

Bond orientational order in smectic liquid crystals

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Order in the orientations of bond angles in bulk smectic liquid crystals is investigated. A simple model which couples in-plane bond orientations to a tilt degree of freedom is solved in the mean-field approximation. In addition to the usual smectic-*A* and smectic-*C* phases, there is an untilted hexatic phase, with long-range order in the bond angles. Modifications of the mean-field theory due to fluctuations are determined, with the aid of results from the $\epsilon = 4 - d$ expansion. Induced sixfold bond-angle order in smectic-*C* liquid crystals vanishes rapidly near the smectic-*C* to smectic-*A* transition temperature, as $|T - T_c|^{\beta_6}$, where $\beta_6 \approx 3.59$. A form for the coupling of bond orientational order to density fluctuations is proposed.

I. INTRODUCTION

A recent theory of two-dimensional melting¹ suggests the possibility of a new phase of matter, intermediate between a solid and a liquid. Building on ideas due to Kosterlitz and Thouless,² it was found that triangular lattices melt via a dislocation unbinding transition into a hexatic liquid-crystal phase, with persistent order in the orientations of bond angles. A second, disclination unbinding transition is required to produce an isotropic liquid.

Birgeneau and Litster³ have argued that the hexatic phase might have analogs in bulk liquid crystals. They proposed, in particular, that single-domain x-ray-diffraction experiments on smectic-*B* liquid crystals⁴ could be interpreted in terms of long-range bond orientational order in the smectic planes. In-plane translational order would be short range, however. These experiments show a hexagonal x-ray-diffraction pattern of six fuzzy spots in reciprocal space. Unfortunately, more precise scattering measurements^{5,6} indicate that smectic-*B* liquid crystals are, in fact, simply three-dimensional crystals with a large diffuse scattering. Nevertheless, a phase of the kind proposed by Birgeneau and Litster remains a possibility in bulk liquid crystals. This hypothetical phase would be intermediate between smectic-*A* and smectic-*B* liquid crystals, and will be referred to here as the stacked-hexatic phase. The discovery of such a bulk liquid-crystal phase would represent a powerful, although indirect, confirmation of the two-dimensional melting theory proposed in Ref. 1. Hexatic orientational order is much harder to observe in two dimensions, where fluctuations prevent a true broken orientational symmetry.¹

Recently, attention has focused on smectic-*F* liquid crystals.^{7,8} These have tilted nematogens, but are more ordered than smectic-*C* liquid crystals. One might guess that the smectic-*F* phase is a candidate

for a tilted version of the hexatic phase, intermediate between an anisotropic solid (smectic *G*) and a smectic *C*. Possible tilted liquid-crystal phases in a few, isolated, smectic layers have recently been studied in some detail.⁹ Although the emphasis was on coupled tilt and orientation degrees of freedom in *two* dimensions, it was observed that tilted smectics in bulk would have induced long-range order in bond orientations. Thus, there can be no fundamental distinction between smectics-*C* and a tilted hexatic phase. There remains, however, the possibility of a first-order transition between a smectic *C* with very weak induced bond-angle order, and a phase with much stronger bond orientational order.

Here, we study this and related questions by solving a simple model of coupled tilt and bond orientations, using mean-field theory corrected for fluctuations. The bond-angle and tilt-orientation fields are defined in Fig. 1. The model was introduced and studied using different techniques for $d = 2$ in Ref. 9. Fluctuations are much less important in bulk materials than in two dimensions, and one expects mean-field theory to be qualitatively correct. The mean-field phase diagram is shown schematically in Fig. 2. Different phases are shown, as a function of inverse dimensionless stiffness constants K_6^{-1} and K_1^{-1} . Here, K_6 measures the coupling between neighboring bond orientations, while K_1 characterizes the interaction between nearby tilt angles. A factor $1/k_B T$ has been absorbed into the definitions of these quantities. Experiments in which only temperature is varied might trace a path from the lower left to the upper right of the figure.

Both smectic-*A* and stacked-hexatic phase are shown, together with a single tilted hexatic, or smectic-*C* phase. Although bond orientational order changes very rapidly in the vicinity of the dashed line, there is no sharp phase transition. In particular, the model does not display a first-order transition

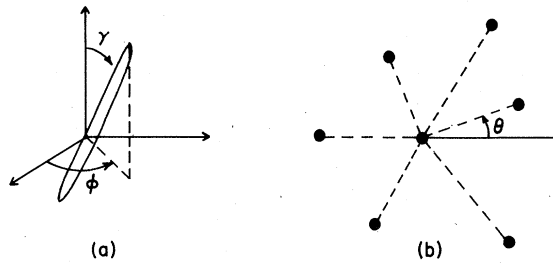


FIG. 1. Degrees of freedom necessary to describe tilted smectic liquid crystals with bond orientational order. If the molecules are tilted by an angle γ within each smectic plane, then the relevant degree of freedom is the orientation angle ϕ made by the projection of the molecule, as shown in (a). (b) shows dashed lines ("bond angles") joining the center of a molecule to its six nearest neighbors within the smectic plane. Each such line defines a bond-orientation angle θ with some in-plane reference axis. Ordinarily, such a field would have an internal sixfold symmetry. Microscopically, one could imagine placing the bond-angle field at the mid-points of the bonds. The field $\psi(\vec{r})$ is a coarsened-grained average of $e^{6i\theta}$, where θ is the microscopic quantity indicated in the figure.

separating two distinct tilted hexatic phases. All three phases meet in a peculiar kind of multicritical point, marking the terminus of three XY -like lines of second-order phase transitions.

Table I reviews the in-plane bond orientational, tilt orientational, and translational order proposed for a variety of smectic phases. In this paper, we do not address ourselves to crystallization of the in-plane fluid phases shown in Fig. 2. The renormalized stiffness K_6^R would be infinite in the smectic- B and smectic- G crystalline phases.

Fluctuation corrections to mean-field theory can be

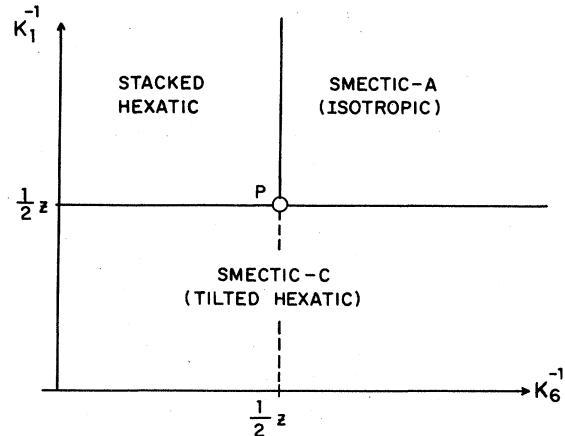


FIG. 2. Phase diagram of a coupled system of bond- and tilt-orientation angles in the mean-field approximation. The stacked-hexatic phase has in-plane long-range orientational or "hexatic" order. The smectic- A phase is like an isotropic liquid within each plane. The smectic- C , or tilted hexatic phase, has long-range bond orientational order, and induced sixfold order in the bond orientations. The orientational order parameter varies rapidly from a large value on the left to a much smaller value on the right across the dashed line. Three XY -like lines of critical points separate these phases, and meet at the multicritical point P . The parameter z is the coordination number in our lattice model.

determined by an expansion in powers of $\epsilon = 4 - d$.¹⁰ Making use of ϵ -expansion results, we can find the behavior of the bond- and tilt-angle order parameters near phase boundaries, and the topology of the phase diagram near the multicritical point in Fig. 2. Fluctuations produce only singular curvature corrections to the XY -like transition lines¹¹; they behave qualitatively as shown in Fig. 2. Perhaps the most useful

TABLE I. In-plane bond orientational, tilt orientational, and translational order for various bulk smectic phases. Many smectic- B and smectic- G liquid crystals are now believed to be simply anisotropic solids. This paper addresses itself only to transitions between the bottom three phases. (Until recently, the smectic- G phase has often been called a smectic- H phase.) LRO means long-range order; SRO, short-range order.

	In-plane bond orientations	In-plane tilt orientations	In-plane translations
Smectic B (Solid)	LRO	SRO	LRO
Smectic G (Anisotropic solid)	LRO	LRO	LRO
Smectic A	SRO	SRO	SRO
Smectic C	LRO	LRO	SRO
Stacked hexatic	LRO	SRO	SRO

result concerns the rate at which induced bond orientational order disappears near the smectic-*A* to -*C* transition. Sixfold bond orientational order is conveniently measured by the thermal average of^{1,9}

$$\Psi(\vec{r}) \propto e^{6i\theta(\vec{r})} , \quad (1.1)$$

where the bond-angle field $\theta(\vec{r})$ is defined in Fig. 1(b). Induced orientational order in the *C* phase disappears quite rapidly near the *C*-to-*A* transition,

$$|\langle \Psi(\vec{r}) \rangle| \sim |T - T_c|^{\beta_6} , \quad (1.2)$$

where we find $\beta_6 \approx 3.59$.

As discussed in Ref. 3, one would expect bond orientational order to show up in single-crystal x-ray-diffraction patterns. These provide a measure of fluctuations in the squared average of $\rho_{\vec{q}}$, the Fourier component of the density at the in-plane reciprocal vector \vec{q} . A simple model of the coupling between the density and bond orientational order, discussed in Sec. IV, predicts that, well below any transition temperatures

$$S(q) \equiv \langle |\hat{\rho}_{\vec{q}}|^2 \rangle = \frac{1}{A_q + B_q \langle \cos[6\theta(\vec{q}) - 6\theta_{\vec{q}}] \rangle} . \quad (1.3)$$

Here, $\theta_{\vec{q}}$ is the angle \vec{q} makes with, say, the *x* axis, and A_q and B_q depend only on the magnitude of \vec{q} . The average on the right-hand side of Eq. (1.3) is over different configurations of bond and tilt angles; density fluctuations have been integrated out. We expect that A_q always exceeds B_q , and has a minimum at $q = q_0$, corresponding to the maximum in the powder average of $S(\vec{q})$. Equation (1.3) implies six maxima in $S(\vec{q})$ for $|\vec{q}| = q_0$. A more speculative formula for the behavior of $S(\vec{q})$ near a phase transition (see Sec. IV) indicates that the difference between $S(q_0, \theta_{\vec{q}_0})$ at the maximum and minimum values of $\theta_{\vec{q}_0}$ vanishes like the bond orientational order parameter,

$$S(q_0, \theta_{\vec{q}_0}^{\max}) - S(q_0, \theta_{\vec{q}_0}^{\min}) \propto \langle e^{6i\theta(\vec{r})} \rangle . \quad (1.4)$$

The limitations of the analysis presented here should also be emphasized. We cannot, of course, predict whether a given smectic liquid crystal will actually display the novel "stacked hexatic" phase. If in-plane translation degrees of freedom were included in the model, we would expect three-dimensional (3D) crystalline phases at low temperatures (large K_1 and K_6). Possible crystalline phases were discussed in Ref. 9. Crystalline in-plane translational order locks the bond orientations, and the renormalized stiffness K_6^R is formally infinite. It is possible that 3D crystallization, i.e., a transformation directly from a smectic-*A* to a solid, could preempt the stacked hexatic phase entirely in many systems.

In Sec. II, we define the model and present its mean-field solution. The effect of fluctuations is discussed in Sec. III. The influence of bond orientational order on density fluctuations is described in Sec. IV.

II. PHASE DIAGRAM IN MEAN-FIELD THEORY

A. Order parameters and model Hamiltonian

In two dimensions the hexatic and tilted hexatic phases are dominated by fluctuations. These fluctuations give rise to power-law decay at large r of the angular correlation function^{1,9}

$$C_6(\vec{r}) \equiv \langle e^{6i\theta(\vec{r})} e^{-6i\theta(\vec{0})} \rangle . \quad (2.1)$$

When layers of hexatic or tilted hexatic are coupled, as in bulk smectics, one expects that fluctuations will be suppressed, except close to a phase transition. If the hexatic phase survives in bulk form, then $C_6(\vec{r})$ should exhibit genuine long-range order³

$$\lim_{r \rightarrow \infty} C_6(\vec{r}) = \text{const} \neq 0 . \quad (2.2)$$

There is also *induced* long-range order of this kind in smectic phases with long-range order in the tilt angle defined by Fig. 1(a). A convenient measure of order in the tilt-orientation angles is

$$C_1(\vec{r}) \equiv \langle e^{i\phi(\vec{r})} e^{-i\phi(\vec{0})} \rangle . \quad (2.3)$$

Although fluctuations prevent long-range tilt-angle order in fluid phases for $d=2$, in three dimensions one can have

$$\lim_{r \rightarrow \infty} C_1(\vec{r}) = \text{const} \neq 0 . \quad (2.4)$$

Ordered phases may be described by the order parameters

$$\Psi = \langle e^{6i\theta(\vec{r})} \rangle \equiv \psi_0 e^{6i\theta_0} , \quad (2.5a)$$

$$\Phi = \langle e^{i\phi(\vec{r})} \rangle \equiv \Phi_0 e^{i\phi_0} . \quad (2.5b)$$

The quantities ψ_0 , θ_0 , Φ_0 , and ϕ_0 are real amplitudes and phases characterizing the broken symmetries.

In this section, we solve a simple model of interacting bond- and tilt-orientation angles in the mean-field approximation. Possible phases correspond to smectic-*A* liquid crystals, with $\psi_0 = \Phi_0 = 0$ (stacked-hexatic) liquid crystals, with $\psi_0 \neq 0$ and $\Phi_0 = 0$, and smectic-*C* liquid crystals, with both ψ_0 and Φ_0 nonzero. As we shall demonstrate explicitly, phases with $\Phi_0 \neq 0$ but $\psi_0 = 0$ are not possible.

The hexatic to isotropic transition can be described qualitatively by a classical *XY* model with spin angles θ_i defined modulo $\frac{1}{3}\pi$,

$$\mathcal{H}_6 = J_6 \sum_{\langle i,j \rangle} \cos[6(\theta_i - \theta_j)] , \quad (2.6)$$

where the summation goes over nearest-neighbor pairs of, say, a cubic lattice. The angle θ_i gives the angle between a nearest-neighbor bond in the fluid and some fixed axis. Similarly, the transition between smectic *A* and *C* can again be described by an *XY* model

$$\mathcal{H}_1 = J_1 \sum_{\langle i,j \rangle} \cos(\phi_i - \phi_j) . \quad (2.7)$$

The Hamiltonians \mathcal{H}_6 and \mathcal{H}_1 can be viewed as lattice-gas models of the bond- and tilt-angle degrees of freedom within each smectic layer. Strictly speaking, there should be different intralayer and interlayer couplings between molecules. We describe these interactions with isotropic couplings J_6 and J_1 for simplicity, since we do not expect spatial anisotropy to change our results qualitatively.

The lattice of sites in Eq. (2.6) is merely a convenient way of imposing an ultraviolet cutoff. It has absolutely no relation to the in-plane crystalline lattice present in bulk smectic-*B* and smectic-*G* liquid crystals. This artificial lattice is decoupled from the bond tilt orientational degrees of freedom studied here.

In Ref. 9, it was argued that there should be six-fold periodic coupling between the angles θ_i and ϕ_i ,

$$\mathcal{H}_{\text{int}} = -h \sum_i \cos(6\theta_i - 6\phi_i) . \quad (2.8)$$

$$f \equiv \frac{F}{N} = -\frac{1}{2} J_6 z \{ [\text{Tr}(\rho_0 \cos 6\theta)]^2 + [\text{Tr}(\rho_0 \sin 6\theta)]^2 \} - \frac{1}{2} J_1 z \{ [\text{Tr}(\rho_0 \cos \phi)]^2 + [\text{Tr}(\rho_0 \sin \phi)]^2 \} - h \text{Tr}[\rho_0 \cos 6(\theta - \phi)] , \quad (2.13)$$

where z is the number of nearest neighbors. Functionally minimizing f with respect to $\rho_0(\theta, \phi)$ gives

$$\rho_0 = e^{-\beta \mathcal{H}_0} / \text{Tr}(e^{-\beta \mathcal{H}_0}) , \quad (2.14)$$

where

$$\mathcal{H}_0 = -z J_6 [\cos 6\theta (\text{Tr} \rho_0 \cos 6\theta) + \sin 6\theta (\text{Tr} \rho_0 \sin 6\theta)] - z J_1 [\cos \phi (\text{Tr} \rho_0 \cos \phi) + \sin \phi (\text{Tr} \rho_0 \sin \phi)] - h \cos 6(\theta - \phi) . \quad (2.15)$$

But the traces in Eq. (2.15) can be evaluated using Eq. (2.14), giving rise to four self-consistency equations for these averages.

If we first set $h = 0$, the self-consistency equations decouple into pairs of 2. Upon defining a vector order parameter

$$(\Phi_0 \cos \phi_0, \Phi_0 \sin \phi_0) \equiv (\text{Tr}(\rho_0 \cos \phi), \text{Tr}(\rho_0 \sin \phi)) , \quad (2.16)$$

the phase angle ϕ_0 drops out, and the two self-consistency equations reduce to one for Φ_0 ,

$$\Phi_0 = \frac{\int_0^{2\pi} \cos \phi \exp(\bar{J}_1 \Phi_0 \cos \phi)}{\int_0^{2\pi} \exp(\bar{J}_1 \Phi_0 \cos \phi)} = \frac{I_1(\bar{J}_1 \Phi_0)}{I_0(\bar{J}_1 \Phi_0)} \quad (2.17)$$

Our final model Hamiltonian is then

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_6 + \mathcal{H}_1 + \mathcal{H}_{\text{int}} \\ &= -J_6 \sum_{\langle i,j \rangle} \cos(6\theta_i - 6\theta_j) - J_1 \sum_{\langle i,j \rangle} \cos(\phi_i - \phi_j) \\ &\quad - h \sum_i \cos(6\theta_i - 6\phi_i) . \end{aligned} \quad (2.9)$$

B. Mean-field approximation

The density matrix associated with the Hamiltonian (2.9) is

$$\rho = \exp(-\beta \mathcal{H}) / [\text{Tr} \exp(-\beta \mathcal{H})] , \quad (2.10)$$

where $\beta = 1/k_B T$.

The mean-field approximation¹² assumes that ρ factors,

$$\rho = \prod_i \rho_i , \quad (2.11)$$

where ρ_i is a single-spin-density matrix for site i , and should be independent of i for a translationally invariant system ($\rho_i = \rho_0$).

The resulting free energy F

$$F = \text{Tr} \rho H + \frac{1}{\beta} \text{Tr}(\rho \ln \rho) \quad (2.12)$$

is to be minimized with respect to ρ_0 under the condition that $\text{Tr} \rho_0 = 1$.

The free energy f per spin becomes

where $\bar{J}_1 \equiv J_1 z / k_B T$ and $I_n(x)$ is a modified Bessel function of order n . Expanding I_1 and I_0 for small arguments one finds the expected second-order phase transition at $\bar{J}_1^c \equiv 2$.

The self-consistency equation (2.17) could have been derived by minimization of the Gibbs free energy, where

$$\frac{G}{k_B T} = \frac{1}{2} \bar{J}_1 \Phi_0^2 - \ln \left(\int_0^{2\pi} \exp(\bar{J}_1 \Phi_0 \cos \phi) \right) . \quad (2.18)$$

An identical situation holds for θ with the appropriate order parameter

$$\psi_0 e^{i6\theta_0} \equiv \text{Tr} \rho_0 \cos 6\theta + i \text{Tr} \rho_0 \sin 6\theta . \quad (2.19)$$

When the coupling h between ϕ and θ is nonzero,

the invariance under simultaneous shifts of θ and ϕ implies three self-consistency equations for Φ_0 , ψ_0 , and $\theta_0 - \phi_0$. These can be derived from minimization of $G/k_B T$, where

$$G/k_B T = \frac{1}{2} \bar{J}_1 \Phi_0^2 + \frac{1}{2} \bar{J}_6 \psi_0^2 - \ln Z \quad (2.20)$$

and

$$Z = \int_0^{2\pi} d\phi \int_0^{2\pi/6} d\theta \exp[\bar{J}_1 \Phi_0 \cos(\phi - \phi_0) + \bar{J}_6 \psi_0 \cos 6(\theta - \theta_0) + \tilde{h} \cos 6(\theta - \phi)] \quad (2.21a)$$

and where

$$\tilde{h} = h/k_B T \quad (2.21b)$$

The formula for Z can be simplified to

$$Z = \frac{1}{6} \int_0^{2\pi} d\phi \exp(\bar{J}_1 \Phi_0 \cos \phi) I_0(\{\bar{J}_6^2 \psi_0^2 + \tilde{h}^2 + 2\tilde{h}\bar{J}_6 \psi_0 \cos 6[\phi - (\phi_0 - \theta_0)]\}^{1/2}) \quad (2.22)$$

It is easy to see that $\partial G/\partial \theta_0 = 0$ if $\theta_0 - \phi_0 = \frac{1}{6} n \pi$, where n is an integer, while numerical integration of Eq. (2.22) shows that (for $h > 0$) even n corresponds to minima and odd n to maxima. Henceforth, we allow $\theta_0 - \phi_0$ to assume one of the minimum values. Equation (2.22) can then be integrated for a number of limiting cases:

1. $\bar{J}_1 \rightarrow \infty$, \bar{J}_6 remains finite

Using the method of steepest descents we find

$$Z = \frac{1}{6} e^{\bar{J}_1 \Phi_0} I_0(\bar{J}_6 \psi_0 + \tilde{h}) + O(e^{\bar{J}_1 \Phi_0} / \bar{J}_1) \quad (2.23)$$

Minimizing G , we obtain

$$\Phi_0 \approx 1 \quad (2.24a)$$

$$\psi = I_1(\bar{J}_6 \psi_0 + \tilde{h}) / I_0(\bar{J}_6 \psi_0 + \tilde{h}) \quad (2.24b)$$

This is the mean-field equation for an XY model in an external magnetic field \tilde{h} , so no phase transition occurs for any \bar{J}_6 .

2. $\bar{J}_6 \rightarrow 0$, \bar{J}_1 remains finite

Expanding Eq. (2.22) in powers of $\bar{J}_6 \Phi_0 / \tilde{h}$ and performing the integrals one finds

$$\psi_0 = \frac{I_1(\tilde{h})}{I_0(\tilde{h})} \frac{I_6(\bar{J}_1 \Phi_0)}{I_0(\bar{J}_1 \Phi_0)} \quad (2.25)$$

This shows how ordering in Φ_0 induces ordering in ψ_0 even for small \bar{J}_6 .

3. $\bar{J}_6 \rightarrow \infty$, \bar{J}_1 remains finite

In this limit, Z can be directly evaluated from Eq. (2.22). The equation obtained by minimizing G with

respect to Φ_0 is then

$$\Phi_0 = \frac{\int_0^{2\pi} d\phi \cos \phi \exp(\bar{J}_1 \Phi_0 \cos \phi + \tilde{h} \cos 6\phi)}{\int_0^{2\pi} d\phi \exp(\bar{J}_1 \Phi_0 \cos \phi + \tilde{h} \cos 6\phi)} \quad (2.26)$$

A numerical solution of this equation shows a conventional second-order phase transition. The phase transition point \bar{J}_c can be found by expanding about $\Phi_0 = 0$ in Eq. (2.26).

$$\bar{J}_c^{-1} = \frac{\int_0^{2\pi} d\phi \cos^2 \phi \exp(\tilde{h} \cos 6\phi)}{\int_0^{2\pi} d\phi \exp(\tilde{h} \cos 6\phi)} = \frac{1}{2} \quad (2.27)$$

Contrary to case (1), we see that ordering in ψ_0 does not induce ordering in Φ_0 .

4. $\bar{J}_1 \approx 2$ and $\bar{J}_6 \approx 2$

This is a Ginzburg-Landau regime where both order parameters are small or zero. Expanding Z in both Φ_0 and Ψ_0 , we obtain for G ,

$$G = \frac{1}{2} J_6 (1 - \frac{1}{2} J_6) \psi_0^2 + \frac{1}{2} J_1 (1 - \frac{1}{2} J_1) \Phi_0^2 + \frac{1}{64} (\bar{J}_6^4 \psi_0^4 + \bar{J}_1^4 \Phi_0^4) + \alpha (\bar{J}_6^6 \psi_0^6 + \bar{J}_1^6 \Phi_0^6) - \frac{1}{2^6 \Gamma(7)} \frac{I_1(\tilde{h})}{I_0(\tilde{h})} \bar{J}_6 \psi_0 (\bar{J}_1 \Phi_0)^6 + \dots \quad (2.28)$$

where α is a small positive number. Minimizing G , we again see that $\psi_0 \neq 0$ if $\Phi_0 \neq 0$ but not the other way around. The bond-angle field undergoes a second-order phase transition at $\bar{J}_6 = 2$. Bond orientational order develops via a second-order phase transition at $\bar{J}_1 = 2$ if $\bar{J}_6 < 2$. There is merely a rapid change in Φ_0 near $\bar{J}_1 \approx 2$ if $\bar{J}_6 > 2$.

We can now give the complete phase diagram for our model as a function of

$$K_1^{-1} \equiv z\bar{J}_1, \quad K_6^{-1} \equiv z\bar{J}_6 \quad (2.29)$$

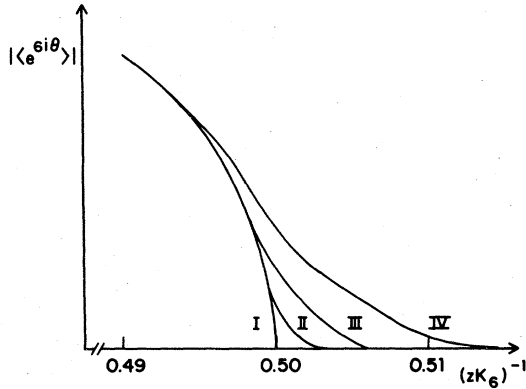


FIG. 3. Variation of the bond-angle order parameter $|\langle e^{6i\theta} \rangle|$ as a function of $(zK_6)^{-1} = \bar{J}_6^{-1}$ for various values of \bar{J}_1^{-1} . The curve labeled I applies for \bar{J}_1^{-1} larger than 0.5, II for $\bar{J}_1^{-1} = 0.45$, III for $\bar{J}_1^{-1} = 0.42$, and IV $\bar{J}_1^{-1} = 0.38$. If \bar{J}_1^{-1} is larger than 0.5 then there will be always bond-angle order for any value of $(zK_6)^{-1}$, although this is undetectable on the scale of the figure. The coupling $\tilde{h} = 80$.

for fixed \tilde{h} (see Fig. 2). The most important effect of \tilde{h} is induced hexatic order in the presence of tilt order. The “unlocked tilted hexatic” phase of Ref. 9 has disappeared. The variation of the bond-angle order parameter for various values of \bar{J}_1 with $\tilde{h} = 80$ is shown as a function of \bar{J}_6 in Fig. 3. This phase diagram agrees with the various limiting cases discussed above, and was checked by numerical minimization of the Gibbs free energy (2.20).

One might consider adding to the Hamiltonian (2.9) a more complicated coupling, of a kind considered in Ref. 9,

$$\mathcal{X}_\times = g \sum_{\langle ij \rangle} \sin(6\theta_i - 6\theta_j) \sin(\phi_i - \phi_j) . \quad (2.30)$$

In Ref. 9, it was found that this term could be generated by a renormalization-group transformation even if initially absent. We have studied the effect of such a term for small g ($g < \sqrt{J_1 J_6}$), and find that the phase diagram in Fig. 2 is qualitatively unchanged.

III. CRITICAL BEHAVIOR

Fluctuations, which are neglected in the mean-field approximation, become important near continuous phase transitions. They can often be accounted for rather accurately in three dimensions by an expansion in powers of $\epsilon = 4 - d$.¹⁰ Here, we refine the mean-field treatment of Sec. II in this way.

The starting point for our analysis is a coarse-grained free-energy functional of $\psi(\vec{r})$ and $\Phi(\vec{r})$. These complex quantities are spatial averages of the microscopic order parameters $e^{6i\theta(\vec{r})}$ and $e^{i\phi(\vec{r})}$ defined in Sec. II A, taken over regions large compared

to the lattice spacing, but still microscopic:

$$\psi(\vec{r}) \equiv \langle e^{6i\theta(\vec{r})} \rangle_{\text{cell}} , \quad (3.1a)$$

$$\Phi(\vec{r}) \equiv \langle e^{i\phi(\vec{r})} \rangle_{\text{cell}} . \quad (3.1b)$$

The hydrodynamic “cells” which are averaged over are centered at \vec{r} . The free-energy functional appropriate near the multicritical point labeled P in Fig. 2 is then

$$\begin{aligned} \frac{F}{k_B T} = \int d^d r \{ & \frac{1}{2} |\bar{\nabla} \psi|^2 + \frac{1}{2} r_6 |\psi|^2 + u_6 |\psi|^4 \\ & + \frac{1}{2} |\nabla \Phi|^2 + \frac{1}{2} r_1 |\Phi|^2 + u_1 |\Phi|^4 \\ & + \frac{1}{2} h [\Phi^6 \psi^* + (\Phi^*)^6 \psi] + w |\psi|^2 |\Phi|^2 \} . \end{aligned} \quad (3.2)$$

The probability of a given configuration of $\psi(\vec{r})$ and $\Phi(\vec{r})$ is proportional to $e^{-F/k_B T}$. A functional of this form without the gradient terms is suggested by the expansion (2.28) of the mean-field Gibbs free energy near the multicritical point. Although there is no coupling like the one proportional to w in Eq. (3.2), such a term could be present in more complicated models. Other interactions which would be permitted by symmetry in Eq. (3.2) turn out to be irrelevant, in the sense used by Wilson.¹⁰ As we shall see, w and h are formally “irrelevant variables” near P as well.

From Eq. (2.28), we expect that r_6 will vanish near the locus of mean-field smectic- A -to-stacked-hexatic transition temperatures. Far above the line of smectic- A -to-smectic- C transition temperatures ($r_1 \gg 0$), $\Phi(\vec{r})$ does not fluctuate strongly, and may be integrated out of the problem in perturbation theory. One is left with a free-energy functional of $\psi(\vec{r})$ only, with slightly altered parameters \bar{r}_6 and \bar{u}_6 ,

$$\frac{F_6}{k_B T} = \int d^d r \left(\frac{1}{2} |\bar{\nabla} \psi|^2 + \frac{1}{2} \bar{r}_6 |\psi|^2 + \bar{u}_6 |\psi|^4 + \dots \right) . \quad (3.3)$$

The critical properties at the smectic- A to smectic- A^* transition are then just those of the three-dimensional XY model. In particular the orientational order parameter $\langle \psi(r) \rangle$ vanishes with the XY critical exponent¹³ $\beta \approx 0.34$,

$$|\langle \psi(\vec{r}) \rangle| \sim |T - T_c|^\beta , \quad (3.4)$$

as $T \rightarrow T_c^-$. The mean-field value would be $\beta = \frac{1}{2}$.

Where r_1 is small, but r_6 large and positive, we are near the locus of smectic- A -to-smectic- C phase transitions. This transition is well-known to be XY -like,¹⁴ so

$$|\langle \Phi(\vec{r}) \rangle| \sim |T - T_c|^\beta , \quad (3.5)$$

as T_c is approached from below. This conclusion can

be checked by integrating the noncritical $\psi(\vec{r})$ field out of Eq. (3.2), and observing that an effective free energy of the form (3.2) in $\Phi(\vec{r})$ remains. Of somewhat more interest is the induced orientational order present when $\langle\Phi(\vec{r})\rangle$ is nonzero. As can be seen from Eq. (3.2), a nonzero $\langle\Phi(\vec{r})\rangle$ acts like an ordering field on $\psi(\vec{r})$.

The way in which $|\langle\psi(\vec{r})\rangle|$ vanishes near T_c can be determined by a simple scaling argument. Consider the quantity $\langle\psi(\vec{r})\rangle$ for large positive r_6 , and T just below T_c . Fluctuations in $\psi(\vec{r})$ can be eliminated by minimizing Eq. (3.2) with respect to $\Psi(\vec{r})$, with the field $\Phi(\vec{r})$ held fixed. For small $\psi(r)$, the minimum occurs for

$$\psi(\vec{r}) \approx \frac{-h}{r_6} [\Phi^*(\vec{r})]^6, \quad (3.6)$$

and one has

$$\langle\psi(\vec{r})\rangle \propto \langle[\Phi^*(r)]^6\rangle. \quad (3.7)$$

The average in Eq. (3.7) is given by an effective free-energy functional F_1 of $\Phi(\vec{r})$ only,

$$\begin{aligned} \frac{F_1}{k_B T} = \int d^d r \{ & (\frac{1}{2} |\vec{\nabla}\Phi|^2 + \frac{1}{2} \bar{r}_1 |\Phi|^2 + \bar{u}_1 |\Phi|^4 + \dots) \\ & + \frac{1}{2} h_6 [\Phi^6 + (\Phi^*)^6] \}, \end{aligned} \quad (3.8)$$

with h_6 set to zero. If the thermodynamic free energy \mathfrak{F}_1 associated with Eq. (3.8)

$$\exp(-\mathfrak{F}_1/k_B T) = \int \mathfrak{D}\Phi \exp(-F_1/k_B T), \quad (3.9)$$

is known, one can determine $\langle(\Phi^*)^6\rangle$,

$$\langle(\Phi^*)^6\rangle = \left. \frac{-\partial(\mathfrak{F}_1/k_B T)}{\partial(h_6/k_B T)} \right|_{h_6=0}, \quad (3.10)$$

Under a renormalization-group transformation, we expect that \mathfrak{F}_1 will transform as a function of $t = (T - T_c)/T_c$ and h_6 , like¹⁰

$$\mathfrak{F}_1(t, h_6) = e^{-d\mathfrak{G}} (e^{\lambda_t t} e^{\lambda_6 h_6}) \quad (3.11)$$

where λ_t is the reciprocal of the XY correlation length exponent, $\lambda_t = 1/\nu$, and λ_6 is the renormalization-group eigenvalue of h_6 . This eigenvalue has been calculated by Wegner and Houghton¹⁵ in an $\epsilon = 4 - d$ expansion,

$$\lambda_6 = -2 - \epsilon + \frac{87}{50} \epsilon^2 + O(\epsilon^3). \quad (3.12)$$

The series appears to oscillate with large coefficients, and a more accurate estimate is probably provided for $d = 3$ by a Padé approximant¹⁶

$$\lambda_6 \approx \frac{-2 - 4.8\epsilon}{1 + 1.74\epsilon}. \quad (3.13)$$

Thus we expect that $\lambda_6 \approx -2.36$ for $\epsilon = 1$. Making

use of Eq. (3.10), we find from Eq. (3.11) that

$$|\langle\psi(r)\rangle| \sim |\langle(\Phi^*)^6\rangle| \sim |t|^\beta, \quad (3.14)$$

where

$$\beta_6 = (d - \lambda_6)\nu \quad (3.15)$$

$$\approx 3.59. \quad (3.16)$$

We have used Eq. (3.13) and the value $\nu \approx 0.67$ for the XY critical exponent ν . Mean-field theory gives $\beta_6 = 3$.

According to Eq. (3.2), nonzero average $\langle\psi(r)\rangle$ does *not* induce order in $\Phi(\vec{r})$. At the locus of stacked-hexatic-to-smectic- C transitions, $|\langle\Phi(\vec{r})\rangle|$ rises from zero as in Eq. (3.5). The average $|\langle\psi(r)\rangle|$ is already finite on this line, however.

To determine the behavior near the special point P in Fig. 2, we study the full free-energy Eq. (3.2). When $h = w = 0$, the behavior at P is that of two decoupled but critical XY models. The importance of the couplings h and w can be determined by a trick first used by Kadanoff and Wegner.¹⁷ The idea is to look at autocorrelations of the couplings which interest us, in the ensemble where $h = w = 0$. The renormalization-group eigenvalue of h or w about the decoupled fixed point can then easily be read off.¹⁷ For example, the eigenvalue of w is easily seen to be

$$\lambda_w = \alpha/\nu. \quad (3.17)$$

Since the XY specific-heat exponent α is slightly negative in three dimensions, the cross coupling proportional to w in Eq. (3.2) is irrelevant. The renormalized coupling $w(l)$ will decay slowly to zero under a renormalization transformation. An analogous computation gives the eigenvalue of h in d dimensions

$$\lambda_h = 1 - \frac{1}{2}d - \frac{1}{2}\eta + \lambda_6, \quad (3.18)$$

where η is the XY critical exponent and λ_6 is given Eq. (3.13). In three dimensions $\eta \approx 0.02$ and $\lambda_h \approx -2.36$, so h is in fact strongly irrelevant near the decoupled fixed point as well! Our conclusion is that the critical behavior near P , at least when approached from the smectic- A phase, should be that of two decoupled XY models. As discussed by Fishman and Aharony,¹¹ in a different context, one expects only singular curvature corrections to the straight lines of critical points terminating at P .

If bond- and tilt-orientation angles were truly decoupled, one would expect *four* lines of critical points coming from P , including one separating a tilted hexatic phase from a tilted phase without bond orientational order. We have seen, however, that bond orientational order is always induced when $\langle\Phi\rangle$ is nonzero. This coupling washes out this extra critical line, even though it is formally irrelevant at P . In this sense, h is a "dangerous irrelevant variable."¹⁸ If h is sufficiently small, the behavior across the dashed line near P in Fig. 2 could mimic many features of a real phase transition.

IV. COUPLING OF ORIENTATIONAL ORDER TO DENSITY FLUCTUATIONS

Order in the tilt orientations of smectic-*C* liquid crystals is readily observed, by looking for in-plane anisotropies in quantities such as the dielectric tensor. Because of its intrinsic sixfold rotational symmetry, bond orientational order is more difficult to observe. As pointed out by Birgeneau and Litster,³ long-range bond orientational order would in fact be detectable as a sixfold pattern of spots in the in-plane monodomain x-ray structure factor,

$$S(\vec{q}) = \langle |\hat{\rho}(\vec{q})|^2 \rangle . \quad (4.1)$$

$$\frac{F_d}{k_B T} = \frac{F}{k_B T} + \frac{1}{2} \int_{\Lambda_0 < q < \Lambda_1} d^d q \{ A_q |\hat{\rho}(\vec{q})|^2 + B_q [z_{\vec{q}}^6 \psi_0^* + (z_{\vec{q}}^*)^6 \psi_0] |\hat{\rho}(\vec{q})|^2 \} . \quad (4.2)$$

Only density fluctuations in an annulus of Fourier space $\Lambda_0 < |\vec{q}| < \Lambda_1$ have been considered. We take this annulus to include the interesting region surrounding the first maximum of the liquidlike in-plane structure factor of the smectic-*A* phase. The quantities A_q and B_q in Eq. (4.2) are functions only of $q = |\vec{q}|$, while the direction dependence is contained in

$$z_{\vec{q}} \equiv q_x + iq_y . \quad (4.3)$$

Density fluctuations in the annulus are coupled to ψ_0 , the $q = 0$ Fourier component of $\psi(\vec{r})$. The coupling term proportional to B_q is invariant under simultaneous sixfold rotations of the axis in Fourier space and ψ_0 , as it should be. One could probably couple density fluctuations to a spatially varying bond orientational order parameter $\psi(\vec{r})$ in a similar way, provided the variations were on a scale much longer than Λ_0^{-1} . The present model is certainly reasonable well below any bond orientational phase transition.

The model (4.2) has virtue that, if we integrate over density fluctuations, we recover a free energy of the form already treated in Sec. III. Upon defining

$$\exp(-\bar{F}/k_B T) \propto \left[\prod_{\Lambda_0 < q < \Lambda_1} \int d\hat{\rho}(\vec{q}) \right] \exp(-F_d/k_B T) \quad (4.4)$$

we find, with $\psi_0 = |\psi_0| e^{i6\theta_0}$

$$\frac{\bar{F}}{k_B T} = \frac{F}{k_B T} + \sum_{\Lambda_0 < q < \Lambda_1} \ln [A_q + B_q q^6 |\psi_0| \times \cos(6\theta_q - 6\theta_0)] , \quad (4.5)$$

Here, $\hat{\rho}(\vec{q})$ is the Fourier component of the density at wavevector $\vec{q} = (q_x, q_y)$. In this section we propose a simple model of the coupling of orientational order to density fluctuations. The model is valid when density fluctuations become decorrelated over distances much shorter than the scale on which $\psi(\vec{r})$ varies appreciably. With this limitation, the model allows us to translate results for $\langle \psi(\vec{r}) \rangle$ contained in Secs. II and III into observable predictions for $S(\vec{q})$.

The model we propose is a modification of the phenomenological Landau-Ginzburg expression for $F/k_B T$, given in Eq. (3.2). The modified free-energy functional F_d which includes density fluctuations is,

where θ_q is the angle \vec{q} makes with, say, the x axis. The dependence on θ_0 drops out upon doing the integration over different directions of \vec{q} . The second term of Eq. (4.5) can be expanded in powers of $|\psi_0|^2$ which simply renormalize the $q = 0$ parts of various terms in Eq. (3.2).

Integrating over density fluctuations in Eq. (4.1), we can find an expression for $S(\vec{q})$.

$$S(\vec{q}) = \left\langle \frac{1}{A_q + B_q [z_{\vec{q}}^6 \psi_0^* + (z_{\vec{q}}^*)^6 \psi_0]} \right\rangle . \quad (4.6)$$

The primed average is now over an ensemble weighted by $\exp(-\bar{F}/k_B T)$. At very low temperatures we can approximate Eq. (4.6) by

$$S(\vec{q}) = \frac{1}{A_q + B_q [z_{\vec{q}}^6 \langle \psi \rangle^* + (z_{\vec{q}}^*)^6 \langle \psi \rangle]} . \quad (4.7)$$

Assuming that A_q has a minimum in the range $\Lambda_0 < q < \Lambda_1$ (corresponding to the maximum in the structure factor when $\langle \psi \rangle = 0$), so that $|B_q|$ is roughly constant and less than A_q in this range, we find the pattern of six spots in $S(\vec{q})$ one expects when orientational order is present. Both A_q and B_q can vary smoothly with temperature.

More generally, we expect a result for $S(\vec{q})$ of the form

$$S(\vec{q}) = \left\langle \frac{1}{A_q(T) + B_q(T) [z_{\vec{q}}^6 \psi^*(\vec{r}) + (z_{\vec{q}}^*)^6 \psi(\vec{r})]} \right\rangle . \quad (4.8)$$

provided fluctuations in $\psi(\vec{r})$ on scales less than Λ_0^{-1} have been filtered out. We can evaluate Eq. (4.8) for simplicity in an ensemble specified by the lattice model (2.9), with $\psi(\vec{r}) = e^{i6\theta(\vec{r})}$. Expanding Eq. (4.6) in a Fourier series near a phase transition, we

obtain a result of the form

$$S(\vec{q}) = \sum_{n=0}^{\infty} c_n(q, T) \cos(6n\theta_{\vec{q}}) \langle \exp[6in\theta(\vec{r})] \rangle. \quad (4.9)$$

The behavior of the averages $\langle \exp[6in\theta(\vec{r})] \rangle$ can be determined by the methods of Sec. III, where the case $n = 1$ is discussed explicitly. The coefficients $c_n(q, T)$ should be finite at any critical temperatures, but may exhibit $|T - T_c|^{1-\alpha}$ singularities as the smectic- A -to-stacked-hexatic transition temperature is approached. Equation (4.9) leads immediately to the prediction (1.4) discussed in the Introduction.

Note added in proof. After the completion of this work, we received a paper by D. E. Moncton and R. Pindak [Proceedings of the International Conference on Ordering in Two Dimensions, Geneva, Wisconsin,

May 1980 (unpublished)]. These authors report observation of a smectic phase with a sixfold modulation of the in-plane x-ray structure factor, but with a finite in-plane translational correlation length. These properties are consistent with those of the stacked hexatic phase discussed here.

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