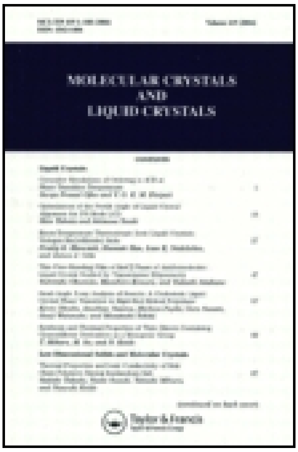

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Heat Capacity Investigations of Extremely Thin Liquid-Crystal Free-Standing Films

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HEAT CAPACITY INVESTIGATIONS OF EXTREMELY THIN LIQUID-CRYSTAL FREE-STANDING FILMS

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Abstract A high-resolution differential ac free-standing film calorimeter has been constructed in our laboratories. We have employed this unique calorimeter to investigate the evolution of the temperature dependence of heat-capacity anomalies through the smectic-A-hexatic-B-crystal-E transition sequence of one liquid crystal compound as the film thickness is reduced from a few hundred to just three molecular layers. The existence of free surfaces in the free-standing liquid-crystal films has a very strong effect on the development of the molecular order through the smectic-A-hexatic-B transition and other unexpected results related to the crystal-E order.

Keywords: heat capacity, free-standing films, phase transition, smectic-A-hexatic-B

INTRODUCTION

In the context of investigating physical properties of two-dimensional systems, to the best of our knowledge, free-standing films possessing a uniform thickness over a macroscopic area (larger than a few millimeter in diameter) are the only unambiguous substrate-free physical systems.[1,2] Although for a given liquid-crystal compound it is not always possible to prepare the desired free-standing films, uniform films of different thickness can be prepared readily from several important and well-characterized liquid-crystal compounds. Our experience from one homologous series indicates that it is easier to prepare uniform films among those compounds with longer alkyl chain(s). Various experimental techniques (e.g., x-ray diffractions,[3] electron diffractions,[4] light scattering,[5] mechanical oscillating,[6] etc.) have been employed to study or explore the nature of this important and unique physical system.

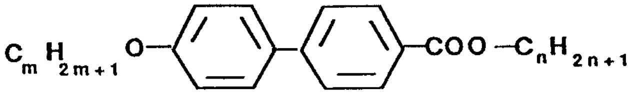
High-resolution heat-capacity investigations have revealed a number of important properties in many different physical systems, such as the phononic and electronic contributions to the thermal properties, the existence of the energy gap in many superconducting materials, the importance of order parameter fluctuations near the majority of continuous phase transitions, etc.. In the context of testing theoretical models and/or obtaining a better understanding of constrained dimensional systems, the effect of free surfaces, the nature of the crossover from three dimensions(3D) to two (2D), and 2D behavior, detailed heat capacity investigations on free-standing liquid-crystal films in conjunction with other measurements (e.g., x-ray, electron, or light scatterings) will provide us with fruitful and essential information.

In our laboratories, we have constructed and continue to improve a high-resolution free-standing film calorimeter which enables us to measure the temperature variation of heat capacity of liquid-crystal free-standing films ranging from three to a few hundred molecular layers thick. The thickness of each molecular layer is about 25 Å. Two essential and innovative ideas which lead to the success of our calorimetric system are the following.[7] First, to minimize the background contributions to the total measured heat capacity, we employ mechanically chopped 3.39 μm laser radiation from a He-Ne laser as the ac heating source on the film. The vibration excitations of CH_2 and CH_3 groups in the alkyl chains of most liquid crystal compounds have absorption peaks in the immediate vicinity of 3.39 μm. The resulting temperature oscillation which is related to the heat capacity of the film is detected by an extremely tiny thermocouple junction (TCJ1) located about 20 μm from the film. 0.5 atmosphere argon exchange gas provide a good thermal link between TCJ1 and the film. Secondly, in the case of thin films (less than one hundred molecular layers), the signal due to direct heating on TCJ1 from the transmitted laser radiation can be more than ten times our measured signal. To minimize this unwanted contribution to our total signal, we have adapted a differential mode. Namely, the direct heating signal from TCJ1 is subtracted by the introduction of another similar thermocouple junction (TCJ2) which is also in the path of the transmitted laser beam but is about 5 mm away from the film. This separation (5 mm) is much larger than the thermal diffusion length (about 0.7 mm) of the argon exchange gas under the operating conditions of the calorimeter. Both thermocouple junctions TCJ1 and TCJ2 are made of chromel and constantan wires 13 μm in diameter. Detailed discussions of our unique calorimeter are given in Ref. 7.

SMECTIC-A-HEXATIC-B TRANSITION

Among the various continuous phase transitions found in the liquid crystal, the smectic-A (SmA)-hexatic-B (HexB) transition displays one of the largest heat-capacity anomalies. Furthermore, the term hexatic was first introduced in the context of theoretical investigations of 2D melting phenomena.[8] Here the HexB phase has 3D long-range hexatic order with short-range translational order. The SmA phase can be viewed as a three-dimensional stack of 2D liquids. Lacking long range translational order, both the SmA and HexB phases in 3D possess a "layer" structure which is actually sinusoidal density waves in which layer-layer correlations decay logarithmically with separation.

In the thin film limit, say a few molecular layers in thickness, we expect to see a 2D liquid-hexatic transition in the compound exhibiting the SmA-HexB transition, provided that no other phase intervenes as the film thickness is reduced. The genuine 2D liquid-hexatic transition can be continuous and can be described by the Kosterlitz-Thouless (KT) theory.[8,9] Theoretical calculations lead to an essential singularity only, exhibiting no anomaly in the temperature variation of heat capacity at the KT transition temperature.[10] Above the KT transition temperature, there exists a heat-capacity maximum due to thermal dissociation of bound vortex pairs. Experimentally, it is not easy to measure the thermal properties of the KT transition. Numerous computer simulations have been carried out to explore the temperature variation of heat capacity near this kind of transition.[11] Many different results were obtained. In principle, a direct comparison with theoretical predictions or results from computer simulations can be made, once the heat capacity from substrate-free films which exhibit 2D thermal properties is measured. These are the main motivations that we chose the SmA-HexB transition found in the nmOBC homologous series as the first candidate in carrying out our free-standing film calorimetric investigations. Here nmOBC refers to n-alkyl-4'-n-alkoxybiphenyl-4-carboxylate. The general chemical structure is



The transition sequence for the 75OBC compound is

Isotropic (81.0 °C) SmA (64.1 °C) HexB (59.8 °C) CryE.

So far we have carried out detailed heat-capacity studies on both 65OBC (Ref. 12) and 75OBC (Ref. 13). Some preliminary data have been obtained from 46OBC (Ref. 14) and 3(10)OBC. Although the major features related to the SmA-HexB transition in the form of free-standing films are the same among these compounds, important differences have been found. As a matter of fact, the work on nmOBC, in particular, the 75OBC and 65OBC compounds is just the beginning of our exploration of new areas in physics, namely, the thermal properties of constrained or reduced dimensional systems without a substrate. So far we have the most complete set of data on the 75OBC compound on which we will concentrate in this invited lecture.

The temperature variations of heat-capacity anomalies near the SmA-HexB transition of 75OBC are shown in Fig. 1 (a) through (f) for a three hundred, 10-, 8-, 7-, 6-, and 5-layer films, respectively. Figure 1(a) displays a pronounced and sharp heat-capacity anomaly associated with the SmA-HexB transition which is similar to the result obtained from the bulk sample.[15] In the case of the 10-layer film data, a small hump is clearly discernible on the high temperature side of the main heat-capacity peak which is located very close to the bulk SmA-HexB transition temperature. On the basis of the following reasonings, we believe that the small heat-capacity hump is due to the development of the hexatic order on the outermost layers of the free-standing film at a temperature slightly higher than the interior (or bulk) SmA-HexB transition temperature. As mentioned previously, along the smectic layer normal both the SmA and HexB phases have a 1D density wave which can not have long range order in 3D. Thus in a 3D system, the layer

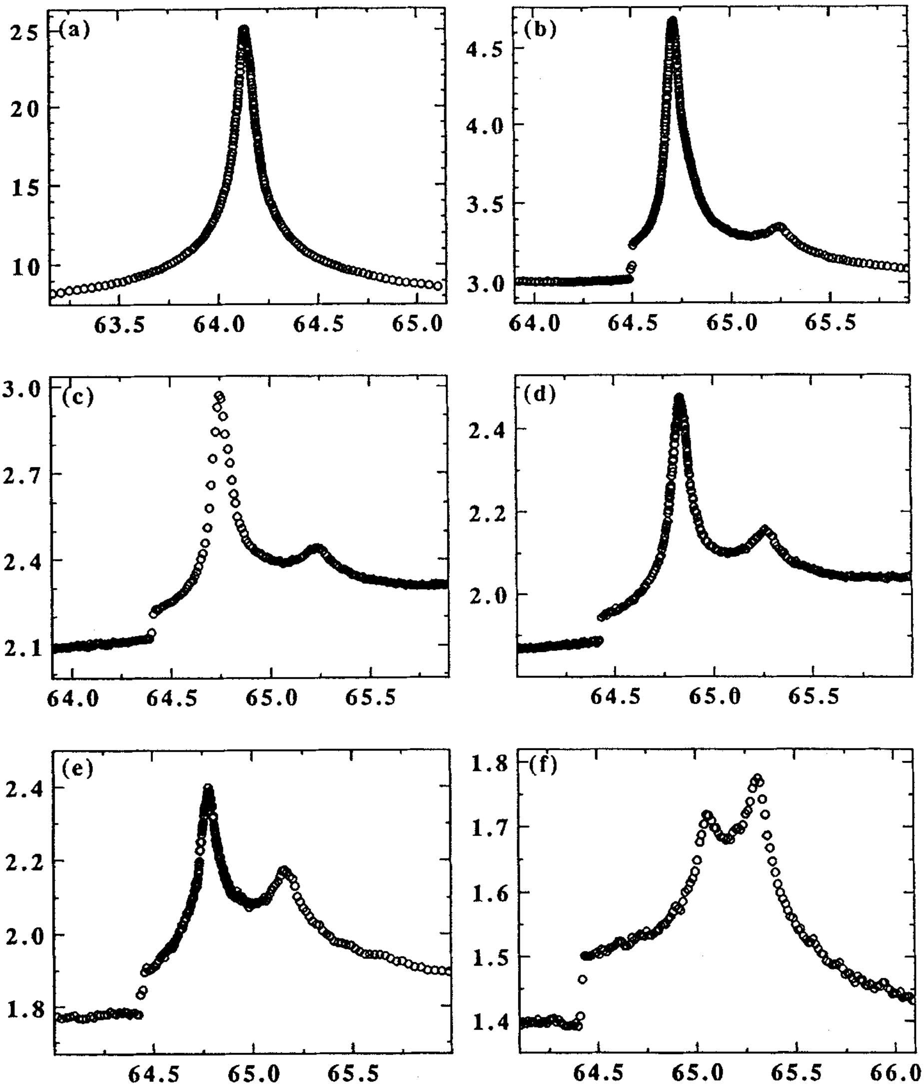


FIGURE 1 Temperature variation of heat capacity near the bulk SmA-HexB transition temperature (64.1 °C) of 75OBC compound. The thickness of free-standing films are (a) approximately three-hundred, (b) ten, (c) eight, (d) seven, (e) six, (f) five molecular layers. The horizontal axes are temperature in °C. The vertical axes of (b-f) are heat capacity in $\mu J/cm^2K$. Heat capacity units for (a) are arbitrary.

structure is not well-defined and layers experience large fluctuations. In the free-standing film configuration, there exist two free surfaces in which the surface tension tends to keep the surfaces flat and suppresses the layer fluctuations. Consequently, the outermost layers have a higher smectic layer order than the interior layers. We believe that this, in turn, will enhance the hexatic order in the outermost layers which leads to the hump on the high temperature side of the main heat-capacity peak indicating the hexatic ordering of the interior layers. Similar surface enhanced order has been identified in several other liquid-crystal systems. This suggests that the "melting" related to the SmA-HexB transition in the free-standing films is very different from the ordinary solid state materials. Namely, the melting process starts from the interior of the film rather than from the outside as temperature rises .

It would be of great interest to experimentally detect the surface hexatic order on top of the interior liquid order in the temperature range between the two liquid-hexatic heat-capacity anomalies. This requires a special experimental geometry.[16] The fact that the higher temperature anomaly increases in size relative to the one occurring at a lower temperature provides additional support for our association of the former with surface hexatic transition (see the evolution in Fig. 1). In the case of 6-layer films (see Fig. 1(e)), the anomaly related to the surface hexatic order, although more prominent than in thick films, remains smaller than the one associated with the interior hexatic order. Eventually in the 5-layer film, the "surface" heat-capacity peak becomes larger than the "interior" one. This is accompanied by a large increase in the "interior" transition temperature.[16] We believe that this is due to a finite penetration depth (ξ_s) of the surface hexatic order. Namely, for films with $N \geq 10$, thickness is much larger than ξ_s. Thus the surface order is localized within the two outermost layers. In the case of 5-layer films, judging from the relative size of the heat-capacity peaks, the surface hexatic order is not limited to the two outermost layers any more. At least, in some degree, the layers next to the two outermost layers participate in the "surface order". Still the surface and interior order remain separate. Finally, for $N \leq 4$, a single and fairly sharp heat-capacity peak associated with the SmA-HexB transition is obtained. The results from 4- and 3-layer films are displayed in Fig. 2. In principle, the fact that the 4-layer film already shows a single heat-capacity peak suggests that the heat-capacity per unit volume should not have changed significantly in reducing the film thickness to three molecular layers. To our great surprise, the height of heat-capacity anomaly decreases by a factor of 5.3 as the film thickness reduces by one layer to a three-layer film. Intuitively, the 2D fluctuations will be enhanced as the film thickness decreases. Here we are dealing with very different physical systems in which surface tension on the free surfaces plays a dominant role in this extremely thin film limit.

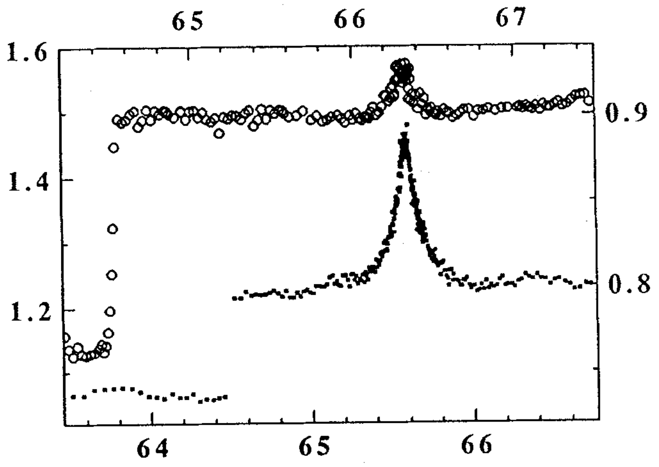


FIGURE 2 The heat capacity anomalies from 4- (solid dots) and 3- (open circles) layer films of 75OBC. The upper (lower) horizontal axis is the temperature (in °C) for the 3- (4-) layer film. The left (right) vertical axis is heat capacity (in $\mu J/cm^2K$) for the 4- (3-) layer film.

To obtain an unambiguous conclusion concerning 2D thermal properties of the liquid-crystal free-standing film, it would be remarkable to be able to measure the temperature variation of heat capacity of 2-layer films. On the basis of our experimental results of 4- and 3-layer films, it would not be surprising if the magnitude of the heat-capacity anomaly will experience another large reduction as the film thickness decreases from three to two molecular layers. At this moment our calorimetric system is incapable of detecting the heat-capacity anomaly from the liquid-hexatic transition of 2-layer films. In order to reach this important milestone in addressing the thermal properties of substrate-free 2D systems, we plan to construct another new calorimetric system with some innovative approaches. However, based on the existing data and following arguments, we believe that the thermal properties of the substrate-free 2D system have been obtained. First, for the films with $N \geq 5$, separate surface and interior order manifest themselves as separate heat-capacity peaks. In the case of $N \leq 4$, single heat-capacity anomaly is obtained. Furthermore, the peak is very sharp. Heat-capacity data of 5- and 4-layer films have full width at half heights (FWHH) about 0.5 K and 0.13 K, respectively. This significant reduction in the FWHH accompanied by a noticeable upward shift in the transition temperature (0.26 K) leads us to rule out the possibility that 4-layer film heat-capacity data are composed of two separate transitions. This indicates that the entire film undergoes a single liquid-hexatic transition. Secondly, after scaling up the heat-capacity anomaly of the three-layer film by a factor of 5.3 and comparing with the data from the four-layer film, they are the same within the experimental resolution of the heat-capacity data from the three-layer film. The results are shown in Fig. 3 (a). Consequently, reducing the film thickness from 4 to 3 molecular layers does not change the major feature of the heat-capacity anomaly. Definitely, it would be nice to confirm this observation by measuring the heat-capacity anomaly from the two-layer film. The comparison between the heat-capacity anomaly from the surface hexatic order of a 10-layer film (see Fig. 1(b)) and that from a 4-layer film is illustrated in Fig. 3 (b). The anomaly from the 4-layer film is slightly sharper. A plausible explanation for the difference is that 4-layer films are a truly substrate-free system and the surface hexatic order has a liquid-like substrate which can be affected by the surface order.

The heat-capacity data of four-layer films near the liquid-hexatic transition can be well described by a simple power law with a scaling correction term. The anomalous part of heat capacity is plotted as a function of $|T-T_C|$ in Fig. 4. In a range of more than one and a half decade in $T-T_C$, the heat-capacity anomaly can be described by the critical exponent α (= 0.30 ± 0.05). This diverging behavior in the heat-capacity anomaly is in disagreement with the theoretical predictions for the 2D liquid-hexatic transition. This does not totally surprise us because the nature of the 3D SmA-HexB transition remains an unresolved and interesting question in critical phenomena. In principle, if the bond-orientation order is the order parameter for the SmA-HexB transition, the transition should belong to the 3D XY universality class. The heat-capacity exponent α should have a value -0.003. We have measured α for many nmOBC compounds as well as their binary mixtures and obtained 0.60 ± 0.03 (Ref. 15,17) which is very different from -0.003. The fact that the value of α is in good agreement with the predicted value for 2D three-state Potts model (α = 1/3) (Ref. 18) may be a coincidence or may provide us with an important hint to the nature of the SmA-HexB transition. Although both electron and x-ray diffraction data fail to reveal any three-state Potts symmetry in the free-standing HexB films, the possibility of a hexatic order accompanied by a herringbone order without translational order cannot be totally ruled out. Addressing this possible scenario requires a detailed intensity analysis for either x-ray or electron scattering profiles.

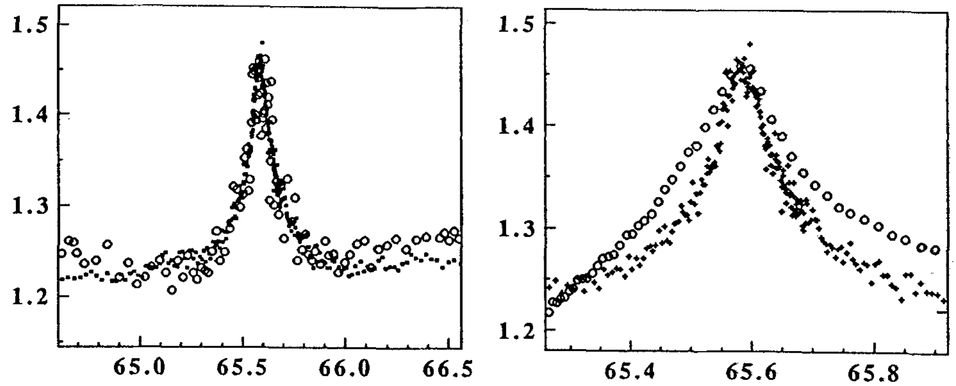


FIGURE 3 Comparison of heat-capacity data (a) from a 4- (solid dots) and 3-layer films (open circles) and (b) from a 4-layer film (solid dots) and surface hexatic order of a 10-layer film (open circles). Horizontal [vertical] axes are the temperature (in °C) [heat capacity] from the 4-layer film data. For the superpositions of these figures, the temperature windows of both data sets are the same, with the vertical scales varied to match peak heights relative to background heat capacity values at higher temperatures. For (b), the background value used to compare the 10-layer surface peak to the 4-layer data lies slightly outside the plot window.

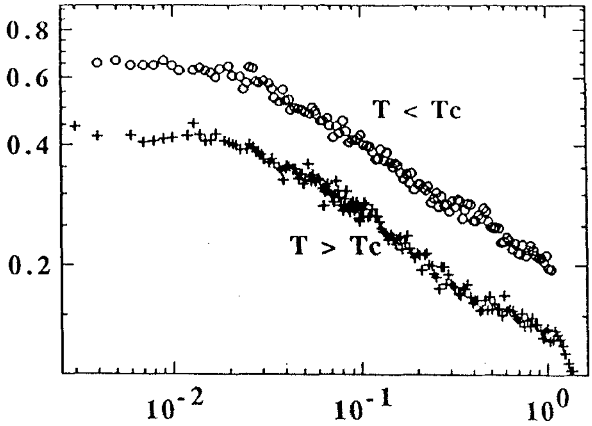


FIGURE 4 A log-log plot of the anomalous part of heat capacity as a function of $|T-T_c|$ from a 4-layer film. For clarity, the $T < T_c$ part was multiplied by a factor of 1.5. The amplitude ratio for the heat-capacity anomaly is about one.

HEXATIC-B-CRYSTAL-E TRANSITION

In Fig. 1 and 2, in addition to the heat-capacity anomalies associated with the hexatic order, there exist sharp heat-capacity jumps about 0.5 K below the main heat-capacity peak. The width of this heat-capacity jump is surprisingly sharp. For the scanning rate of the average sample temperature ranging from 2 to 6 mK/min, the jump occurs within a 5 mK temperature window which is about $1.4 * 10^{-5}$ in reduced temperature. This indicates the existence of a delta-function type of latent heat associated with this transition. The quasi-adiabatic technique which is used in the design of our calorimeter is incapable of resolving such a sharp latent heat.

Based on both x-ray and electron diffraction studies of free-standing films of 75OBC, we[13] conclude that the phase below the heat-capacity jump has surface CryE order accompanied by interior hexatic order. One of the electron diffraction patterns from a four-layer film is shown in Fig. 4 of Ref. 13. One can see very clearly the coexistence of two sets of CryE diffraction peaks and the hexatic diffraction arcs. Due to the existence of the hexatic order in the interior layers, the CryE order on the two outermost layers have slightly different orientations. From many sets of diffraction data, we always obtained two sets of approximately equal intensity diffraction peaks. Thus, we conclude that these two sets of diffraction peaks result from the different CryE domains from the top and bottom layers of the films. For the films as thin as three layers, the x-ray results demonstrate that the inter-layer coupling is similar to the SmA phase while the intra-layer coupling exhibits the CryE type order. In this aspect, the surface CryE order is well-localized on the outermost surfaces of the films with thickness as thin as three molecular layers. Cooling the film down to 59.8 °C (the bulk HexB-CryE transition), the films almost always ruptured. Due to the closeness of the transition temperatures for the surface CryE and interior HexB order, upon heating from the region with the surface CryE order, the film will have a transition into either the HexB phase or the phase with only surface hexatic order. This pronounced hysteretic phenomenon is a strong function of film thickness. Consequently, there exists very interesting interplay between the surface CryE order and the order in interior layers, upon the heating from the phase with the surface CryE order.

The 75OBC sample for this work was provided by J.W. Goodby. We have enjoyed stimulating discussions of this work with R. Pindak, J.T. Ho, D.R. Nelson, and P.S. Pershan. R.G. and T.S. would like to acknowledge the support of an IBM fellowship and a Department of Education fellowship, respectively. This work was partially supported by the Graduate School, University of Minnesota and the National Science Foundation (Solid State Chemistry Program) Grants No. DMR-89-19334.

Note added.--After my presentation and the submission of this work for publication, significant improvements in the stability of our system over a wider temperature window have been made. We have found that the surface liquid-hexatic transition of 75OBC occurs at about 71 °C. Thus, all the experimental data reported here concerning the SmA-HexB transition are from the interior layers. Moreover, we have achieved an important goal, namely, the heat-capacity anomaly near the liquid-hexatic transition of two-layer films has been obtained [Geer, et al., preprint].

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