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Calorimetric investigation of the smectic-C–smectic-I transition in free-standing p-decyloxybenzylidene-p-amino-2-methylbutylcinnamate films

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High-resolution heat-capacity data near the smectic-C–smectic-I transition in free-standing p-decyloxybenzylidene-p-amino-2-methylbutylcinnamate (DOBAMBC) films down to only two molecular layers in thickness have been obtained. The data reveal preferential surface ordering phenomena and surface transitions localized to individual smectic layers. Moreover, the data from two-layer films are not consistent with existing theory, and indicate that the present understanding of the liquid-crystal hexatic phases is not complete.

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The existence of characteristic defects and their ability to mediate phase transitions has been generally acknowledged. However, a complete theoretical picture has proven elusive. In fact, significant progress has been made only for two-dimensional (2D) systems. In 1973, Kosterlitz and Thouless introduced the concept of topological order and demonstrated that the 2D XY model could form topological defects which could mediate a new type of phase transition [1]. This theory was soon extended by Halperin and Nelson to describe the melting of a 2D crystal [2]. One of the most interesting predictions of this analysis was the proposed existence of a novel phase of matter intermediate between the 2D liquid and crystalline phases. Unlike the crystalline state, this phase is predicted to exhibit only short-ranged positional order. However, because the orientations of the local lattices are not distributed randomly, this phase exhibits bond-orientational-order (BOO) and can be distinguished from the isotropic liquid phase. In systems with an underlying sixfold symmetry, BOO is equivalent to the preservation of the angles between imaginary bonds coupling the six nearest neighbors. Such a phase has been termed hexatic and its identification in experimental systems has been the focus of numerous studies [3].

Subsequent to the introduction of these important ideas, Birgeneau and Litster suggested that certain smectic liquid-crystal phases may be three-dimensional (3D) manifestations of the predicted 2D hexatic phase [4]. Smectic liquid crystals are layered systems in which the layer order can be described by a sinusoidal mass density wave. The simplest smectic phases, the smectic-A (Sm-A) and smectic-C (Sm-C) phases, exhibit liquidlike intermolecular interactions within each plane and differ only by the presence of an average tilt angle between the molecular long axis and the mass density wave vector in the Sm-C phase. The Sm-C phase can be referred to as the tilted version of the orthogonal Sm-A phase [5].

One of the most intriguing aspects of many smectic liquid crystals is that, under the appropriate conditions, they can be spread across an opening to form freely suspended films (much like soap films on a ring). The free-standing film geometry has proven to be particularly well suited to the study of smectic phases and, in 1981, Pindak *et al.* first obtained scattering data consistent with the predicted hexatic phase in an x-ray-diffraction experiment on free-standing films of 65OBC (a member of the n-alkyl-4′-n-alkyloxybiphenyl-4-carboxylate, nmOBC, homologous series) [6]. This phase has since been termed the hexatic-B (Hex-B). Unfortunately, the characteristic domain size in the orthogonal Hex-B phase was smaller than the illuminated x-ray spot size and no quantitative data on the increase of hexatic order through the transition region could be obtained. However, domain problems can be avoided in the tilted analogs of the Hex-B phase [such as the smectic-I (Sm-I) phase] since the tilt is expected to couple to the BOO. Because the liquid-crystal molecules are diamagnetic, cooling through the Sm-A–Sm-C transition under a moderate magnetic field (≈ 1 kG) produces films of uniform tilt direction. Due to the coupling, the tilt direction defines the hexatic orientation and further cooling through the Sm-C–Sm-I transition results in single hexatic domain samples. Single domain samples have since been studied extensively by x-ray and optical techniques. These experiments have provided important insight into the nature of hexatic order in liquid crystals presently unobtainable from the orthogonal Hex-B phase.

The coupling has also been predicted to have a profound effect on the nature of the tilted liquid-hexatic transition by inducing finite BOO in the Sm-C phase and formally destroying the Sm-C–Sm-I phase boundary [7]. This prediction has been supported by recent experimental data indicating the existence of BOO above the bulk Sm-C–Sm-I transition in free-standing films of 8OSI [4-(2-methylbutyl)phenyl-4′-(octyloxy)-(1,1′)-biphenyl-4-carboxylate]. Using an intense synchrotron source, Brock *et al.* obtained high-resolution x-ray-diffraction data that convincingly display sixfold intensity modulations characteristic of BOO in the 8OSI films and the data could be quantitatively analyzed in terms of the evolution of hexatic order through the transition [8]. Furthermore, the concept of hexatic order (possessing the symmetry of the XY universality class) is central to the scaling theory developed to describe the n dependence of the successive sixfold Fourier components, C_{6n} [$\approx (C_6)^{\sigma(n)}$], observed in 8OSI [9]. However, we have recently obtained data indicating that the creation of hexatic order alone appears insufficient to describe the Sm-A–Hex-B transition. It is therefore important to also determine the role of hexatic order in the more accessible and better characterized Sm-C–Sm-I transition. Therefore, to understand more fully the nature of the tilted hexatic phases, we have obtained high-resolution heat-capacity data as a function of film thickness near the Sm-C–Sm-I phase transition of p-decyloxybenzylidene-p-amino-2-methylbutyl cinnamate (DOBAMBC). The data display interesting surface ordering effects and unambiguously indicate that our present understanding of the Sm-C–Sm-I transition is incomplete. The results therefore strongly support and generalize our work on the Sm-A–Hex-B transition and point out an important misconception in our understanding of the liquid-crystal "hexatic" phases.

The DOBAMBC films were spread in the oven of the ac calorimetric system described in Ref. [10]. Because of the layer structure, film thickness is quantized in units of molecular layers (denoted by N) and uniform films can be prepared from many hundreds down to only two molecular layers in thickness. Once a film had been spread, its thickness could be determined through a combination of methods. Interference effects between the free surfaces of films of intermediate thickness ($150>N>25$) allow the thickness to be obtained from the characteristic color of reflected white light [11]. Because of destructive interference, thin films ($N<15$) appear dark. However, the thickness is easily determined in this regime since the optical reflectivity increases as N^2 [12]. Finally, the thermal signal from our calorimetric system is also thickness dependent and serves as an independent check of the other methods. The free-standing film geometry is therefore unusual in that studies can be readily performed as a function of sample thickness (and hence, dimensionality). Moreover, the two-layer films have been found to possess 2D thermal properties and have become an important system in which aspects of 2D melting theory can be tested.

The thermal study of such semimicroscopic thin films poses a considerable technical challenge as evinced by the fact that less than 20 ng of sample contribute to the measured signal related to the heat capacity of a two-layer film. Even though the experiment pushed the limits of our present experimental resolution, a remarkable set of data was obtained. The data were all taken at a uniform ramping rate of 15 mK/min and, aside from slight thermal hysteresis (≈ 30 mk), the heating and cooling runs were identical. The transition temperatures were weakly time dependent, decreasing ≈ 15 mK/day, presumably due to sample degradation. To minimize the effects of degradation, fresh sample was loaded every 4–5 days. The heat-capacity data were also found to be independent of the presence of an aligning magnetic field and the data sets presented here were obtained from unaligned films.

The calorimetric data on thick films ($N>100$) cannot be distinguished from the data obtained from bulk samples. However, interesting surface induced effects are revealed as the film thickness is reduced. Distinct anomalies become apparent above the bulk Sm-C–Sm-I transition temperature as shown in Fig. 1. These anomalies are most likely due to transitions localized to individual layers near the surfaces of the films. The surface tension associated with the film-vapor interfaces presumably enhances the ordering of the surface layers, causing the films to freeze from the surfaces inwards. Such surface ordering has been observed in other free-standing film systems, most notably near the Sm-A–Hex-B transition of the nmOBC homologs [13]. Based on these results, it is clear that the anomalies near 66.5 °C correspond to the Sm-C–Sm-I transition in only the two outermost layers of the film [14]. The shoulders near 62.5 °C are due to the layers adjacent to the surface layers and the rest of the interior layers account for the large anomalies near 61.8 °C. Because of our finite experimental resolution, it is not clear whether the layer-by-layer transitions proceed throughout the film (complete wetting) or if the interior layers possess a common transition temperature (incomplete wetting). In principle, the weakly first order nature should inhibit such individual layer transitions. Since significant rounding occurs only within 100 mK of the transition temperatures, the correlation length of the pretransitional fluctuations actually becomes greater than the width of even the 25-layer film and any transition would be expected to involve the entire film [15]. The evident layer transitions are possible only because of the extreme anisotropy of the smectic phases as the layer boundaries effectively limit the extent of fluctuations parallel to the layer normal.

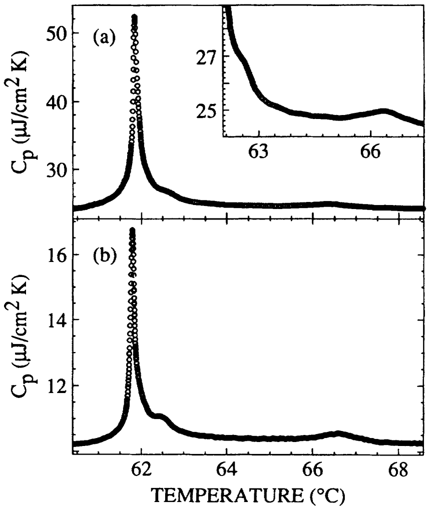

FIG. 1. Heat-capacity data near the Sm-C–Sm-I transition in DOBAMBC films 25 (a) and 11 (b) molecular layers in thickness. The scales are expanded in the inset to better exhibit the surface transitions.

As film thickness decreases further, the interior peak diminishes and the surface transitions become more apparent. Figure 2 displays heat-capacity data from three- and four-layer films. Separate surface and interior anomalies are still present and it is therefore obvious that even films only three molecular layers in thickness (≈ 90 Å) cannot be described as purely 2D since individual layer transitions are possible only when the correlation length parallel to the layer normal remains smaller than the film thickness. The peak heights clearly reflect the asymmetry in boundary conditions. The four-layer interior transition (under the influence of the Sm-I overlayers) is considerably more pronounced than the surface transition, occurring on a liquid substrate. It is also interesting to note that the three-layer interior anomaly exhibits a significantly enhanced transition temperature and is much more than a factor of 2 smaller than the four-layer interior anomaly. Unlike the four-layer interior anomaly, the three-

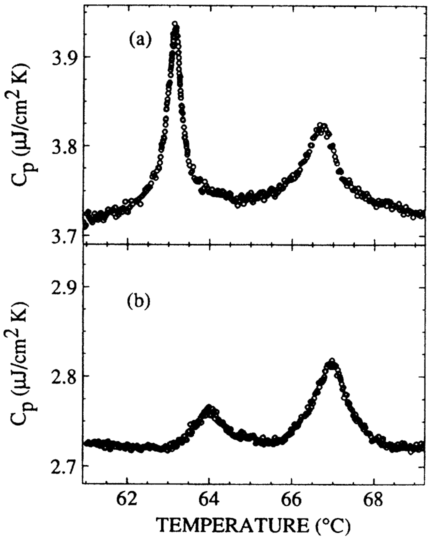

FIG. 2. Heat-capacity data near the Sm-*C*–Sm-*I* transition in DOBAMBC films four (a) and three (b) molecular layers in thickness.

layer interior anomaly is due to the phase transition in only a single molecular layer. The anomalies due to the outermost surface transitions were virtually independent of film thickness, both in magnitude and transition temperature. Furthermore, our preliminary calorimetric studies near the Sm-*C*–Sm-*I* transition in free-standing 8OSI films [16] have revealed qualitatively similar results and layer transitions are again clearly evident.

Unlike thicker films, two-layer films exhibit only a single anomaly, as shown in Fig. 3, finally establishing coherence along the layer normal and may be assumed to possess 2D thermal properties. These data, therefore, represent the anomaly due to a 2D tilted liquid-hexatic transition as discussed in recent theory [7]. As in the case of the other surface transitions, the anomaly is reasonably sharp and symmetric. Moreover, because the transition is only very weakly first-order, the anomaly should be due primarily to pretransitional fluctuations related to the creation of BOO. However, the 2D *XY* model has been predicted to exhibit a very broad, asymmetric anomaly and, although the exact shape is nonuniversal, computer studies suggest that the peak height is on the order of a characteristic step in background heat capacity [17]. The "I" beam in Fig. 3 represents the step calculated under the gross overestimation of one defect per molecular lattice site. As is evident from Fig. 3, the measured anomaly is much more pronounced than expected. This result suggests that the creation of BOO cannot be solely responsible for such a large anomaly and that some other type of molecular order must also be created through the Sm-*C*–Sm-*I* transition. This conclusion is supported by our recent calorimetric work near the Sm-*A*–Hex-*B* transition in *nm*OBC homologs and indicates a basic misconception in our present understanding of the nature of "hexatic" order in liquid-crystal systems [18]. Moreover, since our results indicate that the Sm-*C*–Sm-*I* transition is not a member of the simple *XY* universality class, they do not support the scaling theory [9] generated to explain the x-ray data on 8OSI [8]. We are currently employing Monte Carlo simulation techniques to explore the possibility of herringbone order (described by a three-state Potts Hamiltonian) coupling to the hexatic order so that they are both created through a single continuous transition in 2D and the preliminary results have been promising [19].

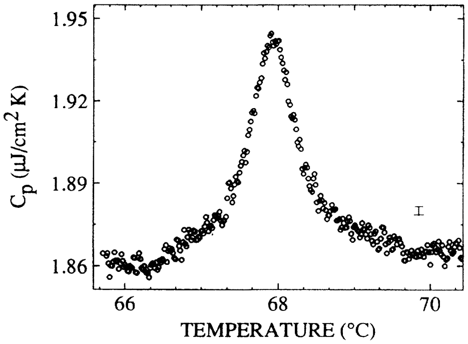

FIG. 3. Heat-capacity data near the Sm-*C*–Sm-*I* transition of a two-layer DOBAMBC film. The "I" beam represents the expected step in the background heat capacity based on 2D melting theory (see text).

In conclusion, we have obtained high-resolution heat-capacity data near the Sm-*C*–Sm-*I* transition in free-standing DOBAMBC liquid-crystal films down to only two molecular layers in thickness. The data on thicker films clearly reveal the presence of transitions localized to individual layers as the films order from the free surfaces inwards. Surprisingly, even films only three layers thick exhibit separate surface and interior transitions and cannot be regarded as truly 2D. The measured two-layer film anomaly is much larger than expected based on the present theory of 2D melting and, as in the case of the Sm-*A*–Hex-*B* transition, the concept of BOO therefore appears insufficient to describe the nature of the Sm-*C*–Sm-*I* transition in these effectively 2D films. This suggests that our current understanding of "hexatic" liquid-crystal phases is not complete and that further study is necessary to reconcile present theory, our calorimetric data, and the x-ray work by Brock *et al.* [8] to resolve these important issues.

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[14] Although detailed x-ray investigations would be the best way to confirm that the phase below the Sm-*C* is the Sm-*I* phase in thin DOBAMBC films, our identification is supported by the evolution of the heat-capacity data and previous studies indicating that the phase sequence in DOBAMBC is independent of film thickness. For example, the torsional relaxation experiments by R. Pindak, W. O. Sprenger, D. J. Bishop, D. D. Osheroff, and J. W. Goodby [Phys. Rev. Lett. **48**, 173 (1982)] yielded no shear response for $T>52$ °C from an eight-layer DOBAMBC film. The optical identification of the Sm-*I* phase has also been reported in free-standing DOBAMBC films by S. M. Amador (Ph.D. thesis, Harvard University, 1989).

[15] Using $\xi \approx \xi_0|t|^{-\nu}$ with ξ_0 taken to be the molecular length ($\xi_0=30$ Å) and a reasonable value for the exponent ν ($\nu \approx \frac{1}{2}$), the value obtained ($\xi \approx 1700$ Å) at $|T-T_c|=100$ mK ($|t|=|T-T_c|/T_c=3\times 10^{-4}$) is much larger than the thickness (≈ 750 Å) of the 25-layer film.

[16] We have found uniform, stable thin 8OSI films much more difficult to prepare than the DOBAMBC films. However, successful calorimetric runs have been completed on 4- and 12-layer 8OSI films.

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