid lines, **c** varies continuously [see Eq. (2)] over a distance scale $O(\kappa^{-1}) \ll L$.

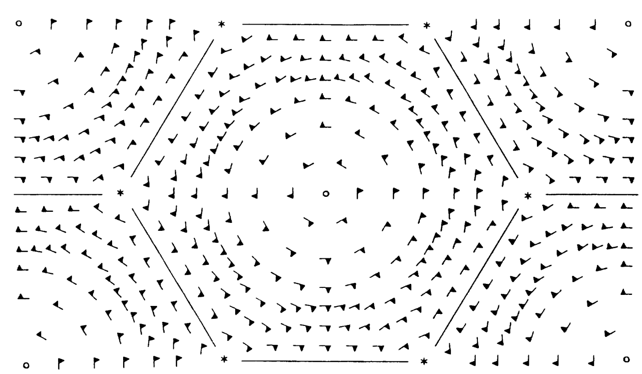

FIG. 2. A hexagonal phase composed of intersecting walls and $+1$ and $-\frac{1}{2}$ disclinations. A $+1$ disclination lies at the center of the hexagonal cell, and $-\frac{1}{2}$ disclinations are present at each corner of the cell. Since three unit cells meet at a corner, the intersection of the three walls at that point represent the core of a $-\frac{3}{2}$ disclination.

energy decreases with increasing chirality all have the same sign for the component of $\hat{\mathbf{z}}\times\hat{\mathbf{c}}$ pointing toward the defect where $\hat{\mathbf{z}}$ is the normal to the film and $\mathbf{c}$ is the order parameter. This implies strain between defects which must be relieved by slow rotation, as in Fig. 1, or by slow rotation and disclinations, as in Fig. 2. The hexagonal unit cell of the lattice in Fig. 2 has a $+1$ disclination at the center and $-\frac{1}{2}$ disclinations at each corner, and is bounded by defect walls. Another possibility is that the uniform state is stable until the chirality is strong enough to drive the bend elastic constant negative, in which case the striped phase forms in a way very different from that studied by Langer and Sethna.

Consider a Landau expansion of the free energy as a function of the order parameter $\mathbf{c}=\sin\theta(\hat{\mathbf{x}}\cos\phi+\hat{\mathbf{y}}\sin\phi)$, where θ is the value of the local tilt angle. A symmetry analysis yields,[7,8]

$$F=\int d^3x\{f_u=\tfrac{1}{2}[(1-\Delta)(\nabla\times\mathbf{c})^2+(1+\Delta)(\nabla\cdot\mathbf{c})^2]+w(\mathbf{c}^2-M^2)(\nabla\times\mathbf{c})_z+u(\mathbf{c}^2-M^2)^2+\cdots\}, \tag{1}$$

where M is the value of $|\mathbf{c}|$ in the uniform state and f_u is the free-energy density therein. The ellipsis indicates terms with higher powers of $\mathbf{c}^2-M^2$ or gradients. The coupling w is a manifestation of the chirality of the system and would be zero in a racemic mixture; the sign of w is determined by the sense of the chirality. For $Z_s\equiv w^2[u(1-\Delta)]^{-1}>2$ the uniform state is linearly unstable[7,8] to a mode parallel to the local ordering direction, corresponding to a bend mode. The bend elastic constant, K_b, can be calculated from Eq. (1) by our assuming that the orientation $\hat{\mathbf{c}}(\mathbf{x})$ is a given, slowly varying, function of $\mathbf{x}$. Our minimizing with respect to the magnitude $|\mathbf{c}|$ yields $\mathbf{c}=[M-(w/4u)(\nabla\times\hat{\mathbf{c}})_z]\hat{\mathbf{c}}$ and $K_b=(1-\Delta)(1-Z_s/2)$. For small positive Z_s-2 walls with negative free energy can appear, described by the order parameter

$$\mathbf{c}=M\{\hat{\mathbf{x}}\cos(\Delta\phi)-\hat{\mathbf{y}}\,\mathrm{sgn}(w)\sin\Delta\phi\tanh[\kappa x\sin(\Delta\phi)]\}, \tag{2}$$

with the assumption that the wall is perpendicular to the x axis and centered at $x=0$, and that $\mathbf{c}$ changes by $2\Delta\phi$ passing through the wall. The quantity $\kappa=M[2u/(1-\Delta)]^{1/2}$ is an inverse correlation length. The free energy of these walls per unit length is[7] $f_w\sim(2-Z_s)\sin^3(\Delta\phi)$ and, thus, these walls for $0<\Delta\phi<\pi$ (and a number of other defects) have negative free energy for $Z_s>2$. This f_w includes surface contributions, e.g., contributions of total gradients $\nabla\times\mathbf{c}$ in the elastic energy. This result is different from $f_w=J_0-4Kq\sin\Delta\phi$, where J_0, K, q are constants derived from a simple fixed-length model with defects by Langer and Sethna.[6] For finite $\Delta\phi$, $(|\mathbf{c}|-M)$ and gradients of $\mathbf{c}$ are finite so that the use of only the terms in the expansion shown in Eq. (1) is illegitimate. Higher-order terms contribute of order $\sin^5(\Delta\phi)$ to f_w and so walls with various $\Delta\phi$ and other defects have negative energies for different values of the chirality. Likely values of $\Delta\phi$ for which the wall energy is first negative with increasing chirality are (i) $\Delta\phi$ small with a negative elastic constant and (ii) $\Delta\phi=\pi/2$, which must be an extremum for reasons of symmetry. These are the possibilities considered in this paper, although any $\Delta\phi$ could in principle first have negative wall energy.

First consider $K_b>0$. We assume that the modulated states are composed of defects separated by distances large compared to their core size so that we can use a fixed-length $\mathbf{c}$ field in the area between the defects, and absorb the length variations of $\mathbf{c}$ into core energies. In the area between the defects we will write the elastic energy density as

$$f_{\mathrm{el}}=\tfrac{1}{2}K[(1+\beta)(\nabla\cdot\hat{\mathbf{c}})^2+(1-\beta)(\nabla\times\hat{\mathbf{c}})^2], \tag{3}$$

where the splay and bend elastic constants are $K_s=K(1+\beta)$ and $K_b=K(1-\beta)$ with $K_s,K_b>0$. Textures with point defects (disclinations) composed of negative core energies can be constructed. However, scaling arguments like those given below show that such states either have a small number of disclinations in a film, however large, or have defects separated by distances comparable to their core size. It is expected that uniform-modulated transitions to such states are first order and will not be considered further.

Consider the phases displayed in Figs. 1 and 2 which can arise through transitions from the uniform state. These transitions are continuous (for the hexagonal state essentially continuous) and the wall separation is infinite (very large) as the transition. We derive the free-energy densities of these phases as functions of the chirality parameter $\Delta\mu=\mu-\mu_c$ where μ is the chemical potential of the minority enantiomer and μ_c is the value of μ at the phase transition. Subsequently we will discuss the competition between these two phases.

The striped phase for $K_b>0$ has been discussed by Langer and Sethna.[6] The total free-energy density relative to the uniform state has the form

$$f_{\mathrm{st}}=\frac{A(\Delta\phi,\beta)}{L^2}-\frac{|f_W(\Delta\phi)|}{L}, \tag{4}$$

where L is the separation between walls, A_S is the elastic free energy associated with the variation of $\hat{\mathbf{c}}$ between the walls, and $f_W\sim\Delta\mu$ is the free energy per unit length of the wall. The minimum of f_{st} occurs when $L=2A_S/|f_W|\sim(\Delta\mu)^{-1}$ and has the value $-f_W^2/4A_S\sim\Delta\mu^2$. It is found that[6]

$$A_S(\beta)=\tfrac{1}{2}K\left[\int_{-\Delta\phi}^{\Delta\phi}d\phi(1-\beta\cos2\phi)^{1/2}\right]^2. \tag{5}$$

The hexagonal phase shown in Fig. 2 requires that the first wall to have negative free energy is characterized by $\Delta\phi=\pi/2$. The free-energy density of a unit hexagonal cell relative to the uniform state has the form

$$f_{\text{hex}}=\frac{2}{3^{1/2}}\left(\frac{A_H\ln(R/R_0)+A_H'}{3R^2}-\frac{|f_W(\pi/2)|}{R}\right), \tag{6}$$

where R is the length of the side of the hexagon. The first term on the right-hand side of (6) is the elastic-energy density due to the presence of both the $+1$ and $-\frac{1}{2}$ disclinations, each of which has core radius R_0. The second term is the energy density associated with the disclination cores and the remainder of the cell, while the third term is the free-energy density of the walls. Both A_H and A_H' will be functions of the elastic anisotropy parameter β. The minimum free energy occurs when

$$R=\left(\frac{2A_H}{3f_W}\right)\ln\left(\frac{R}{R_0'}\right) \text{ or } R\sim\left(\frac{2A_H}{3f_W}\right)\ln\left(\frac{2A_H}{3R_0'f_W}\right), \tag{7}$$

where $R_0'=R_0\exp(\frac{1}{2}-A_H'/A_H)$. At that value of R the free-energy density (6) can be written,

$$f_{\text{hex}}=\frac{-3^{1/2}f_W^2[2\ln(R/R_0')-1]}{4A_H\ln^2(R/R_0')}. \tag{8}$$

Comparing (4) and (8), we see that as $f_W\to 0$, the striped-phase free energy is always logarithmically more negative than that of the hexagonal phase. However, if $\alpha(\beta)\equiv 2\sqrt{3}A_s(\Delta\phi=\pi/2,\beta)/A_H(\beta)\gg 1$, then the hexagonal phase will be the favored state for essentially all values of f_W, i.e., $\ln(1/|f_W|)\leq\alpha$. For arbitrary β, A_H must be determined numerically. However, for $\beta=\pm 1,0$, $A_H(\beta)$ can be calculated analytically with the results of Dzyaloshinskii.[9] We find that $\alpha(-1)=2.00$, $\alpha(0)=3.62$, and $\alpha(+1)=21.5$. Thus for $K_s>K_b$ ($\beta>0$), the hexagonal phase should be favored for a wide range of f_W. Thus mean-field theory predicts a second-order transition to a striped phase, followed by a (weak) first-order transition to the hexagonal phase.

Finally, consider the possibility that the uniform state remains stable until $K_b=0$. Walls with a small value of $\Delta\phi$ first have negative free energy $f_W\sim K_b$. However, from (2) we see that these small-angle walls have widths large compared to κ^{-1}. On length scales greater than κ^{-1} the magnitude of $\mathbf{c}$ can be determined from the local spatial variation of the orientation $\hat{\mathbf{c}}$. Thus, we can analyze a model dependent only on $\hat{\mathbf{c}}$. Since $K_b>0$ we must consider an elastic energy which includes more than two gradients. The relevant terms are

$$F_{\text{el}}=\int d^3x\,\tfrac{1}{2}[K_s(\nabla\cdot\hat{\mathbf{c}})^2+K_b(\nabla\times\hat{\mathbf{c}})^2+G|\nabla\times\hat{\mathbf{c}}|^3+H|\nabla(\nabla\times\hat{\mathbf{c}})_z|^2]. \tag{9}$$

A transition of $K_b=0$ requires that this elastic energy is bounded below by zero, when $K_b>0$. As the term proportional to K_s is nonnegative this is the case when K_s is large enough, e.g, for $K_s>K_s^t$. The elastic energy is bounded below by

$$F_{\text{el}}>\tfrac{1}{2}[K_bf_b+(K_s-K_s^t)f_s]\int d^3x\equiv\int d^3x\,\tfrac{1}{2}[K_b(\nabla\times\hat{\mathbf{c}})^2+(K_s-K_s^t)(\nabla\cdot\hat{\mathbf{c}})^2]. \tag{10}$$

It follows that in the modulated state for $K_b<0$, $f_s/f_b<|K_b|/(K_s-K_s^t)\to 0$ as $K_b\to 0$. This is a very strong constraint and appears to imply a striped phase.

If we consider a striped phase with $K_b<0$ and $\phi\approx 0$, the elastic free-energy density relative to a uniform state is given by

$$f=|K_b^3|\left(F_3-\int dX\,\tfrac{1}{2}\Phi'^2\right)\left(\int dX\right)^{-1}, \tag{11}$$

where

$$F_3=\int dX\,\tfrac{1}{2}[K_s(\Phi\Phi')^2+G\Phi'^3+H\Phi''^2], \tag{12}$$

$\Phi=K_b^{-1/2}\phi$ and the prime indicates differentiation with respect to $X=xK_b^{1/2}$. It follows from this dimensionless form, provided F_3 is bounded below by zero, that the minimum of f will be of order $K_b^3\sim\Delta\mu^3$, that the spatial period L will be of order $K_b^{1/2}\sim\Delta\mu^{1/2}$, and that the angle ϕ will be of order $K_b^{1/2}\sim\Delta\mu^{1/2}$. These results should be compared to the corresponding ones displayed after Eq. (4) which are valid for the striped phase with $\phi\sim 1$ and $K_b>0$. In addition, the geometry of the director pattern will be different from that shown in Fig. 1. The y component of $\hat{\mathbf{c}}$ is of order $(\Delta\mu)^{1/2}$, and goes through a *full* oscillation about zero over the distance L. Since the wall width is of order L there are no sharp walls in this phase, and the periodic pattern of $\hat{\mathbf{c}}$ repeats without a discontinuity at the stripe edge.

The free energy F_3 can be negative when $\gamma\equiv G^2/K_sH>1$. If so, other terms in the free energy are important, and defects in which the order parameter varies on the length scale κ^{-1} are expected. This can be shown explicitly by partial integration of the term proportional to G in Eq. (12) and the completion of the square yielding

$$F_3=\tfrac{1}{2}H\int dX(\Phi''-G\Phi\Phi'/H)^2+\tfrac{1}{2}K_s(1-\gamma)\int dX(\Phi\Phi')^2. \tag{13}$$

The magnitude of the first integral can be made arbitrarily small compared to that of the second integral by our choosing $\Phi(x)$ such that $\Phi'' - GH^{-1}\Phi'\Phi = 0$ for most of the region in which $\Phi' G/H < 0$ and Φ slowly varying elsewhere. As $\gamma \to 1$, the oscillation of the y component of $\hat{\mathbf{c}}$ over the distance L becomes increasingly asymmetric in a continuous way so that for $\gamma > 1$ we return to the geometry of Fig. 1. Thus, despite the very different behaviors near the transition the striped phase is, in fact, a single phase.

In summary, we have studied modulated phases in thin films composed of chiral molecules. While the behavior of a specific system will depend on all orders of a Landau expansion, we have calculated some properties of phases with one- and two-dimensional modulation. The nature of the transition to the striped phase depends on whether it occurs when $K_b > 0$ or $K_b = 0$. Besides the difference in the critical value of K_b, there is different functional dependence of the energy and wall separation on the chirality parameter $\Delta\mu$. For $K_b > 0$, the striped phase may have a higher free energy than a hexagonal phase (Fig. 2). This hexagonal phase is a likely two-dimensional structure as the wall length per unit area is large relative to that of other two-dimensional structures and the elastic energy is relatively small. However, the hexagonal phase requires that a wall with $\Delta\phi = \pi/2$ have negative free energy. Other structures with different wall angles may be possible, and would have the same scaling behavior as that discussed for the hexagonal phase. There is experimental evidence[2b] for a striped phase in one chiral material, but it has not been studied in detail. As our results depend crucially on all orders of a Landau theory we cannot make specific predictions for a given material and we hope that experimentalists will study several chiral systems.

Finally, we emphasize that our discussion has been at the level of mean-field theory. Upon the inclusion of fluctuations we expect the hexagonal phase to have only quasi long-range order (i.e., power-law decay of correlations), while the striped phase will be disordered because of the Landau-Peierls instability.[10] However, we expect that experimentally striped ordering will be seen if $K(\Delta\phi)^2 \gg k_B T$, i.e., for thick films deep in the C phase. These conditions lead to a large correlation length of the stripe undulations compared to L. Thus our predictions should be qualitatively correct except near the $K_b = 0$ transition.

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