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Monte Carlo simulation of a coupled XY model

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Employing the Monte Carlo simulation technique, we have investigated several phase transitions exhibited by a coupled XY model in two dimensions. The model is based on the Hamiltonian proposed by Bruinsma and Aeppli [Phys. Rev. Lett. **48**, 1625 (1982)]. The simulation results demonstrate the existence of a new type of phase transition in which two different orderings are simultaneously established through a continuous transition. The unique nature of this phase transition provides a plausible explanation for our recent high-resolution heat-capacity data near the smectic-A–hexatic-B transition of two-layer free-standing films.

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In light of high-resolution x-ray diffraction studies [1] and heat-capacity measurements [2] near the bulk smectic-A (Sm-A) –hexatic-B (Hex-B) transition in the liquid-crystal compound n-hexyl-4′-n-pentyloxybiphenyl-4-carboxylate (65OBC), many theoretical models [3,4] have been proposed to explain the nature of this intriguing phase transition. The x-ray diffraction study [1] of thick 65OBC films in the Hex-B phase not only revealed long-range bond-orientational order with short-range positional order, indicative of hexatic order in three dimensions, but also displayed additional peaks characteristic of herringbone order. So far, the degree of the herringbone order in the Hex-B phase (short- or long-range order) has not been carefully studied by either x-ray or electron-beam diffraction experiments. Assuming that only the bond-orientational order [$|\Psi|\exp(i6\psi)$] [5] becomes long ranged through the Sm-A–Hex-B transition, this transition should be a member of the XY universality class. The heat-capacity critical exponent should, therefore, be equal to $\alpha=-0.007$ [6]. If the system is near a tricritical point, however, the exponent is predicted to be $\alpha=0.5$. Detailed heat-capacity measurements on bulk samples have yielded very sharp heat-capacity anomalies associated with the Sm-A–Hex-B transition with no detectable thermal hysteresis. Moreover, the temperature variation of the heat capacity near the Sm-A–Hex-B transition of 65OBC has been successfully fit to a power-law expression ($C_p \approx |t|^{-\alpha}$), giving $\alpha=0.60\pm0.03$ [2], which is clearly not consistent with the simple XY critical exponent ($\alpha=-0.007$) in three dimensions. Several theoretical advances [3,4] have therefore been made on the basis of the assumption that the transition is in the vicinity of a tricritical point.

The bond-orientational order (Ψ) can be represented by an XY order parameter [$\Psi=|\Psi|\exp(i6\psi)$] [5]. Because the Hex-B phase exhibits only short-ranged positional order, Bruinsma and Aeppli [3] have argued that the herringbone order (Φ) can also be represented by an XY order parameter [$\Phi=|\Phi|\exp(i2\phi)$]. To formulate the Landau free energy F, which describes both the hexatic and the herringbone order, one notices that the hexatic order possesses sixfold symmetry, while rotating a herringbone pattern by 180° leaves it unchanged. Thus the coupling term should be invariant under the transformations $\psi\rightarrow\psi+m(\pi/3)$ and $\phi\rightarrow\phi+n\pi$, where m and n are integers. Bruinsma and Aeppli formulated the appropriate free energy and considered the fluctuation-induced corrections to mean-field behavior for three-dimensional systems. Their result indicates the existence of two tricritical points, one for the transition between the Sm-A phase ($\Psi=0$, $\Phi=0$) and the stacked hexatic phase ($\Psi\neq0$, $\Phi=0$), and another for the transition between the Sm-A and the phase possessing both hexatic and herringbone order ($\Psi\neq0$, $\Phi\neq0$). While arguments based on the tricritical nature of the Sm-A–Hex-B transition are plausible, it is difficult to understand why seven different liquid-crystal compounds and five binary mixtures, with very different Sm-A and Hex-B temperature ranges, yield $\alpha=0.60\pm0.04$ [7] and should all be in the immediate vicinity of a particular thermodynamic point [8].

To obtain further insight into the nature of this intriguing transition, we have conducted high-resolution calorimetric investigations near the Sm-A–Hex-B transition of several nmOBC compounds in the form of free-standing liquid-crystal films with thickness ranging from two to a few hundred molecular layers. (nmOBC refers to the n-alkyl-4′-n-alkyloxybiphenyl-4-carboxylate homologous series.) In contrast to a broad heat-capacity hump predicted for the two-dimensional XY topological transition [9], the calorimetric investigations of two-layer free-standing films of five different nmOBC compounds yield very sharp heat-capacity peaks near the Sm-A–Hex-B transition. No thermal hysteresis could be detected to within the 10 mK experimental resolution. Moreover, the two-layer film heat-capacity anomaly can be described by a power-law expression with the critical exponent $\alpha=0.30\pm0.05$ [10]. These experimental results

indicate that the system cannot be described by the 2D XY model [11], and that order, in addition to bond-orientational order, may be established through the transition. Since herringbone order can be described by a three-state Potts model, which is predicted to exhibit a continuous transition with $\alpha=\frac{1}{3}$ in two dimensions [12], we have reconsidered Bruinsma and Aeppli's model in two dimensions.

To lowest order in Ψ and Φ, one obtains the following simplified Hamiltonian in a two-dimensional lattice:

$$H=-J_1\sum_{\langle ij\rangle}\cos(\psi_i-\psi_j)-J_2\sum_{\langle ij\rangle}\cos(\phi_i-\phi_j)$$
$$-J_3\sum_i\cos(\psi_i-3\phi_i)\ ,$$

where the coefficients J_1 and J_2 are the nearest-neighbor ($\langle i,j\rangle$) coupling constants for the bond-orientational order (Ψ) and herringbone order (Φ), respectively. The coefficient J_3 denotes the coupling strength between these two types of order at the same lattice site. We are interested in situations in which Ψ and Φ are coupled relatively strongly, and therefore we have chosen $J_3=2.1$ (larger than both J_1 and J_2) for all of the simulations.

Let us first consider the following simple scenario. Take $J_1>J_2$ (say, $J_1=1.0$ and $J_2=0.3$). At sufficiently high temperatures ($T>J_3$), the system is in a completely disordered phase. (The temperature of the system is scaled with respect to the coupling constants.) For $J_3>T>J_1$, the system remains disordered but the phase factors (ψ_i and ϕ_i) of the two order parameters become coupled through the J_3 term. For $3J_2/2<T<J_1$, bond-orientational order is established, and the ordered state corresponds to $\psi_i\approx\psi_j$ for all sites i and j [13]. Without loss of generality, we can choose $\psi_i=0$. Consequently, in this temperature range, there are degenerate minima of the free energy at $\phi_i\approx 0$, $2\pi/3$, and $4\pi/3$ [13]. Further decreasing the temperature below $3J_2/2$ [14], causes the J_2 term to single out one of the three values for ϕ_i to be the lowest-energy state, leaving the other two degenerate states at a higher value. Thus, for $J_3\gg J_1>3J_2/2$, the model exhibits an XY transition at $T_{c1}\approx J_1$ and the three-state Potts transition at $T_{c2}\approx 3J_2/2$ [15].

Employing standard Monte Carlo calculations on a 30×30 lattice, we have obtained the heat-capacity data as a function of temperature, shown in Fig. 1 for $J_1=1.0$ and $J_2=0.3$. During each simulation step, the angles ψ_i and ϕ_i were treated as nonconstrained, continuous variables. To ensure thermal equilibrium, 100 000 Monte Carlo steps were used for each temperature. As expected, no heat-capacity peak is discernible near $T=2.1$. From the preceding discussion, it is clear that the small broad hump near $T=1.0$ signals the XY transition due to the J_1 term. The sharp peak located at $T=0.43$ is expected to signal a transition into the state of three-state Potts symmetry. This result has been confirmed by conducting finite-size scaling analyses [16], using the following lattice sizes: 8×8, 16×16, 24×24, 30×30, and 40×40. The analyses give the ratio $\alpha/\nu=0.44\pm0.05$. Employing the scaling relation $d\nu=2-\alpha$ (here $d=2$) for the two-dimensional system, we obtain $\nu=0.82\pm0.1$ and $\alpha=0.36\pm0.05$, which are in good agreement with the theoretical calculated values $\nu=\frac{5}{6}$ and $\alpha=\frac{1}{3}$ for the three-state Potts transition in two dimensions [12].

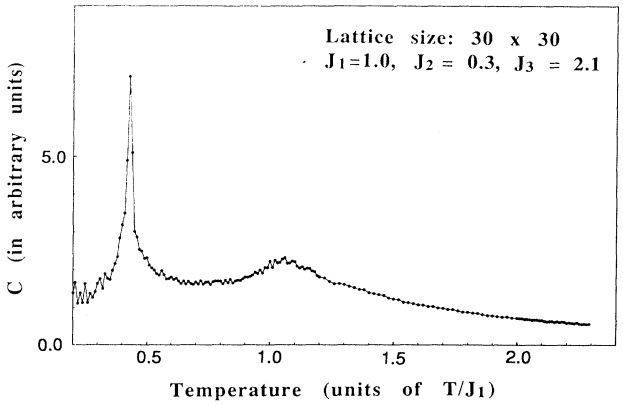

FIG. 1. Temperature dependence of the heat capacity (C) for $J_1=1.0$, $J_2=0.3$, and $J_3=2.1$. The size of lattice is 30×30.

By taking the values of $J_3=2.1$ and $J_1=1.0$ and varying the value of J_2 between 0 and $\frac{2}{3}$, the XY transition (near $T_{c1}=1.0$) is expected to be followed by a three-state Potts transition (at $T_{c2}\approx 3J_2/2$). The expected behavior of the system for $J_2>\frac{2}{3}$ is not entirely clear. Is there a single transition into the state with both herringbone and hexatic order? If so, is it continuous or first order? Or does the system continue to exhibit two separate transitions? Our simulation results demonstrate that a single continuous transition is obtained for $J_2>0.75$ and that two separate transitions are still apparent for $0.75>J_2>\frac{2}{3}$. In addition to the results shown in Fig. 1, we have completed Monte Carlo simulations for $J_2=0.67$, 0.75, 0.85, 0.95, 1.4, and 1.6; part of these results are displayed in Fig. 2. Figure 3 shows a schematic diagram of the phase transition sequences as a function of J_2. In the case of $J_2=0.67$, a sharp heat-capacity peak ($T_{c2}=0.90$) with a small shoulder on the high-temperature side is observed. Apparently, the transition temperature (T_{c2}) in the state with three-state Potts symmetry is noticeably reduced due to the small temperature range of the hexatic (XY) ordered state. Unfortunately, it is not possible to accurately determine the transition temperature (T_{c1}) of the XY transition. Assuming that the value of T_{c1} is not affected by the proximity of the three-state Potts transition, it is expected to be approximately equal to 1 [17]. We have therefore used a dashed line in Fig. 3 to represent part of the isotropic XY phase boundary. For $J_2=0.75$, the heat-capacity maximum occurs at $T=0.99$ and the data also exhibit a small shoulder on the high-temperature side of the larger peak. The cases in which $J_2=0.85$ and 0.95 yield only single, symmetric, sharp peaks at $T_c=1.08$ and 1.18, respectively. Finally, a smaller and broader heat-capacity anomaly is observed for $J_2=1.4$ and 1.6 [18]. The nature of the transition has been established by conducting successive heating and cooling runs with $J_2=0.95$. Since no thermal hysteresis could be detected to within the resolution of the simulation, the transition appears to be continuous.

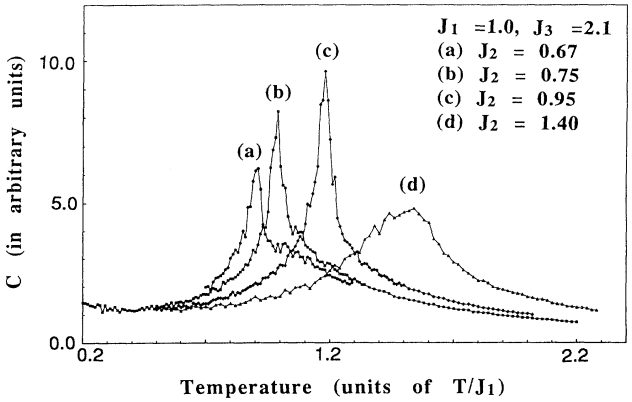

FIG. 2. Temperature dependence of the heat capacity (C). The constants $J_1=1.0$ and $J_3=2.1$ are fixed. The constant $J_2=0.67$, 0.75, 0.95, and 1.4 for curves (*a*), (*b*), (*c*), and (*d*), respectively.

From Fig. 2, it is apparent that only a single large and sharp heat-capacity anomaly is observable for a range of J_2 values. At least this is the case for both $J_2=0.85$ and $J_2=0.95$. Obviously, the transition temperature increases more slowly for $J_2>\frac{2}{3}$ than that responsible for the transition into the three-state Potts state for $J_2<\frac{2}{3}$. Finite-size scaling analyses with $J_2=0.67$, 0.75, 0.85, and 0.95 and lattice sizes 8×8, 16×16, 24×24, 30×30, and 40×40 have also been carried out. The scaling analyses yield $\alpha/\nu=0.44\pm0.05$, which is in good agreement with the ratio characterizing the three-state Potts transition in two dimensions. This indicates that $\alpha=\frac{1}{3}$ can be found in some ranges of the J_1-J_2-J_3 parameter spaces [19].

To identify the nature of the state just above the single heat-capacity peak (with $J_2=0.95$), histograms for ψ_i and ϕ_i at $T=1.20$ have been plotted in Fig. 4(a). This temperature is only slightly above the transition temperature ($T_c=1.18$). To within one standard deviation of the mean value, these histograms demonstrate that the phase above T_c is indeed a disordered one. On the other hand, slightly below T_c (say, $T=1.16$) we found that both ψ_i and ϕ_i exhibit some degree of order, with peaks in the histogram shown in Fig. 4(b). Consequently, this transition establishes both hexatic and herringbone order, and is different from the simple three-state Potts transition.

In summary, employing a Monte Carlo simulation, we have investigated the phase diagram associated with the Hamiltonian proposed by Bruinsma and Aeppli. With $J_1=1.0$ and $J_3=2.1$, the simulation results demonstrate that for $1.4>J_2>0.75$ both ψ_i and ϕ_i can simultaneously establish order through a transition that is continuous to within the resolution of our simulation. Furthermore, the heat-capacity critical exponent characterizing this single transition has a value of $\alpha=0.3$. To the best of our knowledge, this is one of the ways to simultaneously establish the order of two physical parameters through a single continuous transition [19]. This mechanism may be responsible for the experimental results obtained from two-layer free-standing liquid-crystal films near the Sm-A–Hex-B phase of several compounds in the nmOBC homologous series. Experimentally, we have found that the Sm-A–Hex-B transition of two-layer nmOBC liquid-crystal films is characterized by a single heat-capacity peak with critical exponent $\alpha=0.30\pm0.05$ [10]. It should be noted that the transition occurring in the range $0.75<J_2<1.4$ (see Fig. 3) is not a simple three-

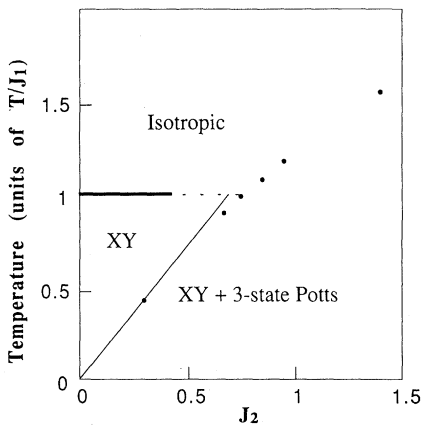

FIG. 3. Schematic of the phase diagram: transition temperature vs J_2 with $J_1=1.0$ and $J_3=2.1$. The solid dots are determined by the peak positions of heat-capacity anomalies. The narrow line is determined by the relationship $T_{c2}=3J_2/2$. The heavy isotropic XY transition line is assumed to be at $T=1.0$. However, as the temperature range for the XY state diminishes, it is very difficult to separate the small heat-capacity hump for the XY transition from the large heat-capacity peak associated with the three-state Potts transition. We have therefore used a dashed line in this region to indicate this uncertainty.

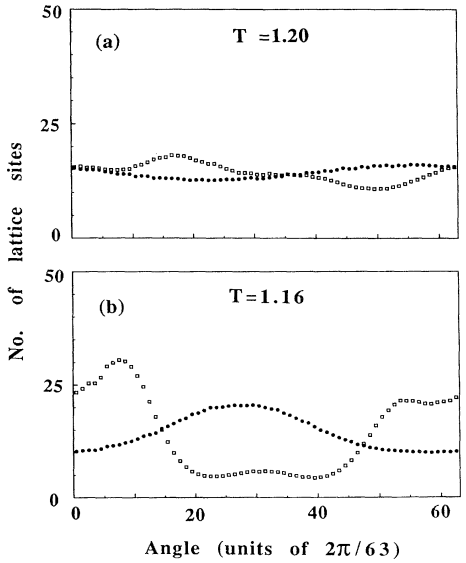

FIG. 4. Histograms for the variables ϕ_i (open squares) and ψ_i (solid dots). Although both ϕ_i and ψ_i are treated as continuous variables in the simulation, to obtain these histograms we have divided 2π into 63 segments. (a) and (b) are the cases for $T=1.20$ ($>T_c$) and $T=1.16$ ($<T_c$), respectively. Here $J_1=1.0$, $J_2=0.95$, and $J_3=2.1$

state Potts transition. It is therefore possible that the corresponding transition in three dimensions may be continuous, unlike the simple three-state Potts transition which exhibits a first-order phase transition in 3D [20]. By adding a weak interlayer coupling term into the Hamiltonian, we are currently investigating this point to see if the results agree with our experimental data on the bulk Sm-*A*–Hex-*B* transition. Further simulation studies in other regions of parameter space are also in progress.

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[14] In the three-state Potts transition, the transition temperature (T_c) is related to the energy difference between two energy states (ΔE), namely, $T_c = \Delta E/1.005$. In our model, $\Delta E = 3J_2/2$; thus $T_c = 3J_2/(2\times 1.005)$.

[15] We believe that finite values of J_1 and J_3 lead to the fact that $T_{c2} < 3J_2/2$.

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