Theory of Hexatic-to-Hexatic Transitions

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(Received 6 June 1988)

A theory of transitions between tilted hexatic-*I* and -*F* phases in liquid-crystal films is developed. A renormalization-group analysis leads to four tilted hexatic phases: the hexatic-*I* and -*F* phases, an intermediate hexatic-*L* phase, and an unlocked phase. All these phases except the unlocked phase also exist if the films are crystalline rather than hexatic. These results are consistent with recent experiments on thermotropic and lyotropic liquid crystals.

PACS numbers: 64.70.Md, 61.30.−v, 64.60.Ak

Layered liquid-crystal systems often exhibit tilted hexatic phases, which have at least quasi long-range order in bond and tilt directions but only short-range crystalline order. Tilted hexatic phases can differ from each other in the relation between the six local in-plane bond directions and the local tilt direction. Recent experiments have investigated transitions among different tilted hexatic phases. Dierker and Pindak (DP)[1] have studied thin tilted hexatic films of thermotropic liquid crystals. They observe a weak first-order transition from the hexatic-*I* phase, in which the local tilt (azimuthal) angle is along one of the local bonds, to the hexatic-*F* phase, in which the local tilt angle is 30° away from a local bond. Smith *et al.* (SSSC)[2] have examined the $L_{\beta'}$ phases of lyotropic liquid crystals, which are probably hexatic but may have finite in-plane crystallites. They find three $L_{\beta'}$ phases: the $L_{\beta I}$ and $L_{\beta F}$ phases (analogous to hexatic *I* and *F*) and a new intermediate $L_{\beta L}$ phase, in which the local tilt angle varies continuously from 0° to 30° away from a local bond. The $L_{\beta I}$-$L_{\beta L}$ and $L_{\beta F}$-$L_{\beta L}$ transitions are second order.

In this Letter we present a Landau theory with fluctuation corrections for transitions among tilted hexatic phases. We extend the theory of Nelson and Halperin (NH)[3] by considering a more general tilt-bond coupling. With this coupling, we find *I*, *L*, and *F* phases as well as the unlocked phase found by NH, and we extract various universal predictions. We also show that all these phases except the unlocked phase exist if there is crystalline as well as bond-orientational order. Our theory therefore applies to the $L_{\beta'}$ phase whether they are hexatic or crystalline.

We consider the Hamiltonian for a tilted hexatic membrane,[3]

$$H/k_BT=\int d^2r[\tfrac{1}{2}K_6|\nabla\theta|^2+\tfrac{1}{2}K_1|\nabla\phi|^2+g\nabla\theta\cdot\nabla\phi+V(\theta-\phi)]\,, \tag{1}$$

in terms of the bond-angle field $\theta(\mathbf{r})$ and the tilt-azimuthal-angle field $\phi(\mathbf{r})$. In this Hamiltonian we neglect elastic anisotropy, which we will discuss briefly below. The function $V(\theta-\phi)$ is general tilt-bond coupling, which can be expressed as

$$V(\theta-\phi)=-\sum_{n=1}^{\infty}h_{6n}\cos[6n(\theta-\phi)] \tag{2}$$

because of the local hexagonal symmetry. NH keep only the h_6 term, but for greater generality we will also keep the h_{12} term. Our aim is to determine the behavior as h_6 passes through 0 for fixed nonzero h_{12}.

In this Letter we consider only low-temperature phases, in which we can neglect disclinations in $\theta(\mathbf{r})$ and vortices in $\phi(\mathbf{r})$. We therefore define the linear combinations[3] $\theta_+(\mathbf{r})=\alpha\theta(\mathbf{r})+\beta\phi(\mathbf{r})$ and $\theta_-(\mathbf{r})=\theta(\mathbf{r})-\phi(\mathbf{r})$, where $\alpha=1-\beta=(K_6+g)/(K_6+K_1+2g)$. The Hamiltonian then simplifies to

$$H/k_BT=\int d^2r[\tfrac{1}{2}K_+|\nabla\theta_+|^2+\tfrac{1}{2}K_-|\nabla\theta_-|^2+V(\theta_-)], \tag{3}$$

with $K_+=K_6+K_1+2g$ and $K_-=(K_1K_6-g^2)/K_+$. The average value of θ_- is 0° (mod 60°) in the *I* phase, 30° (mod 60°) in *F* phase, and between 0° and 30° (mod 60°) in the *L* phase.[2] Variations in $\theta_+(\mathbf{r})$ and $\theta_-(\mathbf{r})$ correspond to "acoustic" and "optical" modes, respectively, with in-phase and out-of-phase variations of bond and tilt angles.[1]

As a first approximation,[4] we neglect fluctuations in $\theta_+(\mathbf{r})$ and $\theta_-(\mathbf{r})$ and just minimize

$$V(\theta_-)=-h_6\cos6\theta_--h_{12}\cos12\theta_-.$$

Suppose that h_{12} is fixed and h_6 decreases from positive to negative values. If $h_{12}>0$, there can be local minima at $\theta_-=0°$ and 30° (mod 60°). For $h_6>0$ the minimum at 0° is deeper, and for $h_6<0$ the minimum at 30° is deeper. We therefore have a first-order *I*-*F* transition at $h_6=0$. If $h_{12}<0$, however, then for $h_6>4|h_{12}|$ the only minimum is

at $\theta_- = 0°$. As h_6 decreases through $4|h_{12}|$, this minimum becomes quartic and then splits into two equally deep minima at $\theta_- = \pm \frac{1}{6}\cos^{-1}(h_6/4|h_{12}|)$. We therefore have a second-order, Ising-type I-L transition at $h_6 = 4|h_{12}|$. As h_6 decreases from $4|h_{12}|$ to $-4|h_{12}|$, the minima in the L phase shift continuously from $\theta_- = 0°$ to $\pm 30°$. At $h_6 = -4|h_{12}|$ there is a second-order, Ising-type L-F transition, and F remains the stable phase for all $h_6 < -4|h_{12}|$.

Fluctuations will produce only small corrections to the mean-field theory discussed above in a three-dimensional (3D), stacked, tilted hexatic liquid-crystal system. However, the films studied by DP are only five layers thick, and hence are effectively 2D. Likewise, the $L_{\beta'}$ phases studied by SSSC exhibit no correlations across bilayers, and hence also appear to be effectively 2D. In a 2D system, fluctuations in $\theta_-(\mathbf{r})$ may invalidate mean-field theory. To assess the significance of fluctuations in 2D, we use the renormalization group. Following the method of Kogut,[5] we work to second order in the potential $V(\theta_-)$ and use smooth momentum-space slicing. We obtain the differential recursion relations

$$dh_6(l)/dl = \left(2 - 9/\pi K_-(l)\right) h_6(l) + [36\alpha_1/K_-(l)\Lambda^2] h_6(l) h_{12}(l), \tag{4a}$$

$$dh_{12}(l)/dl = \left(2 - 36/\pi K_-(l)\right) h_{12}(l) - [9\alpha_1/K_-(l)\Lambda^2] h_6(l)^2, \tag{4b}$$

$$dK_-(l)^{-1}/dl = [162\alpha_2/K_-(l)^3\Lambda^4][h_6(l)^2 + 16 h_{12}(l)^2], \tag{4c}$$

where α_1 and α_2 are positive constants of order 1 that depend on the details of the slicing procedure,[5] and Λ is an ultraviolet cutoff of order the inverse particle spacing. These recursion relations describe a "lock-in" transition[6] at a critical stiffness $K_- = K_{c,6} \lesssim 9/2\pi$, above which h_6 is relevant and $\langle \exp(6i\theta_-) \rangle$ acquires long-range order. Similarly, if $h_6 = 0$, there is a lock-in transition at $K_- = K_{c,12} \lesssim 18/\pi$, above which h_{12} is relevant and $\langle \exp(12i\theta_-) \rangle$ acquires long-range order. $K_{c,6}$ and $K_{c,12}$ depend on the initial values h_6 and h_{12}.

If $K_- > K_{c,6}$, an initially small value of $|h_6|$ increases with increasing length scale. If $K_- > K_{c,12}$, an initially small value of $|h_{12}|$ also increases. When $l = l^*$ such that $\max[|h_6(l^*)|, |h_{12}(l^*)|] = \mathcal{O}(K_-\Lambda^2)$, we can match directly onto an approximation that is valid for *large* $V(\theta_-)$. The renormalized potential at this length scale, $V_{l^*}(\theta_-)$, consists of a series of "valleys" separated by high-energy barriers. Fluctuations in θ_- are then confined to one valley. Four types of behavior are possible:

(1) If $K_- > K_{c,12}$, both h_6 and h_{12} are relevant. If $h_{12} < 0$, $V_{l^*}(\theta_-)$ consists of a series of valleys with Ising-type subvalleys for small enough $h_6(l^*)$. Because θ_- is confined to one valley, our problem is equivalent to a 2D continuum Ising model with fluctuations. We therefore obtain second-order, Ising-type I-L and L-F transitions. If we neglect fluctuations in the Ising model, these transitions occur when $h_6(l^*) = \pm 4|h_{12}(l^*)|$; with fluctuations they occur at a reduced value of $|h_6(l^*)|$. Using the nonlinear recursion relations (4), we can find the critical initial values of h_6. As $K_- \to K_{c,12}^+$, we obtain[7]

$$h_{6c} \propto \pm \exp\left[-c(K_- - K_{c,12})^{-1/2}\right]. \tag{5}$$

(2) If $K_- > K_{c,12}$ and $h_{12} > 0$, $V_{l^*}(\theta_-)$ may have valleys at $\theta_- = 0°$ (mod 60°) and 30° (mod 60°). If $h_6 > 0$, the valleys at $\theta_- = 0°$ (mod 60°) are deeper, and θ_- fluctuates inside one of those valleys, in the I phase. If $h_6 < 0$, the valleys at $\theta_- = 30°$ (mod 60°) are deeper, and θ_- fluctuates in the F phase. As h_6 passes through 0, there is a first-order I-F transition.

(3) If $K_{c,6} < K_- < K_{c,12}$, h_6 is relevant but h_{12} is irrelevant. If $h_6 > 0$, θ_- fluctuates in the I phase, and if $h_6 < 0$, θ_- fluctuates in the F phase. If $h_6 = 0$, the potential $V(\theta_-)$ iterates to 0, and our problem becomes a 2D xy model with no symmetry-breaking field. In that case there is no long-range order in θ_-. We therefore obtain a second-order rather than a first-order I-F transition as h_6 passes through 0. The line of critical points at $h_6 = 0$ for $K_{c,6} < K_- < K_{c,12}$ is a fluctuation effect, peculiar to two dimensions.[6]

(4) If $K_- < K_{c,6}$, h_6 and h_{12} are both irrelevant. The potential $V(\theta_-)$ then iterates to 0, and there is no long-range order in θ_-. We therefore obtain the unlocked tilted hexatic phase studied by NH.[3] In this phase $\theta(\mathbf{r})$ and $\phi(\mathbf{r})$ fluctuate independently.

By combining the behaviors in regimes (1)–(4), we obtain a phase diagram in the initial parameters h_6, h_{12}, and K_-^{-1}. Figure 1 presents two cross sections of that phase diagram for fixed positive and negative h_{12}. For $K_- \to \infty$ mean-field theory is valid, because in that limit all fluctuations are quenched. For $K_- > K_{c,12}$, the phase diagram depends on the sign of h_{12}. If $h_{12} < 0$, the phase diagram shows I, L, and F phases with second-order, Ising-type I-L and L-F transitions. The L phase boundaries come together in a triple point at $K_- = K_{c,12}$ as in Eq. (5). If $h_{12} > 0$, the phase diagram shows a first-order I-F transition, which now ends in a tricritical point at $K_- = K_{c,12}$. For $K_{c,6} < K_- < K_{c,12}$, both cross sections of the phase diagram show a direct, second-order I-F transition. For $K_- < K_{c,6}$, both cross sections show the unlocked phase.

The renormalized θ_- stiffness constant is $K_-^R \equiv \lim K_-(l)$. Along the second-order I-F phase boundary, for $h_6 = 0$ and $K_{c,6} < K_- < K_{c,12}$, Eqs. (4) imply the universal results

$$\lim_{K_- \to K_{c,12}^-} K_-^R = 18/\pi$$

and

$$\lim_{K_- \to K_{c,6}^+} K_-^R = 9/2\pi.$$

Similarly, in the unlocked phase, for $K_- < K_{c,6}$ and all values of h_6, we find

$$\lim_{K_- \to K_{c,6}^-} K_-^R = 9/2\pi.$$

An order parameter which describes the entire phase diagram is $M_- \equiv \langle \exp(6i\theta_-) \rangle$. This order parameter is 0 in the unlocked phase (where its correlations decay algebraically[3]), real and positive in the I, real and negative in the F, and complex in the L phase. For small h_6 and h_{12}, M_- obeys the scaling relation

$$M_-(h_6, h_{12}, K_-) = \exp\left[-\frac{9}{\pi} \int_0^l dl' K_-(l')^{-1} \right] M_-(h_6(l), h_{12}(l), K_-(l)). \tag{6}$$

For $K_{c,6} < K_- < K_{c,12}$, Eqs. (4) and (6) imply the power law

$$|M_-| \propto |h_6|^{9/(2\pi K_-^R - 9)} \tag{7}$$

for small h_6, near the second-order I-F transition. For $K_- > K_{c,12}$, the discontinuity ΔM_- across the first-order I-F transition is given by

$$\Delta M_- \propto \exp[-c'(K_- - K_{c,12})^{-1/2}] \tag{8}$$

as $K_- \to K_{c,12}^+$, near the tricritical point. Similarly, M_- vanishes with an essential singularity at the boundary of the unlocked phase.[6]

We can now consider the effect of elastic anisotropy. On a microscopic length scale, K_1 and g are really anisotropic tensors with eigenvalues $K_\uparrow^B$, $K_\uparrow^S$, g^B, and g^S, corresponding to bend and splay. The stiffness K_6 is always isotropic because of local hexagonal symmetry. If we now change variables for θ and ϕ to θ_+ and θ_-, the acoustic "polarization" constants α and β depend on the wave-vector direction in reciprocal space. In general K_- will also depend on the wave-vector direction in a complicated way. However, in the limit $K_6 \gg K_\uparrow^B$, $K_\uparrow^S$, g^B, and g^S the tensor K_- becomes K_1, just as in the isotropic case. By rescaling distances parallel and perpendicular to the local tilt direction, we find that $(K_\uparrow^B K_\uparrow^S)^{1/2}$ takes the place of K_- in the recursion relations for h_6 and h_{12}. Nelson and Pelcovits[8] have shown that $K_\uparrow^B$ and $K_\uparrow^S$ [and hence $(K_\uparrow^B K_\uparrow^S)^{1/2}$] evolve toward a common value $(K_\uparrow^B + K_\uparrow^S)/2$, which is independent of length scale at first order in $V(\theta_-)$. To be precise, at each length scale the recursion relations are determined by the value of $(K_\uparrow^B K_\uparrow^S)^{1/2}$ at that length scale. However, as an approximation, we can simply use the asymptotic value $(K_\uparrow^B + K_\uparrow^S)/2$ in place of K_- in the recursion relations.

As a final theoretical note, consider how the phase diagrams of this paper are modified if the membrane is crystalline rather than hexatic. In that case K_6 becomes infinite, and $\theta(\mathbf{r})$ is replaced by the fixed orientation θ_0 of the crystal axes. In the Hamiltonian, we must now include the coupling of $\phi(\mathbf{r})$ to the lattice strain field $u_{ij}(\mathbf{r})$. NH[3] argue that the Hamiltonian for a crystalline membrane becomes

$$H/k_B T = \int d^2 r [\mu u_{ij}^2 + \tfrac{1}{2}\lambda u_{kk}^2 + \tfrac{1}{2} K_1 |\nabla \phi|^2 + w(u_{ij} - \tfrac{1}{2}\delta_{ij} u_{kk}) s_i s_j + V(\theta_0 - \phi)], \tag{9}$$

where $\mathbf{s} \equiv (\cos\phi, \sin\phi)$. They show that if $w \neq 0$ the unlocked phase becomes unstable, and the tilt direction is locked with respect to the crystal axes. They assume $h_6 > 0$ and $h_{12} = 0$, so that the stable phase is the crystalline analog of the I phase. However, by generalizing their argument to arbitrary h_6 and h_{12}, one can show that the crystalline analogs of

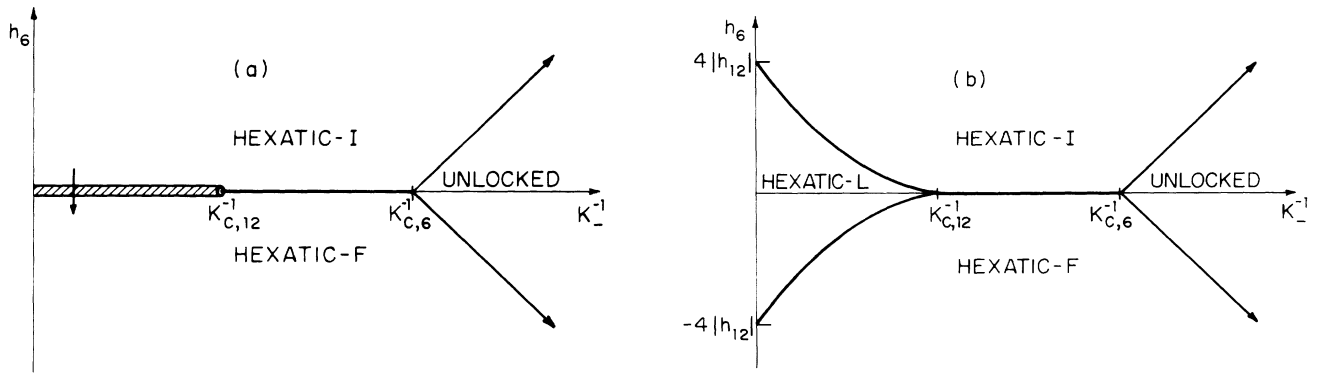

FIG. 1. Two cross sections of the theoretical phase diagram, for (a) constant $h_{12} > 0$ and (b) constant $h_{12} < 0$, as a function of h_6 and the temperaturelike variable K_-^{-1}. The double lines represent first-order and the single lines second-order transitions. The arrow in (a) indicates the approximate position of the I-F transition in Ref. 1.

F and L are also stable phases. Our theory therefore applies to those crystalline phases, and the phase diagrams in Fig. 1 remain correct except that the unlocked phase becomes crystalline I for $h_6 > 0$ and crystalline F for $h_6 < 0$. The transitions among the crystalline I, F, and L phases are the same as the transitions among the corresponding hexatic phases.

Our theory is consistent with DP's observation[1] of a weak first-order I-F transition in five-layer thermotropic liquid-crystal films. From the theoretical phase diagram, we expect a weak first-order transition if $h_{12} > 0$ and $K_- \gtrsim 18/\pi$. The experiments do not directly determine the sign of h_{12}, but they do indicate the value of K_- at light-scattering length scales. DP find $K_\parallel^B$ and $K_\parallel^S$ in the smectic-C phase of a two-layer film. By extrapolating $K_\parallel^B$ and $K_\parallel^S$ from the smetic-C phase into the hexatic-I phase, we can estimate their values in the hexatic-I phase. Their mean, which plays the role of K_- on long length scales, is $K_-^{\text{eff}} = (K_\parallel^B + K_\parallel^S)/2 \approx 40/\pi$ (when normalized by $k_B T$). Because elasticities are roughly proportional to film thickness, we expect $K_-^{\text{eff}} \approx 100/\pi$ in five-layer films. That value is indicated in Fig. 1(a). It is well within the first-order I-F transition region, but the form of Eq. (8) suggests that the jump in M_- should still be rather small. We predict that the I-F transition will be more strongly first order in systems with higher tilt elasticities. In particular, the optical-mode relaxation rate at the I-F transition, which is a measure of $|h_{12}|$ at light-scattering length scales, should increase with increasing tilt elasticities. We also predict that experiments will show an I-F tricritical point in systems where $(K_\parallel^B + K_\parallel^S)/2$ is reduced to approximately $18/\pi$.

Our theory also agrees with the experiments on $L_{\beta'}$ phases by SSSC,[2] whether these phases are hexatic or crystalline. Note that the possibility of dislocation buckling in these systems tends to favor hexatic instead of crystalline order.[9] The theoretical phase diagram shows that the intermediate $L_{\beta L}$ phase should be present, and that the $L_{\beta I}$-$L_{\beta L}$ and $L_{\beta F}$-$L_{\beta L}$ transitions should be second order, if $h_{12} < 0$ and $K_- \gtrsim 18/\pi$. Because SSSC did not measure $K_-^{\text{eff}} = (K_\parallel^B + K_\parallel^S)/2$, we do not have an experimental check of our prediction for the elasticity. We can, however, begin to understand the $L_{\beta L}$ phase in the framework of a theory that covers both lyotropic and thermotropic liquid crystals.

We thank S. B. Dierker, R. Pindak, H. S. Seung, E. B. Sirota, and T. J. Sluckin for helpful discussions. This work was supported by the National Science Foundation through Grant No. DMR 85-14638 and through the Harvard Materials Research Laboratory.

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