Chiral Symmetry Breaking in Langmuir Monolayers and Smectic Films

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Langmuir monolayers and freely suspended smectic films can exhibit a spontaneous breaking of chiral symmetry. The order parameter that characterizes this symmetry breaking is coupled to variations in the direction of molecular tilt. As a result, chiral symmetry breaking leads to the spontaneous formation of complex equilibrium patterns with either 1D or 2D modulations in the direction of molecular tilt. A Landau theory for this pattern formation gives a general phase diagram, which includes a uniform nonchiral phase, a striped pattern, a square lattice, and a uniform chiral phase.

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It has long been recognized that there is a close connection between molecular chirality and pattern formation in liquid crystals. In bulk three-dimensional (3D) systems, chiral molecules can form a cholesteric phase, with a helical pattern of twist in the molecular director, and a smectic-C^* phase, in which the director rotates from layer to layer [1]. In thin films, chiral molecules can form a striped pattern of parallel defect walls [2], as well as spiral star defects [3]. More recently, experiments on Langmuir monolayers [4,5] and freely suspended smectic films [6] have found that similar striped patterns and spiral star defects can occur in 2D systems of *nonchiral* molecules. In these systems, chiral symmetry is spontaneously broken, leading to a chiral phase composed of nonchiral molecules [7]. To understand these experiments, we must examine how chiral symmetry breaking leads to pattern formation in 2D systems.

In this paper, we construct the free energy for a pseudoscalar chiral order parameter $\psi(\mathbf{r})$, which is coupled to the curl of the 2D tilt director field $\hat{\mathbf{c}}(\mathbf{r})$. By minimizing this free energy, we obtain the mean-field phase diagram of Fig. 1. At high temperatures, the phase diagram shows a uniform nonchiral phase with $\psi=0$. At a critical temperature, there is a transition into a striped phase, with a uniaxial modulation of both ψ and $\hat{\mathbf{c}}$. (This striped phase is a generalization of the bend stripes discussed in Ref. [7].) The amplitude of the modulation of ψ grows with the mean-field critical exponent $\beta=1$, in contrast with the Ising mean-field exponent $\beta=\frac{1}{2}$. The striped phase exhibits two distinct regimes: a sinusoidal regime with smooth variations of ψ and $\hat{\mathbf{c}}$ and a soliton regime with a series of sharp domain walls. Between these regimes, the system can form a 2D modulated phase, with a square lattice of tilt vortices separated by domain walls. At low temperatures, there is a uniform chiral phase. In addition to the phase diagram, we also investigate chiral fluctuations in the high-temperature, nonchiral phase, and we examine the effects of these fluctuations on the transition to the striped phase.

In a Langmuir monolayer, chiral symmetry can be broken through several possible mechanisms. First, if the monolayer is in a tilted hexatic phase (as is suggested by the observation of star defects [4]), the tilt direction can be locked at an angle between 0° and 30° from one of the local bond directions. This relation between tilt order and bond-orientational order breaks chiral symmetry. As discussed in Ref. [7], the chiral order parameter would be $\psi(\mathbf{r})=\sin\{6[\phi(\mathbf{r})-\theta(\mathbf{r})]\}$, where ϕ is the tilt azimuth and θ the bond orientation. Second, even if the monolayer is not in a tilted hexatic phase, the molecules might pack on the 2D surface in two inequivalent ways that are mirror images of each other. The chiral order parameter would be the difference in the densities of the two packings. Third, if the monolayer is composed of a racemic mixture of two opposite enantiomers, the racemic mixture can separate to form chiral domains. In that case, the chiral order parameter would be the difference in densities of the two enantiomers.

In a freely suspended smectic film, the mechanism for chiral symmetry breaking depends on the thickness of the film. In a thin film, the 3D molecular director $\hat{\mathbf{n}}$ is uniform across the thickness of the film. If the top and bottom surfaces are equivalent, $\hat{\mathbf{n}}$ is equivalent to $-\hat{\mathbf{n}}$. Thus, a tilted hexatic film of cylindrical molecules always has an inversion symmetry, regardless of the relation between

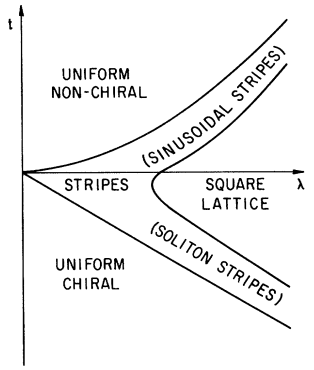

FIG. 1. Mean-field phase diagram for chiral symmetry breaking in a 2D film. The parameter t represents temperature, while λ is the coupling between the chiral order parameter ψ and the curl of the tilt director field $\hat{\mathbf{c}}$. This phase diagram is a schematic view, not drawn to scale.

tilt order and bond-orientational order. Hence, $\sin[6(\phi-\theta)]$ is not a chiral order parameter for a thin smectic film. Chiral symmetry can still be broken by the other two mechanisms described above—either packing of molecules in the film or phase separation of a racemic mixture. By contrast, in a thick film, $\hat{\mathbf{n}}$ is not uniform across the thickness of the film. Hence, the top and bottom layers are each equivalent to Langmuir monolayers, and all three mechanisms are possible.

The general free energy for chiral symmetry breaking in a Langmuir monolayer or a smectic film can be written as

$$F=\int d^2r[\tfrac{1}{2}\kappa(\nabla\psi)^2+\tfrac{1}{2}t\psi^2+\tfrac{1}{4}u\psi^4+\tfrac{1}{2}K_1(\nabla\cdot\hat{\mathbf{c}})^2+\tfrac{1}{2}K_3(\nabla\times\hat{\mathbf{c}})^2-\lambda\psi\nabla\times\hat{\mathbf{c}}]\,. \quad (1)$$

Here, the 2D tilt director $\hat{\mathbf{c}}=(\cos\phi,\sin\phi)$ is the (normalized) projection of the 3D molecular director $\hat{\mathbf{n}}$ into the x-y plane. (We neglect variations in the magnitude of the tilt.) The 2D curl $\nabla\times\hat{\mathbf{c}}$ can be written as $\hat{\mathbf{z}}\cdot\nabla\times\hat{\mathbf{n}}$ in a Langmuir monolayer, and as $\hat{\mathbf{n}}\cdot\nabla\times\hat{\mathbf{n}}$ in a thin smectic film. The first three terms in F are the standard Ginzburg-Landau expansion in powers of ψ. The coefficient t passes through 0 as a function of temperature. The next two terms are the Frank free energy for splay and bend variations in $\hat{\mathbf{c}}$. We will make the single-Frank-constant approximation $K_1=K_3\equiv K$, so that these terms simplify to $\frac{1}{2}K(\nabla\phi)^2$. The final term is the coupling between the chiral order parameter and the director field. It is permitted by symmetry because both ψ and $\nabla\times\hat{\mathbf{c}}$ change sign under reflection. This coupling term is similar to the $\nabla\times\hat{\mathbf{c}}$ term that has been considered in theories of smectic films of chiral molecules [8–11], but here $\nabla\times\hat{\mathbf{c}}$ is multiplied by a chiral order parameter that can itself vary across the film.

The mean-field phase diagram is shown schematically in Fig. 1. It was found by numerical minimization of the free energy using the conjugate-gradient algorithm on a 100-site 1D lattice and on a 100×100 square lattice, with periodic boundary conditions. This phase diagram is expressed in terms of the temperature t and the coupling λ for fixed K, κ, and u. Figure 2 illustrates the resulting patterns as t is decreased with λ constant. From the uniform nonchiral phase, there is a second-order transition to the striped phase. Just below the transition, both $\psi(\mathbf{r})$ and $\phi(\mathbf{r})$ are modulated sinusoidally [Fig. 2(a)]. The wavelength of the modulation decreases as t decreases. At lower temperature, the striped pattern becomes more disordered [Fig. 2(b)]. This disordered pattern may be only a metastable state, but experimental systems exhibit similar metastable labyrinth states [12]. As t decreases further, there is a transition to a square lattice of cells with alternating positive and negative chirality [Fig. 2(c)]. Finally, the striped phase reappears at low temperatures [Fig. 2(d)]. The stripes now appear as domains with constant ψ and linear variation in ϕ, separated by domain walls (or solitons) in which ψ changes sign. The width of the stripes now *increases* as t decreases, and it diverges at the transition to the uniform chiral phase.

To understand the behavior in the sinusoidal-stripe regime, we make the variational ansatz $\psi(\mathbf{r})=\psi_0\cos qx$, $\phi(\mathbf{r})=\phi_0\sin qx$. Inserting this ansatz into Eq. (1) gives the free energy per unit area,

$$F/A=\tfrac{1}{4}\kappa q^2\psi_0^2+\tfrac{1}{4}t\psi_0^2+\tfrac{3}{32}u\psi_0^4+\tfrac{1}{4}Kq^2\phi_0^2-\lambda q\psi_0 J_1(\phi_0)\,. \quad (2)$$

By minimizing this free energy over the amplitudes ψ_0 and ϕ_0 and the wave vector q, we find that there is a second-order transition from the uniform nonchiral phase ($\psi_0=\phi_0=0$) to the striped phase at the critical temperature $t_c=\lambda^2/K$. Near this transition, we obtain

$$\psi_0\propto(t_c-t)\,, \quad (3a)$$

$$\phi_0\propto q\propto(t_c-t)^{1/2}\,. \quad (3b)$$

In this mean-field theory, the striped phase forms at infinite wavelength at t_c, and the wavelength then decreases as the temperature decreases. The critical exponent $\beta=1$ for the amplitude ψ_0 is surprising because it differs from the Ising critical exponent $\beta=\frac{1}{2}$ in mean-field theory. Of course, we would expect thermal fluctuations (discussed below) to modify the mean-field predictions for the critical exponents.

In the lower-temperature soliton-stripe regime, the behavior of $\psi(\mathbf{r})$ and $\phi(\mathbf{r})$ is quite different. Here, we have a series of stripes in which $\psi\approx\pm(|t|/u)^{1/2}$ is approximately constant and ϕ increases linearly, separated by discrete solitons, i.e., sharp domain walls across which ψ changes sign. The free energy is the sum of the solid free energy, the Frank free energy for variations in ϕ, and the λ coupling. If the width of each stripe is l, the resulting free energy density is

$$\frac{F}{A}\approx-\frac{1}{l}\left[\frac{2\lambda|t|^{1/2}}{u^{1/2}}-\frac{\kappa^{1/2}|t|^{3/2}}{2^{1/2}u}\right]+\frac{\pi^2K}{2l^2}\,. \quad (4)$$

Minimizing this expression over l gives

$$l\approx\frac{2^{1/2}\pi^2Ku}{2^{3/2}\lambda u^{1/2}|t|^{1/2}-\kappa^{1/2}|t|^{3/2}}\,. \quad (5)$$

Note that the stripe width l now *increases* as the temperature decreases (as t becomes more negative), the opposite trend from the sinusoidal-stripe regime. When $t\approx-\lambda(8u/\kappa)^{1/2}$, the positive soliton free energy exceeds the negative λ coupling, and hence the stripe width diverges. At this point, there is a transition into the uniform chiral phase.

In addition to the striped phase, we also find a 2D modulated phase, which consists of a square lattice of $l\times l$ cells. Inside each cell, the chiral order parameter $\psi\approx\pm(|t|/u)^{1/2}$ is approximately constant. The cells are separated by sharp walls across which ψ changes sign. This lattice of alternating chirality induces a vortex in $\hat{\mathbf{c}}(\mathbf{r})$ at the center of each cell and an antivortex at each

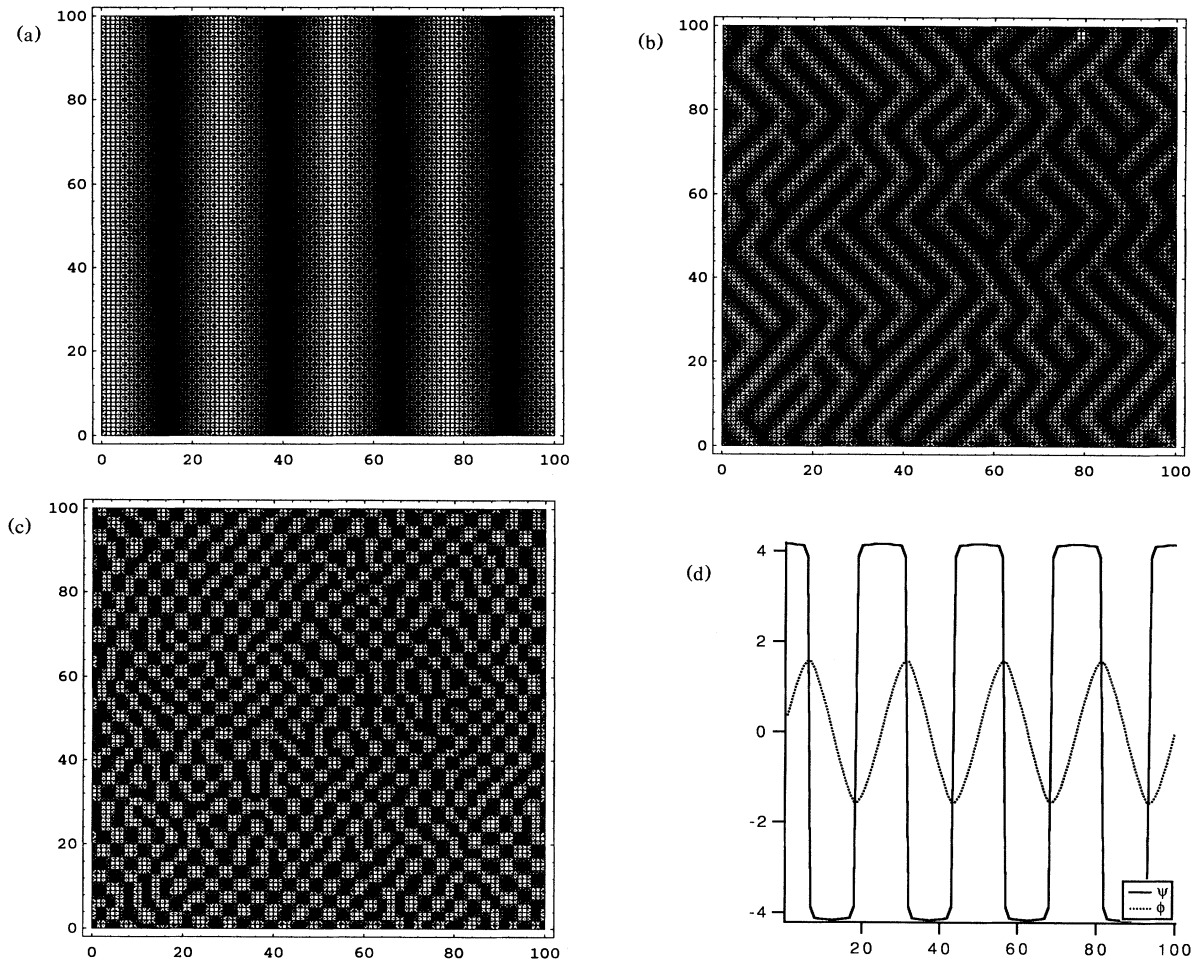

FIG. 2. Patterns formed at several temperatures along the line $\lambda=4$, $K=\kappa=u=1$ (in units where the lattice constant is 1): (a) $t=15$; (b) $t=7$; (c) $t=-1$; (d) $t=-17$. In (a)-(c), the positive or negative value of ψ is indicated by the gray scale. In (d), both ψ and ϕ are shown as functions of x across the stripes.

corner where four cells meet. The free energy of this lattice is again the sum of the soliton free energy, the Frank free energy, and the λ coupling, but now the Frank free energy is logarithmic in l because of the vortex-antivortex interaction:

$$\frac{F}{A} \approx -\frac{2}{l}\left[\frac{2\lambda|t|^{1/2}}{u^{1/2}} - \frac{\kappa^{1/2}|t|^{3/2}}{2^{1/2}u}\right] + \frac{2\pi K}{l^2}\ln\left[\frac{l}{a}\right], \quad (6)$$

where a is the vortex core radius. Comparing Eqs. (4) and (6) shows that the square lattice is preferred over the striped phase if $\ln(l/a) \lesssim \pi$. Thus, the square lattice is favored only when the spacing l is of order the vortex core radius. For that reason, the square lattice appears in the region of the phase diagram between the sinusoidal stripes and the soliton stripes, where l is minimal.

To gain further insight into chiral symmetry breaking and pattern formation, we go beyond mean-field theory by integrating over the thermal fluctuations in the director field (*without* assuming $\phi \ll 1$) to obtain an effective free energy in terms of the chiral order parameter alone. This integration can be performed as an expansion in powers of ψ. The leading-order terms gives

$$F_{\text{eff}} = \frac{1}{2}\int d^2r\left[\kappa(\nabla\psi)^2 + \left(t - \frac{\lambda^2}{2K}\right)\psi^2\right] + \frac{\lambda^2 k_B T}{16\pi K^2 a^2}\int d^2r\, d^2r'\,\psi(\mathbf{r})\psi(\mathbf{r}')\left|\frac{\mathbf{r}-\mathbf{r}'}{a}\right|^{-\eta-2}, \quad (7)$$

where a is the short length scale cutoff, and $\eta = k_B T/2\pi K$. (In any tilted phase $0 < \eta < \frac{1}{4}$, because tilt order is destroyed by thermal fluctuations for $\eta > \frac{1}{4}$ [13].) Equation (7) shows that fluctuations in ϕ induce an effective "antiferromagnetic" long-range, power-law interaction in ψ. This interaction is similar to the dipole-dipole interaction in monolayers of polar molecules, which also leads to pattern formation [14], except that the exponent varies continuously as a function of temperature. Equation (7)

gives the spectrum of chiral fluctuations in the uniform nonchiral phase:

$$\langle|\psi(\mathbf{q})|^2\rangle = \frac{k_B T}{t + \kappa q^2 - (\lambda^2/2K) b(\eta)(qa)^\eta}, \quad (8)$$

where $b(\eta) = 2^{-\eta}\Gamma(1-\eta/2)/\Gamma(1+\eta/2) \approx 1$. As the temperature t decreases, Eq. (8) predicts an instability at the nonzero wave vector $q = [\lambda^2 \eta b(\eta) a^\eta / 4\kappa K]^{1/(2-\eta)}$, whereas mean-field theory predicts an instability at $q = 0$. This finite-wave-vector instability is the 2D analog of the 3D Brazovskii instability [15]. Because of this instability, we expect the transition from the uniform nonchiral phase to the striped phase to be weakly first order.

The predictions of this paper could be tested experimentally in several ways. First, one could measure the stripe width as a function of temperature in both the sinusoidal and soliton regimes. Experiments on smectic films [6] have found that the stripe width increases as temperature decreases in the soliton regime, in agreement with Eq. (5). Second, one could measure the chiral order parameter in a tilted hexatic phase using x-ray scattering, and compare the critical behavior with our predictions. Third, one could apply a strong magnetic field h in the layer plane, which couples to the director $\hat{\mathbf{c}}$. A straightforward extension of our mean-field theory predicts that the striped pattern will set in at the finite wave vector $q = (ht_c/K\kappa)^{1/4}$, and that the amplitude of the chiral order parameter will scale with the Ising mean-field exponent $\beta = \frac{1}{2}$. Fourth, one could study Langmuir monolayers of "bola-lipids" with *two* headgroups per molecule. In these monolayers, there is a symmetry under $\hat{\mathbf{c}} \rightarrow -\hat{\mathbf{c}}$, which forbids the λ coupling in the free energy and destroys the mechanism for pattern formation discussed here.

As a final point, the theory presented here also applies to *splay stripes* in the nonchiral phases of Langmuir monolayers [7] if we replace the coupling $\lambda\psi\nabla\times\hat{\mathbf{c}}$ by $\lambda\Psi\nabla\cdot\hat{\mathbf{c}}$ in the free energy and rotate $\hat{\mathbf{c}}$ by 90°. Here, $\Psi(\mathbf{r})$ can be any scalar order parameter that varies across the monolayer. Earlier papers [10,11] have taken Ψ to be a stiff order parameter with a nonzero average value. However, Ψ could also represent the concentration difference in a two-component monolayer. As we pass through the phase separation transition, this order parameter would become a soft mode, analogous to the chiral order parameter ψ considered above. Thus, phase separation should also induce pattern formation in monolayers. From the phase diagram of Fig. 1, we would predict stripes of alternating composition and a square lattice with cells of alternating composition. This phenomenon should not occur in thin smectic films, because the coupling $\lambda\Psi\nabla\cdot\hat{\mathbf{c}}$ is forbidden by the $\hat{\mathbf{n}} \rightarrow -\hat{\mathbf{n}}$ symmetry.

In conclusion, we have developed a general theory for chiral symmetry breaking and pattern formation in 2D systems. In future work, this theory could be extended in two ways. First, one could study the effects of thermal fluctuations on the low-temperature, ordered phases, and on the phase transitions discussed in this paper. Second, one could investigate whether similar chiral symmetry breaking could occur in bulk 3D systems. For example, a racemic mixture of chiral, cholesteric-forming molecules could separate into regions of each chirality. We conjecture that this system would form a pattern of cholesteric slabs with alternating directions of molecular twist, or perhaps a 2D square lattice of cholesteric bars or a 3D cubic lattice of cholesteric cubes. By examining such systems, one could determine how the general connection between chiral symmetry breaking and pattern formation extends to higher dimensions.

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