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Modulated structures in Langmuir monolayers and in smectic films

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Modulated structures have been observed in nonchiral systems such as Langmuir monolayers and freely suspended smectic films, and a mechanism involving spontaneous chiral symmetry breaking has recently been suggested to account for the occurrence of these structures. We study a simple model corresponding to this mechanism in the mean-field approximation. We find that the model exhibits two uniaxially modulated phases (the director field is colinear or noncolinear) and a vortex-lattice phase, in addition to the two uniform ordered phases (one chiral and one nonchiral) and the disordered phase. The high-temperature transition from the uniform nonchiral phase to the noncolinear uniaxial phase is found to be of third order; it belongs to a peculiar, intermediate class of transitions that has previously been suggested to occur in chiral systems. The low-temperature transition from the noncolinear uniaxial phase to the uniform chiral phase is second order, but also peculiar, because the wave number vanishes linearly at the transition; the modulated phase just above the transition is best described as a spatially varying commensurate phase with walls.

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I. INTRODUCTION

Langmuir monolayers and freely suspended thin smectic films have attracted considerable interest because their reduced dimensionality allows a variety of modulated structures [1–11] and hexatic phases [12,13], in addition to the common smectic phases of the bulk. These modulations reflect an inhomogeneous, periodic ordering of the molecular tilt (which is perpendicular to the layers in the smectic-A phase and tilted in the smectic-C phase). In uniaxially modulated phases, the tilt forms a striped pattern of parallel defect walls separating homogeneously ordered regions [1–3]. Two-dimensional spiral star defects have also been observed [4]. The appearance of modulated structures in related systems was first observed in materials composed of chiral molecules [1–3]. Theoretical understanding of these structures has been provided within a general framework of competing interactions which are expected to exist in chiral systems [2,8,9]. More recently, however, observation of modulated textures in smectic films composed of nonchiral molecules has been reported [4–7]. A mechanism for inducing inhomogeneous patterns in nonchiral films has been suggested [10]. The effect of a coupling, which may exist in thin films, of the director field to the hexatic order parameter has also been considered [14].

To analyze the possible phase diagrams and the phase transitions separating the various phases in these systems, one usually introduces a Landau-Ginzburg (LG) model corresponding to the order parameter. In the case of tilted molecular films or monolayers, the order parameter is the local director field $\mathbf{c} = (c_x, c_y)$, which represents the projection of the molecular tilt onto the layer plane. The LG model must be invariant under the symmetry operations of the disordered phase; for chiral systems it must be invariant under rotations and translations, and for nonchiral systems it must also be invariant under a mirror symmetry in the plane. The free energy corresponding to chiral systems takes the form

$$F = \int d^2r\ \mathcal{F}_0[\mathbf{c}(\mathbf{r})], \tag{1a}$$

where the free-energy density is [2,8,9]

$$\mathcal{F}_0[\mathbf{c}(\mathbf{r})] = \tfrac{1}{2}\alpha c^2 + \tfrac{1}{4}\beta c^4 + \tfrac{1}{2}K_1(\nabla\cdot\mathbf{c})^2 + \tfrac{1}{2}K_3(\nabla\times\mathbf{c})^2 + \mu c^2\nabla\cdot\mathbf{c}\ . \tag{1b}$$

Here K_1 and K_3 are the Frank elastic constants; the parameters α and β control the magnitude c of the vector order parameter $\mathbf{c}$. The free-energy density is invariant under rotations and translations; as expected, for chiral systems it is not invariant under the mirror symmetry $\mathbf{c} \to -\mathbf{c}$. An appropriate free energy for the nonchiral case is given by the model (1) with $\mu = 0$. The μ term contributes to the free energy only when c^2 varies with $\mathbf{r}$; otherwise it becomes a surface term and may be neglected. The phase diagram of this model exhibits a disordered phase (in which $\mathbf{c} = 0$), a uniform phase with constant order parameter $\mathbf{c}$, and modulated phases

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in which $\mathbf{c}$ is a periodic function of $\mathbf{r}$. The modulated structures are driven in this model by the μ term, which is linear in the gradient operator and therefore favors inhomogeneous ordering; this term competes with the elastic terms K_1 and K_3, which favor homogeneous ordering when they are positive.

The phase diagram of the model (1) with $K_1, K_3 > 0$ has been studied in some detail [2,8,9,15–18]. The model exhibits two types of modulated phases, one uniaxial (striped) and the other hexagonal. The second-order transition from the disordered to the uniaxial phase is of a peculiar type, with characteristics of both first- and second-order transitions, intermediate between the two common types (instability and nucleation) of second-order transitions; further, the structure is universal, independent of the parameters which enter the LG model. Section III discusses this third, intermediate type of second-order transition in more detail.

In studying the phase diagram of *nonchiral* systems, one has to consider the model (1) with $\mu = 0$. Here modulated structures may be obtained when one of the elastic constants becomes negative; in this case, one has to add higher-order terms to the model (1b), say $(\nabla \cdot \mathbf{c})^4$ or $(\nabla \times \mathbf{c})^4$, to stabilize it.

An exceptionally interesting paper [10] suggested a simple mechanism which drives the effective constant K_3 negative in nonchiral systems; such systems may undergo a phase transition in which chiral symmetry is *spontaneously* broken. When this happens, the constant K_3 is reduced and may become negative, yielding modulated structures. Reference [10] suggested several ways in which chiral symmetry may be spontaneously broken in a Langmuir monolayer: (i) in a racemic mixture, a phase separation may take place forming chiral domains; (ii) the molecules in the two-dimensional surface may pack locally in two inequivalent ways which are mirror images of each other; (iii) in a tilted hexatic phase, the tilt can be at an arbitrary angle to the local bond direction. Corresponding ways were suggested for freely suspended smectic films.

To analyze this mechanism in more detail, one introduces a pseudoscalar chiral order parameter $\psi(\mathbf{r})$ in addition to the director field $\mathbf{c}(\mathbf{r})$. The LG free-energy density [10]

$$\mathcal{F} = \tfrac{1}{2}\kappa(\nabla\psi)^2 + \tfrac{1}{2}t\psi^2 + \tfrac{1}{4}u\psi^4 + \tfrac{1}{2}K_1(\nabla\cdot\mathbf{c})^2 + \tfrac{1}{2}K_3(\nabla\times\mathbf{c})^2 + \tfrac{1}{2}\alpha c^2 + \tfrac{1}{4}\beta c^4 - \lambda\psi\hat{z}\cdot(\nabla\times\mathbf{c}) \quad (2)$$

corresponding to these two order parameters is a sum of the usual densities for a pseudoscalar ψ and a director field $\mathbf{c}$ plus a coupling term with coefficient λ; this term is permitted by symmetry since both ψ and $\nabla\times\mathbf{c}$ change sign under reflection. To see that this coupling effectively reduces K_3, consider the system near (but above) the transition from a nonchiral $\psi = 0$ phase to a chiral $\psi \neq 0$ phase; here $t \geq 0$ and one may neglect the κ and u terms. Minimizing the free energy with respect to ψ, one finds

$$\psi \sim (\lambda/t)\hat{z}\cdot(\nabla\times\mathbf{c}) \ . \quad (3)$$

Inserting this relation into (2), one obtains an effective LG model for the director field $\mathbf{c}$; in this model the effective constant K_3 is $K_3 - \lambda^2/(2t)$, and so may become negative near the transition to the chiral phase.

The model (2) was studied by Selinger *et al.* [10] within the mean-field approximation, but numerically only for a unit director field $\mathbf{c} = (\cos\phi, \sin\phi)$; four ordered phases were found, two uniform and two modulated, and a schematic (λ, t) phase diagram was suggested. One uniform phase is nonchiral ($\psi = 0$) and the other chiral ($\psi \neq 0$). One modulated phase is uniaxial (striped), with constant amplitude $|\mathbf{c}|$, and the other two-dimensionally modulated (a square lattice of cells with alternating positive and negative chirality).

In this paper we study the model (2) without imposing the constraint $|\mathbf{c}| = \text{const}$. We carry out a detailed numerical study of the mean-field (λ, t) phase diagram, and we analyze the various phase transitions. Our main findings are the following.

(1) We find a fifth ordered phase, in addition to the four ordered phases found in Ref. [10]. The new phase is uniaxial with a colinear structure. It is striped (like the "stiff" noncolinear striped phase found previously [10] under the constraint $|\mathbf{c}| = \text{const}$), but "soft" because the magnitude of the director field vanishes periodically; it cannot be obtained under the above constraint.

(2) The transition from the uniform nonchiral phase to the stiff striped phase is a *third*-order transition, rare in the theory of modulated systems. Moreover, this transition is rather different from ordinary continuous transitions leading to modulated structures, for it belongs to an intermediate class of transitions in which the harmonic content of the modulated phase close to the transition is nontrivial, even though the order parameter is vanishingly small (explicitly, the amplitudes of the higher harmonics do not become negligibly small compared to that of the fundamental as the transition is approached). In previous studies, transitions of the intermediate class were induced by terms like the μ term of Eq. (1); here, however, no such term exists, and the transition is driven by the coupling between the order parameters ψ and $\mathbf{c}$.

(3) The transition between the soft and stiff striped uniaxial phases belongs to the Ising universality class.

(4) The transition from the stiff striped phase to the uniform chiral phase is unusual because the wave number vanishes linearly and because the modulated phase near the transition contains no regions where the order parameters are even roughly constant; the source is the continuous degeneracy of the uniform state.

II. PHASE DIAGRAM AND PHASES

This section describes the phase diagram and the structures of the various phases; the next section describes the nature of the phase transitions.

We obtained the mean-field (λ, t) phase diagram by numerical minimization of the free energy for the density (2) for the choices $K_1 = K_3 = K$, $\kappa = K = u = -\alpha = \beta = 1$ of the parameters; the results are more general, for there are four scaling parameters (the magnitude of ψ, the magnitude of $\mathbf{c}$, the magnitude of the free energy, and the distance scale). All coefficients but t are assumed to be independent of temperature T (in particular, the assumption that α is independent of T means that the transition from the disordered phase $\mathbf{c} = \mathbf{0}$ occurs well above the other transitions). The corresponding Euler-Lagrange equations were solved with periodic boundary conditions, either in a segment of length L for one-dimensional (1D) patterns, or in an $L \times L$ cell for 2D structures (for the latter, the solutions were obtained by minimizing the free energy using a conjugate-gradient method); the average free-energy density of these solutions was then optimized with respect to the cell size L.

The Euler-Lagrange equations for $\mathbf{c}$ and ψ have uniform solutions and many modulated solutions; all solutions are continuously degenerate (can be rotated arbitrarily in the x-y plane).

Uniform solutions. The disordered phase $\mathbf{c} = \mathbf{0}$, $\psi = 0$ is of no interest. Both the uniform nonchiral (UNC) phase and the uniform chiral (UC) phase are described by a uniform director field $\mathbf{c}$ of magnitude $|\mathbf{c}| = c_0$ [where $c_0 = (-\alpha/\beta)^{1/2} = 1$ for the above parameters] and arbitrary direction in the x-y plane. In the UNC phase, which is the equilibrium structure for $t > \lambda^2/K$, the order parameter ψ is zero. In the UC phase, which is the equilibrium structure for t sufficiently less than zero, $|\psi| = \psi_0$, where $\psi_0 = (-t/u)^{1/2}$; the UC phase is additionally degenerate with respect to the sign of ψ.

Striped solutions. For the solutions modulated in one dimension, we choose the x axis to lie along the modulation direction so that c_x, c_y, and ψ are independent of y. We f‑d two classes of striped solutions: For the "stiff" striped phase, which is noncolinear, c_y and ψ oscillate about zero while c_x and $|\mathbf{c}|$ oscillate about nonzero values; for this class, there exist two subclasses of solutions, those which are winding in character and those which are nonwinding (we find that the latter have the lower free energy). For the "soft" striped phase, c_x is identically zero, while c_y and ψ oscillate about zero; this phase is colinear ($\mathbf{c}$ is everywhere parallel or antiparallel to some direction).

Two-dimensional solutions. Solutions modulated in both directions are of course far more numerous; we find that the best 2D solutions are those for the square vortex lattice. Two other classes of solutions were found, the first with nodes of $\mathbf{c}$ on a triangular lattice (without sixfold symmetry, however), and the second labyrinth solutions [like that of Fig. 2(b) of Ref. [10]]; these other solutions are optimal at nonoptimal values of q, but decay to those for the square vortex lattice as q is optimized.

Figure 1 gives the numerical (*not* schematic) phase diagram which we find for the above choice of the Landau parameters; it shows five ordered phases described above. The major differences from the schematic diagram of Ref. [10] are the region of soft stripes and the order of the transition from the uniform nonchiral phase. For $\lambda = 0$, there is a second-order transition at $t = 0$ between the UNC and UC phases; for $\lambda \neq 0$, we find as few as two transitions and as many as six.

Figures 2 through 5 display the structures of the modulated phases at selected points on the line $\lambda = 2$, along which the phase sequence with decreasing t is uniform nonchiral ($t = 4$, third-order), stiff stripes ($t = 2.59$, first-order), vortex lattice ($t = -0.23$, first-order), soft stripes ($t = -5.226$, second-order), stiff stripes ($t = -6.604$, second-order), and uniform chiral.

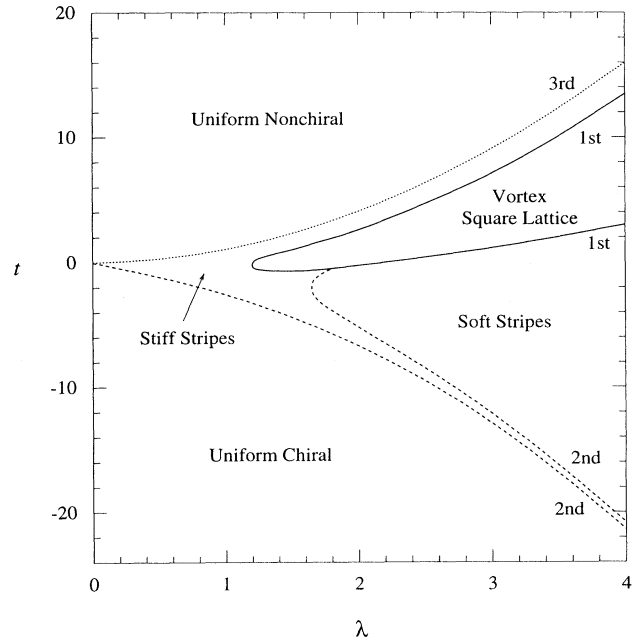

FIG. 1. The mean-field (λ, t) phase diagram of the model (2) showing the regions of stability of the five ordered phases. First-order transitions are plotted with solid lines, second-order transitions with dashed lines, and the third-order transition with a dotted line; orders of the transitions are also indicated next to the lines. The Landau coefficients are $\kappa = K_1 = K_3 = u = -\alpha = \beta = 1$.

Figure 6 shows the x component of the wave vector $\mathbf{q}$ as a function of t along the same line. Discontinuities occur at the first-order transitions to and from the vortex state. The wave number vanishes linearly at the low-temperature transition to the uniform chiral phase, due to the continuous degeneracy (as discussed in Sec. III).

The following provides additional detail on the phases. At $t = \lambda^2/K$, there is a third-order transition from the UNC phase to the stiff striped phase in which both $\mathbf{c}$ and ψ are uniaxially modulated along some direction. The amplitudes of the oscillations in all three quantities (c_x, c_y, and ψ) are small just below the transition, and grow with decreasing t, as shown in Fig. 2; the average value of the amplitude $|\mathbf{c}|$ is the uniform value c_0 at $t = \lambda^2/K$, and decreases with t. The system is locally chiral (since $\psi \neq 0$), although it is nonchiral when spatially averaged. For lower t and for sufficiently large $|\lambda|$, the optimal structure is a square lattice of cells with alternating positive and negative chirality; the cells are separated by walls across which ψ changes sign. The director field has vortices at the centers of the cells, and antivortices at the corners, as shown in Fig. 3. Of course this structure can be obtained only if the magnitude $|\mathbf{c}|$ of the director field is free to vanish, for the phase changes by $\pm 2\pi$ around each vortex. The director field $\mathbf{c}$ circulates about each vortex, like the superfluid velocity $\mathbf{v}$ for vortices in superconductors, but the similarity is only superficial: In superconductors, the optimal packing is the triangular lattice because all vortices have the same chirality and **v** vanishes on the cell boundaries (and diverges at the cores); the uniaxial phase always has higher energy than some other phase. Here, on the other hand, the optimal packing is the square lattice because the vortices have both chiralities (there also antivortices) and $|\mathbf{c}|$ is large on the cell boundaries (and vanishes at the cores of the vortices and antivortices); there are two uniaxial phases, each stable in part of the phase diagram.

At still lower t, for sufficiently large $|\lambda|$, the system next becomes uniaxial with soft stripes, as shown in Figure 4. A reentrant transition to the stiff striped phase takes place at yet lower t; Fig. 5 shows typical structures of this phase. The domain walls occur where $\psi = 0$; the peaks in c_y would likely be suppressed on including higher-order terms in c^2 in the density. The structure of the domains is unusual, for the director field **c** is not constant within the domains (although its magnitude is almost constant at the lower value of t). A second unusual feature is that the wave number vanishes linearly at the transition to the UC phase. The explanation lies in the continuous degeneracy of the uniform state.

III. PHASE TRANSITIONS

We now discuss the nature of the transitions between the various phases, beginning with some general comments on second-order transitions from unmodulated phases (either disordered or uniform) to modulated phases. These transitions are broadly divided into three classes: instability, nucleation, and an intermediate class which has characteristics in common with the other two.

(1) Instability transitions (such as transitions from

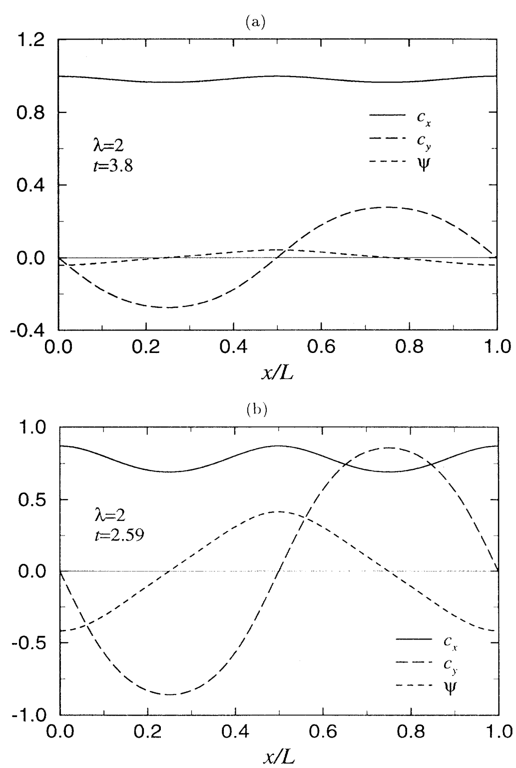

FIG. 2. Structure of the stiff striped phase for $\lambda = 2$: (a) at $t = 3.8$ (near the transition from the uniform nonchiral phase, $q = 0.257$) and (b) at $t = 2.59$ (at the transition to the vortex phase, $q = 0.704$).

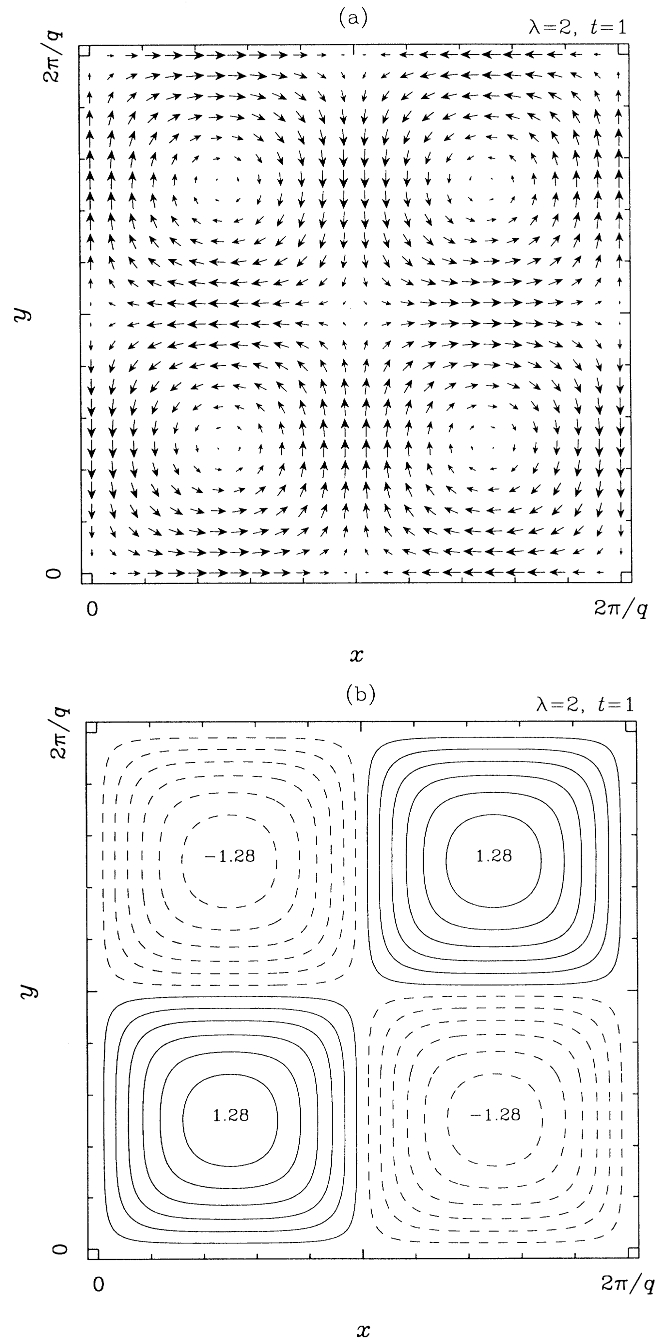

FIG. 3. Structure of the vortex phase for $\lambda = 2$ and $t = 1$; $q_x = q_y = q = 0.624$. Part (a): local director field $\mathbf{c}(x, y)$; the length of the arrows is proportional to the magnitude of **c**. Part (b): contour plot of $\psi(x, y)$; solid and dashed lines represent $\psi > 0$ and $\psi < 0$, respectively; contours are drawn at $\psi = \pm 0.1, \pm 0.3, \ldots$.

disordered to spin-density-wave or charge-density-wave structures) are characterized by a small order parameter, usually the Fourier amplitude $S(\mathbf{q})$ of the local order parameter $S(\mathbf{r})$; here $2\pi/q$ is the wavelength of the modulated structure, and $q = |\mathbf{q}|$ is the wave number. Two features are typical of these transitions. First, q is nonzero at the transition, meaning that the modulated structure has a finite wavelength at the transition. Second, the amplitudes of the higher harmonics of the order parameter, namely $S(n\mathbf{q})$ with $n > 1$, become negligibly small compared with that of the fundamental as the transition is approached; that is, the ratios $S(n\mathbf{q})/S(\mathbf{q})$ for $n > 1$ vanish at the transition. The modulated phase thus has trivial structure at the transition, a fundamental mode only.

(2) Nucleation transitions (which usually occur between uniformly ordered and modulated phases) are rather different, taking place via condensation of localized domain-wall-like structures separating regions which are locally uniform. These transitions have no small local order parameter, since the domain-wall-like objects are large perturbations of the uniform phase. As the transition is approached from the modulated side, the average distance between the localized domain walls diverges, resulting in a transition to a uniform phase. Unlike instability transitions, here the characteristic wave number approaches zero at the transition. Moreover, because of the localized nature of the domain walls, the structure of the modulated phase near the transition is nontrivial, and higher harmonics are of the same order as the fundamental.

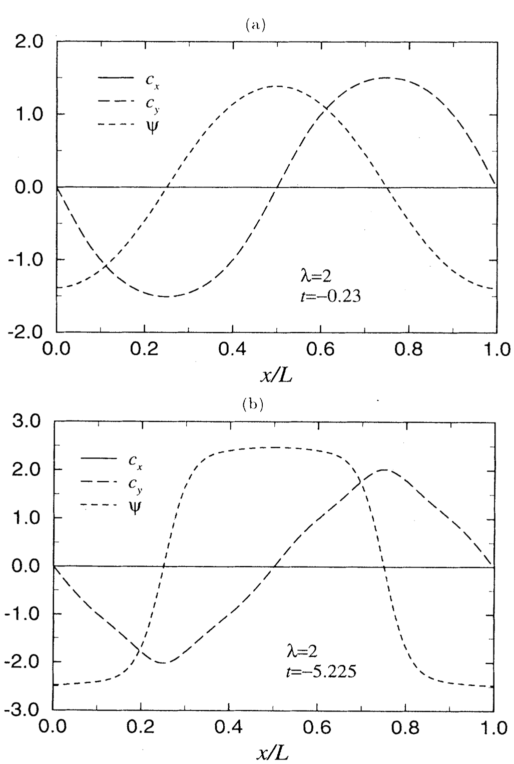

FIG. 4. Structure of the soft striped phase for $\lambda = 2$: (a) at $t = -0.23$ (at the transition from the vortex phase, $q = 0.979$) and (b) at $t = -5.225$ (just above the transition to the stiff striped phase, $q = 0.659$).

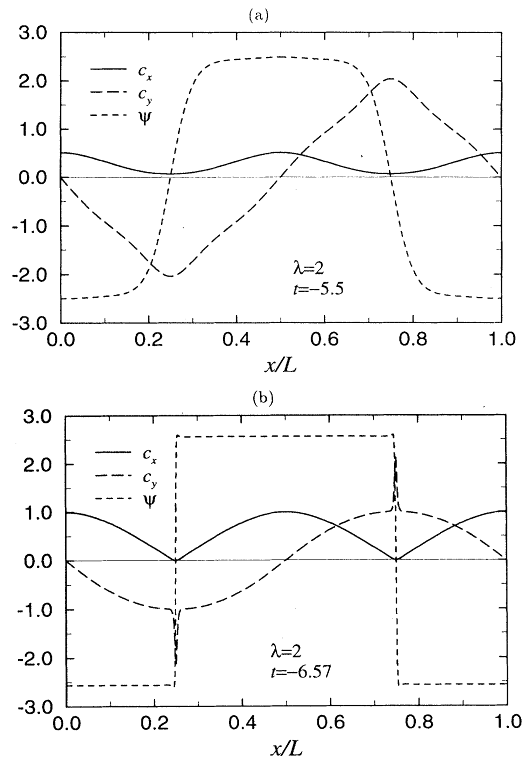

FIG. 5. Structure of the stiff striped phase for $\lambda = 2$: (a) at $t = -5.5$ (below the transition from the soft striped phase, $q = 0.567$) and (b) at $t = -6.57$ (close to the transition to the uniform chiral phase, $q = 0.0243$).

(3) A third, intermediate, type of transition to modulated phases may occur [9,15–18] in systems characterized by a vector order parameter $\mathbf{p}$ (e.g., ferroelectrics or chi-

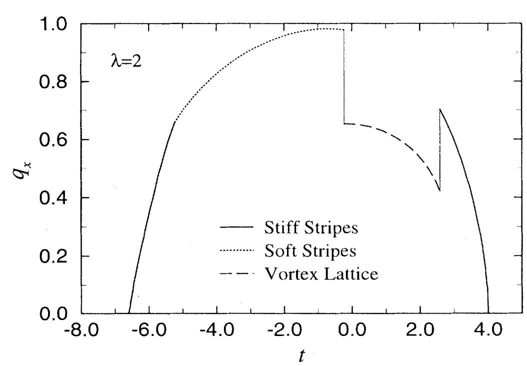

FIG. 6. x component of the wave vector $\mathbf{q}$ as a function of the Landau parameter t for $\lambda = 2$ for the optimal modulated phase. The wave number is continuous at the second-order transition between the soft and stiff uniaxial solutions, and discontinuous at the first-order transitions to and from the vortex phase. It vanishes as $(t_c - t)^{1/2}$ at the high-temperature transition to the uniform nonchiral phase, and as $t - t_c'$ at the low-temperature transition to the uniform chiral phase, as explained in the text.

ral films) and for which a cubic term like $p^2\nabla\cdot\mathbf{p}$ occurs in the Landau expression for the free energy. As in instability transitions, the transition into a modulated phase (induced by the cubic term) is characterized by a small local order parameter $\mathbf{p}(\mathbf{q})$ which goes continuously to zero at the transition. As in nucleation transitions, however, the wave vector $\mathbf{q}$ vanishes at the transition and the harmonic content of the modulated phase is nontrivial; the amplitudes of the higher harmonics are of the same order as the fundamental mode and therefore may not be neglected.

For the model of Eq. (2), we find that the transition from the uniform *nonchiral* phase to the stiff striped phase is of this intermediate type, even though the density contains no cubic term like that discussed above. The transition from the uniform *chiral* phase to the stiff striped phase is of nucleation type, as obtained in Ref. [10], but it too is unusual. The following provides a detailed analysis of the phase transitions found in this model.

A. Transition from the uniform nonchiral phase

The uniform nonchiral phase is described by the order parameters $c_x = c_0\cos\phi$, $c_y = c_0\sin\phi$, and $\psi = 0$, where ϕ is an arbitrary constant phase which we can take to be zero. Reference [10] showed that this phase is unstable when t is less than the value $t_c = \lambda^2/K$: a perturbation of the form $c_y \propto \sin(qx)$ to the particular state $c_x = c_0$, $c_y = 0$, $\psi = 0$ drives ψ away from zero, generating a chiral, one-dimensionally modulated phase, as can be seen from Eq. (5a) below.

Our initial analysis of this transition involves two restrictions, both removed later. (1) The amplitude $|\mathbf{c}|$ in the uniaxial phase has the constant value c_0 of the uniform nonchiral phase. This restriction allows us to write $(c_x(x), c_y(x)) = c_0(\cos\phi(x), \sin\phi(x))$; the Landau coefficients are normalized so that $c_0 = 1$. (2) The elastic constants K_1 and K_3 have the same value (denoted by K). With these restrictions, the free-energy density $\mathcal{F}$ (relative to the uniform nonchiral phase) and the corresponding Euler-Lagrange equations for the functions $\psi(x)$ and $\phi(x)$ are

$$\mathcal{F} = \tfrac{1}{2}\kappa(\psi')^2 + \tfrac{1}{2}t\psi^2 + \tfrac{1}{4}u\psi^4 + \tfrac{1}{2}K(\phi')^2 - \lambda\psi\phi'\cos\phi\ , \tag{4}$$

$$-\kappa\psi'' + t\psi + u\psi^3 - \lambda\phi'\cos\phi = 0\ , \tag{5a}$$

$$-K\phi'' + \lambda\psi'\cos\phi = 0\ . \tag{5b}$$

Suitable boundary conditions are $\phi(0) = \phi(L) = 0$ and $\psi'(0) = \psi'(L) = 0$, where $L = 2\pi/q$ is the spatial period; $\phi(x)$ and $\psi(x)$ are odd and even functions of x, respectively.

We expand in $\epsilon = t_c - t$ about the particular uniform nonchiral state with $c_y = 0$, using the following results [10] for the scaling behavior as $\epsilon \to 0^+$: $\psi(x) = O(\epsilon)\Psi(qx)$, $\phi(x) = O(\epsilon^{1/2})\Phi(qx)$, and $q = O(\epsilon^{1/2})$; the last means that $\psi'(x) = O(\epsilon^{3/2})$, for example. The free-energy density and the differential equations are then

$$\mathcal{F} = \tfrac{1}{2}\kappa(\psi')^2 + \tfrac{1}{2}t\psi^2 + \tfrac{1}{2}K(\phi')^2 - \lambda\psi\phi'(1-\tfrac{1}{2}\phi^2) + O(\epsilon^4)\ , \tag{6}$$

$$-\kappa\psi'' + t\psi - \lambda\phi'(1-\tfrac{1}{2}\phi^2) = O(\epsilon^3)\ , \tag{7a}$$

$$-K\phi'' + \lambda\psi'(1-\tfrac{1}{2}\phi^2) = O(\epsilon^{7/2})\ ; \tag{7b}$$

here and in the following we keep only the leading terms explicitly. Equation (7b) and the boundary conditions allow us to eliminate $\psi(x)$ using $\psi(x) = K\phi'(x)/\lambda + \tilde{\psi}(x)$; an explicit expression is not needed for the function $\tilde{\psi}(x)$, which is of order ϵ^2 and whose derivative is

$$\tilde{\psi}'(x) = K\phi^2\phi''/(2\lambda) + O(\epsilon^{7/2})\ , \tag{8}$$

because the density is stationary in leading order. Equations (6) and (7) reduce to

$$\mathcal{F} = \frac{K^2}{\lambda^2}\left[\frac{\kappa}{2}(\phi'')^2 - \frac{\epsilon}{2}(\phi')^2 + \frac{t_c}{2}(\phi\phi')^2\right] + O(\epsilon^4)\ , \tag{9}$$

$$-\kappa\phi'''' - \epsilon\phi'' + t_c[\phi(\phi')^2 + \phi^2\phi''] = O(\epsilon^{7/2})\ . \tag{10}$$

To simplify these results we change variables to $X = qx$, $\Phi(X) = (t_c/\epsilon)^{1/2}\,\phi(x)$, and $Q = (\kappa/\epsilon)^{1/2}\,q$; both the function $\Phi(X)$ (which has period 2π, independent of ϵ) and the constant Q are of order ϵ^0. The density and the differential equation are then

$$\mathcal{F} = \frac{\epsilon^3K^3}{2\kappa\lambda^4}\left[Q^4(\Phi'')^2 - Q^2(1-\Phi^2)(\Phi')^2\right] + O(\epsilon^4) \tag{11}$$

$$-Q^2\Phi'''' - \Phi'' + \Phi(\Phi')^2 + \Phi^2\Phi'' = O(\epsilon) \tag{12}$$

with boundary conditions $\Phi(0) = \Phi(2\pi) = 0$ and $\Phi''(0) = \Phi''(2\pi) = 0$. All terms on the left-hand side of Eq. (12) are of order ϵ^0.

The two important results for the phase transition are obtained by inspection of Eqs. (11) and (12). First, the free-energy difference of Eq. (11) vanishes as ϵ^3, and so the transition from the uniform nonchiral phase is *third* order (not second order as found previously, accounting for the unusual critical exponents obtained in mean field). The characteristic critical exponents of this transition may, of course, be modified when fluctuations are taken into account. It would be interesting to carry out renormalization-group calculations of this transition and to characterize its universality class. Second, as $\epsilon \to 0$, the function Φ and the constant Q become independent of the temperature. Therefore $\Phi(X)$ is a universal function; in fact it is independent of all the Landau parameters. Further, the universality is nontrivial because all Fourier coefficients are of the same order at the transition; explicitly (except in the trivial case $\Phi_0 = 0$), $\Phi(X) = \Phi_0\sin X$ is not a solution of Eq. (12), although the harmonic content turns out to be small. The transition from the uniform nonchiral phase is then of the third (intermediate) type discussed above.

The optimal constant Q (which determines the spatial period) and the optimal function $\Phi(X)$ are determined by minimizing the free-energy difference $F = \int \mathcal{F} dx$ with respect to Q; for given Q, Eq. (12) (with the right-hand side set to zero) is solved for $\Phi(X)$ and the result substituted into Eq. (11). We find that $Q = 0.557$, and that the average free-energy density $\langle\mathcal{F}\rangle = L^{-1}\int_0^L \mathcal{F}\, dx$ is $-0.0394\epsilon^3$ to leading order in ϵ; the maximum value of Φ is 1.191. The amplitudes of the higher harmonics are proportional to that of the fundamental, but are rather small (the amplitude of the third harmonic is less than 0.04 times that of the fundamental), and decrease geometrically with increasing order. The numerical solution is thus well approximated by the trial function [10]

$$(\psi(x)\,,\, \phi(x)) = (\psi_0 \cos(qx)\,,\, \phi_0 \sin(qx)), \qquad (13)$$

which gives $Q = 0.577$, the free-energy difference as $-\epsilon^3 K^3/(27\kappa\lambda^4)$, and the maximum value of Φ as 1.155, all within a few percent of the numerical values.

We now remove the restrictions $c_x^2 + c_y^2 \equiv c_0^2$ and $K_1 = K_3$, only quoting results. The transition temperature becomes $t_c = \lambda^2/K_3$. The square of the amplitude is

$$c_x^2 + c_y^2 = c_0^2 + \tfrac{1}{2}K_1(c_y^2)''/\alpha + O(\epsilon^3)\ ; \qquad (14)$$

the leading correction [the second term on the right-hand side of Eq. (14)] is of order ϵ^2. Equation (11), from which generalizations of Eqs. (9), (10), and (12) can be obtained, becomes

$$\mathcal{F} = \frac{\epsilon^3 K_3^3}{2\kappa\lambda^4}\frac{K_3 c_0^2}{K_1}\left[Q^4 (C'')^2 - Q^2(1-C^2)(C')^2\right] + O(\epsilon^4) \qquad (15)$$

where $C(X) = [K_1 t_c/(K_3 c_0^2 \epsilon)]^{1/2}\ c_y(x)$. The important points are that the modulated structure remains universal and that the transition remains third-order when the restrictions are removed.

B. Transition from the uniform chiral phase

This transition is of nucleation type, as discussed in Ref. [10]. Its nature can be simply understood in the $|\mathbf{c}| = 1$ limit; letting the director magnitude $|\mathbf{c}|$ vary with x makes no qualitative difference.

Near the transition to the uniform chiral phase, the modulated phase is composed of stripes in which, to a very good approximation, ψ alternates between $\pm\psi_0$ [see Fig. 5(b)]. Within each stripe, the phase ϕ varies linearly between $\pm\phi_0$; the extremal phase ϕ_0 is determined by minimizing the free energy, and it approaches $\pi/2$ at the transition. The stripes are separated by narrow domain walls, or solitons, in which ψ and ϕ vary rapidly. With these approximations, the average free-energy density takes the form

$$\langle\mathcal{F}\rangle \approx \frac{a}{l} + \frac{b}{l^2}, \qquad (16a)$$

where l is the width of the stripes, and the coefficients are

$$a = (-\kappa t/2)^{1/2}\ \psi_0^2 - 2\lambda\psi_0\ , \qquad (16b)$$

$$b = \pi^2(K_1 + K_3)/4\ ; \qquad (16c)$$

this is a modest generalization of Eq. (4) of Ref. [10]. The coefficient a represents the effective free energy of a domain wall, while the term b represents the positive free energy due to the spatial variation of $\mathbf{c}$ within the stripes, as seen in Fig. 5; the interaction energy of the domain walls is discussed below. As long as a is positive, the free energy is minimized by $l = \infty$, and the state is uniform. For sufficiently large λ, a becomes negative (as does the free energy), resulting in a condensation of solitons. The average width of the stripes diverges as $l \sim (\lambda - \lambda_c)^{-1}$, where $\lambda_c = -t[\kappa/(8u)]^{1/2}$; this is a good approximation for the critical line in the small t limit of the phase diagram. Correspondingly, the wave number q ($\propto 1/l$) vanishes linearly at the transition, as seen in Fig. 6.

The expression (16a) for the free energy, and the linear vanishing of q, are unusual. In a typical model of the Lifshitz-invariant class of incommensurate systems, the expression corresponding to (16a) is [19]

$$\langle\mathcal{F}\rangle = a'q + b'q\exp(-c'/q), \qquad (17)$$

where a' vanishes at the transition, and $b', c' > 0$; the second term results from the repulsive interaction of domain walls. Correspondingly, q vanishes as $-c'/\ln(-a'/b')$ rather than linearly. Linear behavior was also found for the incommensurate state of $CsCuCl_3$ in a transverse magnetic field [20], for the same reason: the commensurate state is continuously degenerate and the modulated phase near the transition is a succession of nearly commensurate states, a spatially varying commensurate phase with walls. The overshooting of the order parameters seen in Fig. 5 (the phenomenon was apparently first noticed in Ref. [21]) usually indicates an exponentially damped, oscillatory interaction between domain walls and a first-order transition [22]. But this interaction (whether attractive or repulsive) is exponentially weak and negligible compared to the energy from the spatial variation within the domains, and so does not appear in Eq. (16a).

C. Transition between the soft and stiff striped phases

Simple symmetry considerations indicate that this transition belongs to the Ising universality class. The soft striped phase consists of a colinear director field $\mathbf{c} = (0, c_y(x))$ and an oscillating chiral order parameter $\psi(x)$. The functions $c_y(x)$ and $\psi(x)$ are periodic in x, satisfying $c_y(x) = -c_y(-x)$ and $\psi(x) = \psi(-x)$. This structure is thus invariant under rotation by π:

$$\mathbf{r} \to -\mathbf{r}:\ \ \mathbf{c} \to -\mathbf{c}\,,\ \ \psi \to -\psi\ . \qquad (18)$$

At the transition to the stiff striped phase, the component c_x of the director field becomes nonzero. The order parameter associated with this transition is thus $c_x(x)$, which satisfies $c_x(x) = c_x(-x)$. The precise functional form of $c_x(x)$ can be calculated by solving the Euler-Lagrange equations corresponding to the model (2), but is not needed for the present analysis. The relevant important feature is that when $c_x(x)$ becomes nonzero, the twofold symmetry (17) is broken. The transition is therefore described by a scalar order parameter [say the amplitude of the function $c_x(x)$], and thus belongs to the Ising universality class.

A second-order transition occurs between the two uniaxial states at $t = -5.226$ for $\lambda = 2$; the stiff state is unstable (cannot be obtained numerically) for larger t, and the soft state is metastable for smaller t. Another second-order transition between these two states occurs at $t \approx 1$ (for $\lambda = 2$), but in this region the vortex state is optimal; the stiff state is unstable (in the same sense) at smaller t, and the soft state metastable at higher t.

D. Transitions to the vortex phase

The phase transitions from the two striped phases to the vortex-lattice phase are expected (and found) to be of first order since there is no group-subgroup relation between the phases which are separated by the transition.

IV. SUMMARY

The phase diagram and the nature of the phase transitions of nonchiral Langmuir monolayers and smectic films were analyzed. The phase diagram displays two types of striped phases, corresponding to colinear and noncolinear director fields. It also exhibits two uniform phases (one chiral and one nonchiral) and a vortex-lattice phase. The transition from the uniform nonchiral phase is found to be of intermediate type, which has previously been expected to exist in chiral systems. This transition was analyzed within the mean-field approximation. It would be interesting to examine experimental results concerning this transition in view of the theoretical predictions obtained in this study. It would also be interesting to analyze the effect of fluctuations (by, say, renormalization-group techniques) on the nature of this phase transition.

In the present work we considered the structures of the director field and the chiral order parameter which may occur on isotropic smectic films or in Langmuir monolayers. We did not consider textures corresponding to hexatic systems. The coupling between the director field and the hexatic order has been considered in some detail by Fischer *et al.* [14]. Experimentally, smectic films were found to exist in both liquid and hexatic phases [6,12,13]. On the other hand, in Langmuir monolayers the tilt order is usually found to be accompanied by some structural hexatic order [23].

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