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Heat-capacity anomalies from four-layer liquid-crystal films: Experimental results and simulation results

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Our recent heat-capacity measurements on four-layer free-standing liquid-crystal films near the smectic-*A* –hexatic-*B* transition of *n*-heptyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (75OBC) exhibit separate heat-capacity anomalies associated with the distinct ordering of the interior and surface layers. Employing the Metropolis Monte Carlo technique, we have simulated these transitions in a layered system with finite thickness (for example, $30\times30\times4$). Comparison between our experimental and simulation results indicates that the anisotropy between inter- and intralayer interactions plays an important role in our experimental findings. Furthermore, the ratio of intra- to interlayer interactions strength should be more than 100.

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Liquid crystals are highly anisotropic organic molecules which possess intermediate phases (mesophases) with different degrees of translational and orientational order between the conventional isotropic liquid and crystalline phases. Two such mesophases, which are relevant to this paper, are the smectic-*A* (Sm-*A*) and hexactic-*B* (Hex-*B*) phases. Both phases possess one-dimensional density waves along the long axis of the molecule. This one-dimensional order cannot be long ranged. The Sm-*A* phase can be though of as a stack of two-dimensional liquid layers and the Hex-*B* phase exhibits three-dimensional long-range bond-orientational order [1,2]. Because of their layer structure (each layer is about 25 Å thick and approximately equal to the molecular length), free-standing films, similar to soap films, can be prepared in these two phases. Using appropriate liquid-crystal compounds, we can prepare uniform, free-standing liquid-crystal films of different thicknesses over an opening about 1 cm in diameter. The films can be as thin as two molecular layers and are very stable. Upon cooling, some liquid-crystal compounds undergo a transition into the crystal-*E* (Cry-*E*) phase in which the molecules posses both long-range positional order and herringbone order. Without the complication of the substrate, free-standing liquid-crystal films offer a unique physical system to study crossover from three to two dimensions and the nature of two-dimensional melting phenomena in substrate-free systems.

Many experimental techniques have been employed to investigate the physical properties of free-standing liquid-crystal films. Recently, we have constructed a state-of-the-art free-standing film calorimetric system [3] which enables us to measure the temperature variation of the heat capacity near several important phase transitions in liquid crystals. For example, we have studied in great detail the nature of the Sm-*A* –Hex-*B* transition of *n*-heptyl-4′-*n*-pentyloxybiphenyl-4-carboxylate (75OBC) with various film thicknesses [4–6]. The combination of the surface tension at the film-vapor interface and anisotropy between inter- and intralayer interaction yields extremely interesting results in the temperature variation of the heat capacity as a function of film thickness [4–6]. Specifically, separate interior and surface liquid-hexatic transitions were observed for film thicknesses down to a three-molecular-layer film where the single interior layer transition could still be resolved. The liquid-hexatic transition was also discerned in a two-layer film which presumably exhibits two-dimensional behavior [5]. In the case of four-layer films, distinct and well-separated interior and surface liquid-hexatic transitions were seen. In light of these experimental results, we have carried out computer simulations employing the Metropolis Monte Carlo technique [7] to study the temperature variation of the heat capacity of a system with a finite thickness, e.g., $30\times30\times4$. Qualitative comparison between the experimental and simulation results enables us to estimate that the ratio of the intralayer to the interlayer interaction strength should be larger than 100.

Details of our experimental setup have been reported in Ref. [3]. Figure 1 displays our experimental heat-

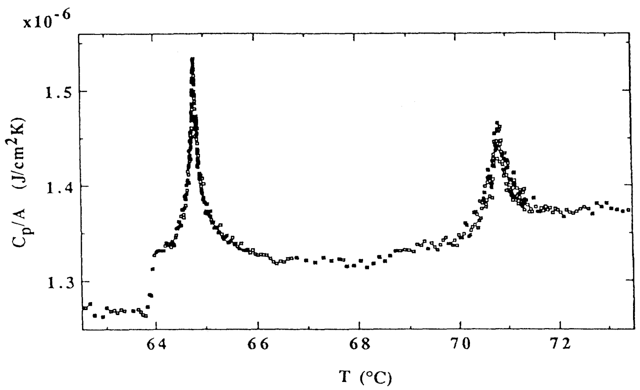

FIG. 1. Temperature variation of heat capacity (per unit area) of a four-layer film of 75OBC.

capacity data as a function of temperature of a four-layer film of 75OBC. The heat-capacity peaks near 71 °C and 65 °C signal the surface and interior liquid-hexatic transitions, respectively. The heat-capacity jump near 64 °C marks the surface hexatic–Cry-*E* transition. While both the surface and interior liquid-hexatic transitions have been demonstrated to be reproducible between the cooling and heating runs, the surface hexactic–Cry-*E* transition exhibits pronounced thermal hysteresis [8]. The interior two layers would presumably undergo the hexatic–Cry-*E* transition at about 59 °C which is the bulk Hex-*B*–Cry-*E* transition temperature for 75OBC. Unfortunately, almost all the 75OBC films studied spontaneously ruptured near this temperature, so the interior transition temperature could not be determined.

It is clear that the heat-capacity anomaly associated with the interior liquid-hexatic transition is symmetric and quite sharp. As a result, a critical fitting could be done over one and a half decades in reduced temperature, yielding the heat-capacity critical exponent $\alpha=0.30\pm0.05$ (Ref. [4]). Figure 1 shows the following three salient features. First, the surface and interior transition temperatures are well separated. This indicates that the interlayer coupling strength is relatively weak. Second, the outermost layers, under the influence of the surface tension, have the liquid-hexatic transition temperature enhanced to approximately 6 K above the bulk Sm-*A*–Hex-*B* transition temperature ($T_{AB}=65$ °C). To the best of our knowledge, there exists no symmetry-breaking field acting on the surface layers. On the other hand, the interior layers undergo the liquid-hexatic transition under the influence of the surface ordering through a weak interlayer coupling. Consequently, the interior layers exhibit a slightly higher transition temperature than the T_{AB} for a bulk sample. Under this circumstance, one expects that the heat-capacity anomaly associated with the interior liquid-hexatic transition should be somewhat rounded due to the effective ordering field. It is therefore surprising to note that the interior anomaly is sharper than the surface anomaly. Third, the critical exponent $\alpha=0.30$ associated with the interior liquid–hexatic transition is in excellent agreement with the value of α $(=\frac{1}{3})$ for the three-state Potts model in two dimensions [9]. The plausibility of the three-state Potts order has been demonstrated by x-ray diffraction studies [2] on thick free-standing liquid-crystals films of 65OBC (a homolog of 75OBC). The experimental data clearly show the existence of the herringbond diffraction peaks along with the hexatic order. However, no detailed x-ray diffraction through the herringbone peak position has yet been performed to determine whether the herringbone order is short or long ranged. In principle, long-range herringbone order can exist in a system with long-range hexatic order without long-range translational order. Unfortunately, the scattering intensity from the herringbone order is too weak to be discernible in the electron diffraction from thin liquid-crystal films [10].

Employing Metropolis Monte Carlo technique, we have performed simulations on $20\times20\times4$ systems with *XY* nearest-neighbor interactions and $30\times30\times4$ systems with three-state Potts interactions. To more closely approximate our experimental system, periodic boundary conditions were used along the two long axes. To achieve equilibrium, we used more than 50 000 Monte Carlo steps for each lattice site at each individual temperature. The heat capacity can be calculated from either the energy fluctuations or temperature derivative of the total energy. The good agreement between these two approaches gives us confidence in our simulation results. Because the hexatic order can be represented by an *XY* order parameter [11], the simulation on the *XY* model was tried first.

The simulation Hamiltonian with the nearest-neighbor *XY* interaction had the following form:

$$H_{XY}=-\sum_{\alpha=1}^{4}\sum_{\langle i,j\rangle}(J_{h,\alpha}/T)\cos(\theta_i^\alpha-\theta_j^\alpha) -\sum_{\alpha=1}^{3}\sum_{i}(J_v/T)\cos(\theta_i^\alpha-\theta_i^{\alpha+1}) \;,$$

where α ranging from 1 to 4 is an index for different layers, T is temperature, J_v is the interlayer coupling constant, and J_{hs} $(=J_{h,1}=J_{h,4})$ $[J_{hi}$ $(=J_{h,2}=J_{h,3})]$ are the intralayer coupling constants for the surface (interior) layers. Recent work facilitated the determination of the relative magnitudes of the coupling constants. Due to the competition between the finite size and surface ordering effects in free-standing liquid-crystal films, a unique thickness dependence of the Sm-*A*–HeX-*B* transition temperatures of the interior layers has been theoretically predicted by Li *et al.* [12] and subsequently experimentally confirmed in the 75OBC compound [13]. Comparisons between the experimental data and theoretical prediction yield $J_{hs}/J_{hi}\approx2$ (Ref. [13]). Thus we chose the following coupling constants in this simulation work: $J_{hs}/T=2.0$, $J_{hi}/T=1.2$, and $J_v/T=0.02$. The fact that $J_{hs}>J_{hi}$ is due to the surface enhanced order. As expected [14], the *XY* model simulations yield a very broad heat-capacity hump (see Fig. 2) which is a combination of the two broad humps due to the surface and interior transitions. The result is clearly different from our experimental data as shown in Fig. 1. The small difference $(\approx2\times10^{-3})$ between the constant volume heat capacity (C_V) calculated from simulations and the constant pressure heat capacity (C_P) obtained from experimental measurements is discussed in Ref. [15].

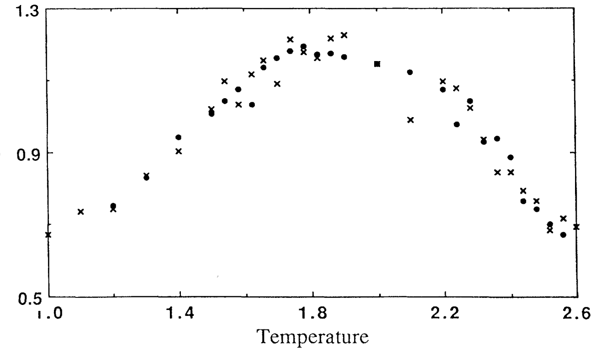

FIG. 2. Simulation result for a four-layer system (20×20×4) with a nearest-neighbor XY interaction. The intralayer coupling strength of the two surface layers ($J_{hs}/T=2.0$), which is larger than that of the two interior layers ($J_{hi}/T=1.2$). The interlayer coupling strength $J_v/T=0.01$. For comparison, the heat-capacity data calculated from energy fluctuation formula (crosses) and from derivative of energy (solid dots) are shown.

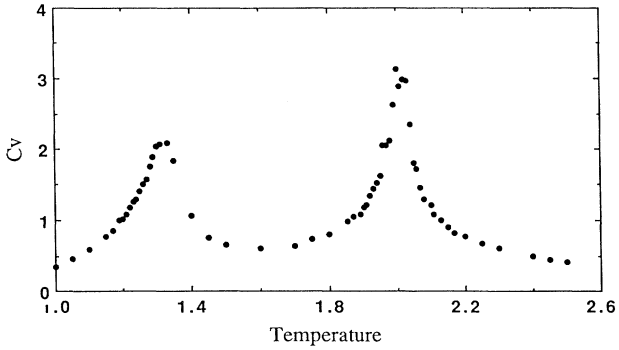

FIG. 4. Simulation results for a four-layer system (30×30×4) with three-state Potts interaction. The intralayer coupling strength of the two surface layers ($J_{hs}/T=2.0$), which is larger than that of the two interior layers ($J_{hi}/T=1.2$). The interlayer coupling strength $J_v/T=0.05$, which is five times larger than that used in the case for Fig. 3. There is no surface ordering field.

The sharp features in the four-layer-film heat capacity suggest that, although the electron diffraction studies from the thin films fail to reveal any additional order besides hexatic order, the development of the hexatic order alone is not sufficient to explain the observed heat-capacity anomalies, there are two clues. First, the heat-capacity anomaly at 64.8 °C as shown in Fig. 1 can be fitted to a power-law expression with the critical exponent $\alpha=0.30$ consistent with the three-state Potts model which possesses a continuous transition with $\alpha=\frac{1}{3}$ in two dimensions (2D). Second, x-ray diffraction from thick films of 65OBC yield a peak associated with the herringbone order. Herringbone order in a system with bond-orientational order exhibits three-state Potts symmetry. These facts support the supposition that the Hex-B phase may possess not only bond-orientational order but also herringbone order. To test this hypothesis, Monte Carlo simulations with nearest-neighbor three-state Potts interactions (Ref. [16]) were performed on a 30×30×4 system. Figure 3 displays the temperature dependence of the heat capacity for the following parameters: $J_{hs}/T=2.0$, $J_{hi}/T=1.2$, and $J_v/T=0.01$. In order to produce a wider surface heat-capacity peak, a small surface ordering field ($H_s/T=0.05$) was included in these simulations. At this moment, we do not know of any physical origin for the existence of the surface ordering field (H_s/T). Systematic measurement of the heat capacity of thin films of various liquid-crystal compounds is in progress. Hopefully, this will shed new light on the physical origin of the wider surface heat-capacity peak for the 75OBC compound (see Fig. 1).

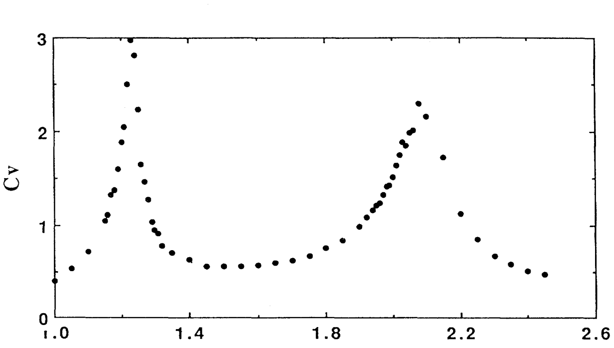

FIG. 3. Simulation result for a four-layer system (30×30×4) with nearest-neighbor three-state Potts interaction. The intralayer coupling strength of the two surface layers ($J_{hs}/T=2.0$), which is stronger than that of the two interior layers ($J_{hi}/T=1.2$). The interlayer coupling strength $J_v/T=0.01$. The surface ordering field $H_s/T=0.05$.

The simulation results are qualitatively similar to our experimental results shown in Fig. 1. Even though the heat-capacity anomaly of the surface layers is broad due to the surface ordering field (H_s/T), the heat-capacity anomaly from the interior layers remains fairly sharp.

In order to investigate the effect of the interlayer coupling strength on the sharpness of the heat-capacity anomaly from the interior layers, we performed another simulation with the following parameters: $J_{hs}/T=2.0$, $J_{hi}/T=1.2$, $J_v/T=0.05$, and $H_s/T=0$. The value of J_v/T is increased from 0.01 to 0.05. The results are displayed in Fig. 4. Noticeable rounding of the interior peak is evident. We have therefore concluded that the ratio of the interlayer to the intralayer coupling strength is less than about 0.01.

In conclusion, we have reported simulation results related to the heat-capacity data obtained from free-standing liquid-crystal films. The simulation results suggest that the Sm-A–Hex-B transitions in thin films of the nmOBC liquid-crystal compounds cannot be described as simple XY transition. Although the supposition that the additional order results from the introduction of the three-state Potts symmetry requires direct experimental justification, computer simulations are a powerful method of obtaining clues regarding the phenomena associated with pseudo-two-dimensional systems only a few molecular layers thick. Further simulation work is in progress to gain more insight into the nature of free-standing liquid-crystal films.

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[15] Here we compare the experimental heat-capacity data (C_P) with the results (C_V) obtained from simulations. In the case of liquid crystals, we have calculated $(C_P - C_V)/C_P = [VT\alpha_t^2/\kappa]C_P \approx 2 \times 10^{-3}$. Here we use x-ray data [S.C. Davey *et al.*, Phys. Rev. Lett. **53**, 2129 (1984)] to obtain the thermal expansion coefficient (α_t) and ultrasonic data [K. Miyano and J. B. Ketterson, Phys. Rev. A **12**, 615 (1975)] to obtain the compressibility (κ) in our calculation. Consequently, the difference between C_P and C_V can be ignored.

[16] The interaction Hamiltonian we used for the nearest-neighbor three-state Potts interactions is

$$\begin{aligned} H = &- \sum_{\alpha=1}^{4} \sum_{\langle i,j \rangle} (J_{h,\alpha}/T)\delta_{s_i^\alpha, s_j^\alpha} \\ &- \sum_{\alpha=1}^{3} \sum_{i} (J_v/T)\delta_{S_i^\alpha, S_i^{\alpha+1}} \\ &- \sum_{i,\alpha=1,4} (H_s/T)\delta_{S_i^\alpha, 1} , \end{aligned}$$

where $s_i^\alpha = 1$, 2, and 3 represent three different states for the three-state Potts model; $J_{h,1} = J_{h,4} = J_{hs}$, the intralayer coupling strength for the surface layers and $J_{h,2} = J_{h,3} = J_{hi}$, the intralayer coupling strength for the interior layers.