Hexatic Order and Herring-Bone Packing in Liquid Crystals

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A model is proposed for coupled bond-orientational and herring-bone packing degrees of freedom in layered liquid crystals. Three distinct phases are possible: isotropic, and bond-orientationally ordered stacked hexatic with and without herring-bone order. The transition between the two ordered phases is first order. The isotropic-hexatic transition can be driven first order by fluctuations and becomes second order at a tricritical point. Available experimental data are consistent with our model.

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In ordinary three-dimensional (3D) systems, melting proceeds via a first-order transition directly from solid to liquid. Recently, there has been a growing awareness that matters may be different in two dimensions. In particular, Halperin and Nelson[1] proposed a 2D melting process where the solid is first transformed into an intermediate "hexatic" phase, characterized by short-range positional order and algebraic decay of bond-orientational order. Upon further heating, a continuous disclination unbinding transition into the isotropic liquid phase takes place. It was soon realized that hexatic phases, with short-range positional order and true long-range bond-orientational order, might exist in highly anisotropic 3D systems.[2] The smectic-B and -F phases of liquid crystals, where the molecules form hexagonally ordered layers, were regarded as potential 3D, or "stacked," hexatics. Very recently, x-ray studies of free-standing films have demonstrated that the smectic-B phase of one material, n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate (65OBC), is indeed a stacked hexatic.[3] In addition to the hexagonal pattern of diffuse spots which is the signature of the hexatic phase, Pindak *et al.* observed somewhat broader peaks corresponding to correlations in the molecular orientations about their long axes. The positions of these peaks indicate that locally, the molecules are packed according to a herring-bone scheme.[4]

The x-ray work[3] and subsequent specific-heat measurements[5] showed that in 65OBC, the transition from the smectic-B to the smectic-A phase, with isotropic intralayer correlations, is continuous. Contrary to expectations that the critical behavior here should be He like, a large and positive specific-heat exponent ($\alpha = 0.64$) was found. As the temperature is decreased in the hexatic phase, a first-order transition into a crystalline phase with long-range herring-bone order (smectic E) takes place.

Because of the x-ray evidence for unusually strong local herring-bone order in both the smectic-A and -B phases of 65OBC, we have formulated a model for a liquid crystal with coupled herring-bone and bond-orientational degrees of freedom. With this model, it is possible to understand the peculiar critical behavior at the smectic-A–hexatic transition. In this paper, we describe our model, explore its phase diagram within mean-field theory, and show how fluctuations substantially alter the mean-field results.

The local order parameter associated with bond-orientational order is defined[1] by $\Psi(\vec{r}) = \exp[i6\psi(\vec{r})]$ where ψ is the bond-angle field defined in Fig. 1(a). To obtain also a convenient measure for herring-bone order, we recall that three orientationally inequivalent herring-bone patterns can be superposed on a triangular lattice[6] [Fig. 1(b)]. Furthermore, each of these

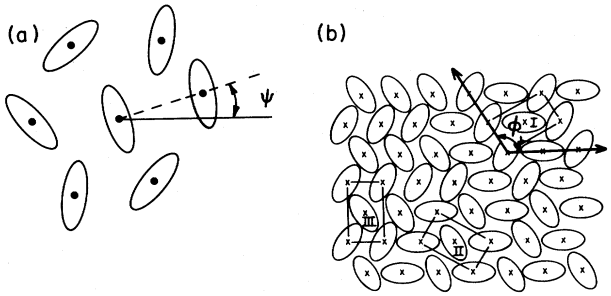

FIG. 1. The two coupled order parameters necessary to describe liquid crystals like 65OBC. (a) Shows how the lines joining the centers of neighboring molecules define a bond-orientation angle ψ with respect to a reference axis. (b) Shows the three possible herring-bone orientations and how the angle between the axis along which nearest neighbors have parallel body orientations and the reference direction define the herring-bone angle φ.

may be translated over a lattice vector to produce a different herring-bone pattern, though with the same orientation. Consequently, the herring-bone order parameter for a triangular lattice is a three-component spin variable.[6] However, smectic-A and stacked-hexatic fluids are characterized by a finite in-plane positional correlation length ξ. There are no means to decide whether two orientationally equivalent herring-bone patterns, superposed on two regions separated by $r > \xi$, have been translated with respect to one another. Thus, as long as we do not study solidification, it is sufficient to describe local herring-bone order by $\Phi(\vec{r}) = \exp[2i\varphi(\vec{r})]$, where φ, defined in Fig. 1(b), gives the angle between the local herring-bone axis and a reference direction.

Recall now that the hexatic is sixfold symmetric, while rotating a herring-bone pattern by 180° leaves it unchanged. Consequently, the Ginzburg-Landau free energy F which describes the problem of coupled herring-bone and hexatic degrees of freedom should be invariant with respect to the transformations $\varphi(\vec{r}) \to \varphi(\vec{r}) + n\pi$ and $\psi(\vec{r}) \to \psi(\vec{r}) + m(2\pi/6)$ where n and m are integers. Thus, to lowest order in Ψ and Φ,

$$F/k_B T = \int d^3r \{ \tfrac{1}{2} |\nabla\Psi|^2 + \tfrac{1}{2} r_6 |\Psi|^2 + u_6 |\Psi|^4 + \tfrac{1}{2} |\nabla\Phi|^2 + \tfrac{1}{2} r_2 |\Phi|^2 + u_2 |\Phi|^4 + w |\Phi|^2 |\Psi|^2 + h\,\mathrm{Re}(\Psi^* \Phi^3) \} . \quad (1)$$

The condition for thermodynamic stability of F is (if $w = 0$)

$$h^{4/3} < (4^{4/3}/3) u_2 u_6^{1/3} . \quad (2)$$

Free-energy functionals similar to F are relevant not only to liquid crystals,[7] but also to monolayers of diatomic molecules,[6] and to magnetic systems with two coupled spin degrees of freedom.[8]

We first discuss the mean-field phase diagram. For $w = 0$ and $h = 0$, Eq. (1) simply represents two decoupled xy models, and the resulting phase diagram in the r_2-r_6 plane will include four distinct phases ($\Psi = \Phi = 0$; $\Psi = 0, \Phi \neq 0$; $\Psi \neq 0, \Phi = 0$; $\Psi \neq 0, \Phi \neq 0$), separated by lines of second-order transitions. If $h \neq 0$, one of these phases, namely that with herring-bone but without hexatic order ($\Psi = 0, \Phi \neq 0$), will be eliminated because Φ acts as a field on Ψ. Conversely, if we set $\psi = \text{const}$, F describes a system with the symmetry of the three-state Potts model. Since the ordering transition in a 3D three-state Potts model is first order, the transitions between the pure hexatic and hexatic plus herring-bone phases should be first order. Within mean-field theory, the transition lines between the isotropic and ordered phases remain second order for $h \neq 0$, and terminate together with the first-order line at a bicritical point, as shown in Fig. 2(a).

We now discuss the fluctuation-induced corrections to mean-field behavior. For $h = 0$ and $w = 0$, we have two decoupled 3D xy models with critical exponents $\alpha \simeq -0.02$, $\eta \simeq 0.02$, and $\nu = 0.67$. The renormalization group (RG) eigenvalues of h and w at the decoupled fixed point are determined by the method of Kadanoff and Wegner,[9] giving

$$\lambda_w = \alpha/\nu \simeq 0.03 , \quad (3a)$$

$$\lambda_h = 1 - \tfrac{1}{2} d - \tfrac{1}{2} \eta + \lambda_3 = 0.36 + O(\epsilon^3) , \quad (3b)$$

where[10] $\lambda_3 = 1 - 0.1\epsilon - 0.03\epsilon^2$ and $\epsilon = 4 - d$. So, w is an *irrelevant* perturbation. To understand the effect of h, one finds the RG flow equations and solves them close to the decoupled fixed point.

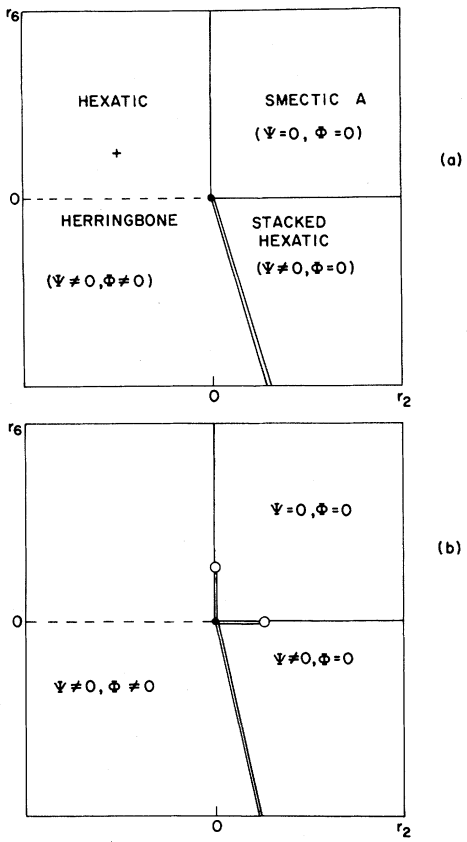

FIG. 2. Mean-field (a) and fluctuation-corrected (b) phase diagrams for a system with coupled hexatic (Ψ) and herring-bone (Φ) degrees of freedom. Single and double lines denote second- and first-order transitions, respectively.

To first order in ϵ, we have

$$\frac{dr_2}{dl} = 2r_2 + \frac{16u_2K_4}{(1+r_2)} + \frac{2wK_4}{(1+r_6)}, \tag{4a}$$

$$\frac{dr_6}{dl} = 2r_6 + \frac{16u_6K_4}{(1+r_6)} + \frac{2wK_4}{(1+r_2)}, \tag{4b}$$

$$du_2/dl = \epsilon u_2 - 40u_2^2K_4 - 2w^2K_4 - 9h^2K_4, \tag{4c}$$

$$du_6/dl = \epsilon u_6 - 40u_6^2K_4 - 2w^2K_4, \tag{4d}$$

$$dw/dl = \epsilon w - 16wu_6K_4 - 16wu_2K_4 - 8w^2K_4, \tag{4e}$$

$$dh/dl = \epsilon h - 24hu_2K_4, \tag{4f}$$

with $K_4 = 1/8\pi^2$.

The decoupled fixed point is given by $r_2^* = r_6^* = -\frac{1}{5}\epsilon$ and $u_2^* = u_6^* = \epsilon/40K_4$. [The *isotropic* fixed point ($n = 4$) is known to be unstable[11] if $n \geq 3.1$.] There is no fixed point with $h \neq 0$. For $r_2(l), r_6(l) \ll 1$, and $w = 0$, Eqs. (4c) and (4f) can be integrated numerically, and the RG flow goes into the unstable region (see Fig. 3). This usually indicates a first-order-phase transition.[12] The transition occurs when $l^* \sim \ln(\epsilon/40K_4h)/\lambda_h$, and $r_2(l^*)$ and $r_6(l^*)$ will still be small if the starting parameters r_2 and r_6 are $\ll (40K_4h/\epsilon)^{1/(\lambda_h \nu)}$. Thus, close to the multicritical point, fluctuations convert the two second-order lines found in the mean-field treatment [Fig. 2(a)] into first-order lines [Fig. 2(b)].

On the other hand, if r_6 is small and r_2 is of order unity, we can integrate out the fluctuations in Φ to obtain an effective free energy functional

$$F_{\text{eff}} = \int (\tfrac{1}{2}|\nabla\psi|^2 + \tfrac{1}{2}\tilde{r}_6|\Psi|^2 + \tilde{u}_6|\Psi|^4) d^3r, \tag{5}$$

where $\tilde{r}_6 = r_6 - c_1h^2\ln(\Lambda^2/r_2)$ and $\tilde{u}_6 = u_6 - c_2h^4/r_2^{1.5}$, with c_1 and $c_2 > 0$ and Λ an ultraviolet cutoff. As long as $\tilde{u}_6 > 0$, a *second-order phase transition* with xy-like critical behavior will occur. The simplest means of connecting this second-order line with the corresponding first-order line near the multicritical point is through a tricritical point where $\tilde{u}_6$ vanishes,[13] as shown in Fig. 2(b). Similarly, there should be a tricritical point on the line separating the isotropic from the herring-bone plus hexatic phases.

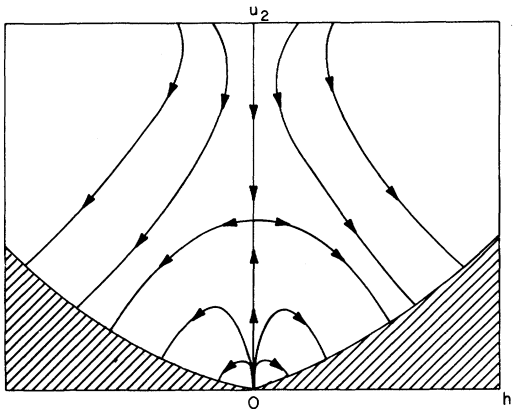

FIG. 3. Renormalization-group flow diagram for the herring-bone coupling u_2 and the coupling h between herring-bone and hexatic order. In the hatched region the Landau-Ginsberg-Wilson free energy [Eq. (5)] is unstable.

We now discuss the relevance of our model to real hexatic liquid crystals, in particular 65OBC. Firstly, the unusual specific-heat exponent $\alpha_{\text{exp}} = 0.64$ observed at the smectic-A–hexatic transition can be explained in terms of this transition occurring near the tricritical point in Fig. 2(b). The discrepancy between α_{exp} and the 3D Gaussian value, $\alpha = 0.5$, is not significant in the context of experiments on tricritical behavior in systems other than He_3-He_4 mixtures: for example, $\alpha_{\text{exp}} = 0.57$ in NH_4Cl and 0.65 in $FeCl_2$.[14] To test the existence of the tricritical point, experiments should be performed on mixtures of 65OBC with similar compounds, for example 75OBC, where phase separation is unlikely.

In summary, we have presented a theory for stacked hexatics which takes into account the tendency of the anisotropic liquid-crystal molecules towards forming a close-packed herring-bone array. Our model will yield qualitatively different results in two rather than three dimensions,[15] and consequently, we are looking forward to x-ray scattering studies of both thin films and surface layers of bulk 65OBC. Finally, the coupling of herring-bone order to density fluctuations and the possibility of a noncrystalline smectic phase with long-range herring-bone order remain to be investigated.

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