

Unusual Thickness-Dependent Heat-Capacity Anomalies in Free-Standing Hexatic Liquid-Crystal Films

C. Y. Chao,^{1,*} C. R. Lo,¹ P. J. Wu,¹ T. C. Pan,¹ M. Veum,² C. C. Huang,³ V. Surendranath,⁴ and J. T. Ho⁵

¹*Department of Physics and Astronomy, National Central University, Chung-Li 32054, Taiwan, Republic of China*

²*Department of Physics and Astronomy, University of Wisconsin at Stevens Point, Stevens Point, Wisconsin 54481*

³*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*

⁴*Department of Physics, Kent State University, Kent, Ohio 44242*

⁵*Department of Physics, University at Buffalo, The State University of New York, Buffalo, New York 14260*

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High-resolution heat-capacity and optical-reflectivity measurements have been conducted near the smectic-*A* to hexatic-*B* transition in thin free-standing films of the liquid-crystal compound 64COOBC. We find an unexpected dependence on film thickness of the integrated magnitude of the heat-capacity anomalies as the films undergo layer-by-layer transitions. We measure the penetration depths of the ordering from the surface and next-to-surface layers which are pertinent to the highly correlated thermal behavior.

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Surface ordering in free-standing liquid-crystal films has generated considerable experimental and theoretical interest over the past ten years [1–9]. In contrast to conventional solids, the surface tension at the film-vapor interface acts to promote smectic order at the surface, resulting in the surface layers ordering at a higher temperature than the interior. It is generally expected that rough interfaces cause the surface region to grow continuously, whereas smooth interfaces favor layer-by-layer growth [10]. The study of such layer-by-layer freezing behavior is extremely useful because it can yield quantitative information about the nature of the intermolecular forces [8] and about the effective surface penetration depth [6]. In this Letter, we report the results of heat-capacity (C_p) and optical-reflectivity (OR) experiments on thin free-standing films of *n*-hexyl-4'-*n*-pentanoyloxy-biphenyl-4-carboxylate (64COOBC). We find an unexpected dependence of the magnitude of the C_p anomalies associated with the layer-by-layer transitions from the smectic-*A* (Sm-*A*) to the hexatic-*B* (Hex-*B*) phase on film thickness. We also measure a large effective penetration depth of the next-to-surface layer which bears relevance to the unusual C_p behavior.

The techniques for making C_p and OR experiments in free-standing liquid-crystal thin films have been described elsewhere [11,12]. The compound 64COOBC exhibits the following bulk phase sequence [13]: isotropic (68.5 °C) Sm-*A* (56.7 °C) Hex-*B* (49 °C) crystal-*B* (Cry-*B*), with a weakly first-order Sm-*A*–Hex-*B* transition [14]. The exact number of smectic layers N in our films was determined by laser reflectivity [15]. Our preliminary structural measurement of these films by electron diffraction indicates that the C_p and OR phenomena observed here all involve Sm-*A*–Hex-*B* transitions.

We measured the temperature dependence of C_p in 64COOBC films of thickness between 2 and 30 layers. Figure 1 displays the C_p data in 3- and 4-layer films.

Two separate Sm-*A*–Hex-*B* transitions are evident, one at 63.5 °C and the second at 58.3 °C and 57.4 °C for 3- and 4-layer films, respectively. In the 3-layer film, the high-temperature peak is associated with the liquid-hexatic transition of the two surface layers, while the low-temperature peak corresponds to the liquid-hexatic transition of the single interior layer. This interpretation is reinforced quantitatively by the fact that the integrated intensity of the high-temperature peak is twice that of the low-temperature peak. In the 4-layer film, the high- and low-temperature C_p peaks have roughly the same integrated intensity, again demonstrating the existence of two liquid-hexatic transitions, first in the two outermost layers and then in the two interior layers. We have also analyzed the single C_p anomaly in a 2-layer film and found it to obey a simple power-law behavior $C_p \sim t^{-\alpha}$, where t is the reduced temperature, yielding an exponent $\alpha = 0.39 \pm 0.03$ [16].

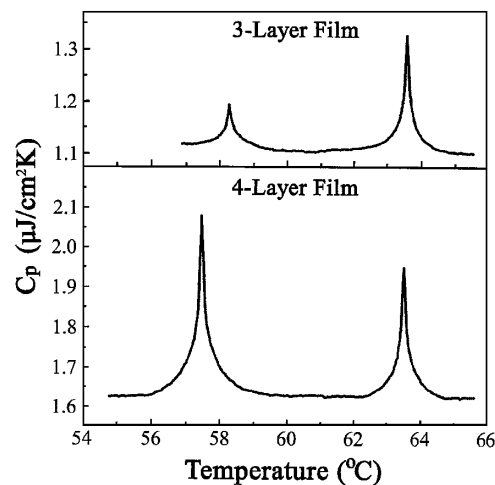


FIG. 1. Temperature dependence of heat capacity in 3- and 4-layer 64COOBC films near the Sm-*A*–Hex-*B* phase transition.

The C_p data upon cooling in films of 5–10 layers are shown in Fig. 2, where three well-defined peaks are clearly seen. The variation of the magnitudes of the C_p peaks as the film thickness is increased does not appear to follow any simple pattern. Surprisingly, with increasing thickness, the first peak grows, while the relative intensities of the second and third peaks change in a nonsystematic manner. These results are not significantly affected by the temperature ramping rate in either direction. From repeated runs using different samples, we have obtained an average thermal hysteresis of 30, 15, and 10 mK (with a resolution of 5 mK in the slowest scans) for the first, second, and third transitions, respectively. Thus the three transitions in these films appear to be continuous to within our resolution.

We have also examined the changes in the optical reflectivity in these films, which is expected to be a measure of the in-plane density [12], as they undergo the phase transitions, as shown in Fig. 3 for $N = 5$ –10. In each case, three steps in the OR can be seen. The three OR steps observed in the 6-layer film have essentially the same magnitude, indicating that each involves a pair of smectic layers undergoing structural changes at the Sm-A–Hex-B transition, propagating inward from the surface with decreasing temperature. For $N > 6$, the OR changes of the surface and next-to-surface transitions are nearly the same,

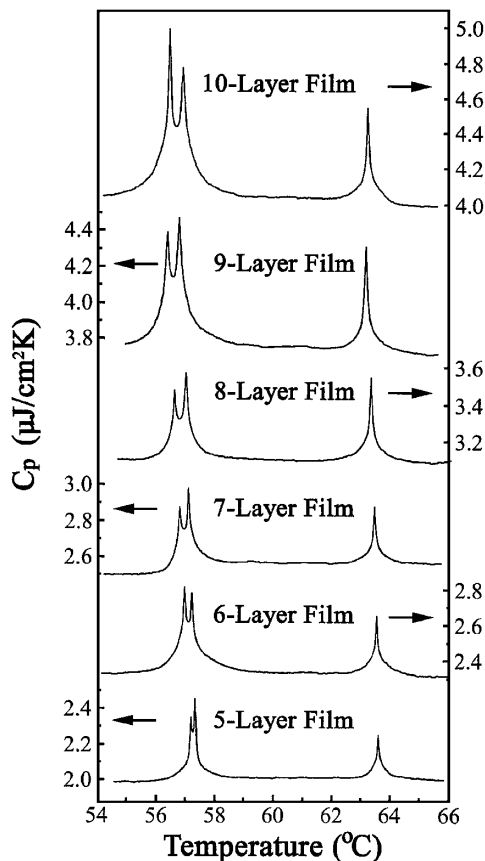


FIG. 2. Temperature dependence of heat capacity in 64COOBC films of 5–10 molecular layers near the Sm-A–Hex-B transition.

and are both equal to that of the surface transition of the 6-layer film. This result suggests that each of the first and second transitions in the films upon cooling involves primarily two smectic layers transforming structurally from the Sm-A to the Hex-B phase, while the third transition then corresponds to the remaining ($N - 4$) interior smectic layers undergoing the same transition. This conclusion is further strengthened by the observation that the third OR step in films with $N > 6$ is larger than the first two, and increases with increasing N . Thus the surface-freezing behavior in these films belongs to the case of incomplete layer-by-layer freezing. Our finding about the number of layers undergoing structural changes at the various steps makes the earlier observation about the nonsystematic variation in the C_p peaks all the more intriguing.

Our C_p data are best seen by comparing the integrated intensities of the various peaks as a function of film thickness. It should be mentioned that a comparison of the magnitude of the C_p signal obtained from different films can be subject to an uncertainty of up to 5% because of the difficulty in making absolute calibrations [17]. However, we believe that the results presented here suggest a general physical picture that is apparent beyond any experimental uncertainty. Figure 4(a) shows the dependence on the film thickness N of the integrated intensities of the first C_p peak, the first and second peaks combined, and all three peaks combined. For $N > 4$, our analysis involved resolving the separate contributions of the second and third peaks. It can be seen in Fig. 4(a) that

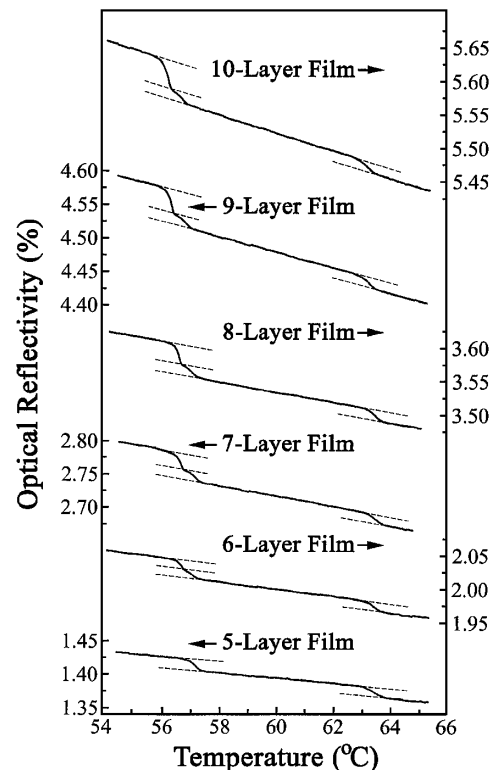


FIG. 3. Temperature dependence of optical reflectivity in 64COOBC films of 5–10 molecular layers near the Sm-A–Hex-B transition.

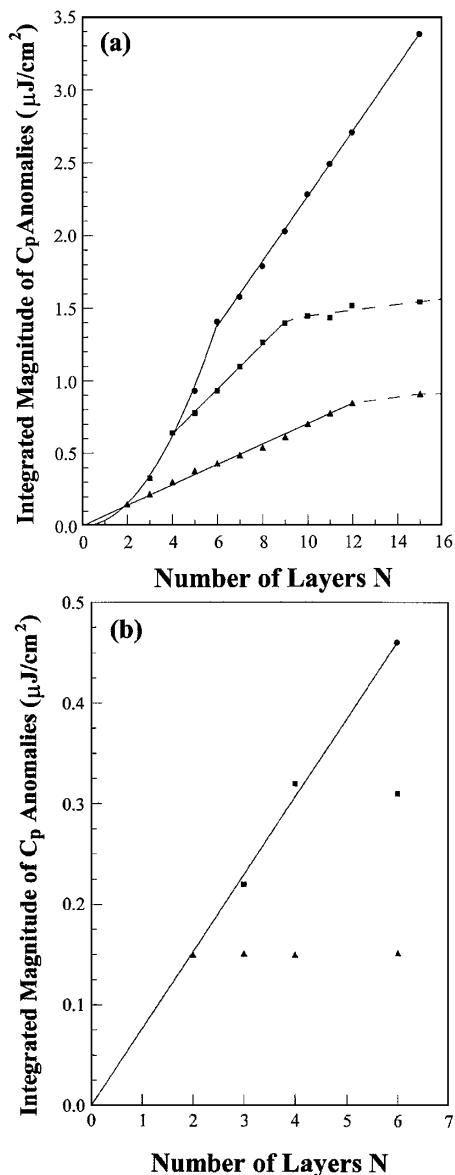


FIG. 4. Integrated magnitude of the first C_p peak (triangles), the first and second peaks combined (squares), and all three peaks combined (circles) as a function of film thickness N in (a) 64COOBC and (b) 3(10)OBC. The line through the data points for the combined integrated intensities in (a) is proportional to N^2 for $N \leq 6$ and to N for $N \geq 6$. The other solid lines are straight lines, and the dashed lines are guides to the eye.

the integrated magnitude of the first C_p anomaly shows a pronounced dependence on N which is almost linear up to $N = 12$. This is in stark contrast to the behavior in the n -alkyl-4'- n -alkoxybiphenyl-4-carboxylate (nm OBC) compounds [4,5], in which the magnitude of the first C_p anomaly is independent of N , as demonstrated in Fig. 4(b) from published data on 3(10)OBC [5]. In fact, all the data in Fig. 4(b) show clearly that the layers undergo phase transitions independently of each other in 3(10)OBC at least up to $N = 6$. On the other hand, both the magnitude and the N dependence of the data in Fig. 4(a) suggest considerable interlayer correlations in the thermal behavior of 64COOBC. In the first two transitions, which involve

structural changes in the outermost and second layers as indicated by the OR data, the C_p anomalies are enhanced by entropic contributions from the interior layers and increase in integrated magnitude with N . Of particular interest is the behavior of the total integrated magnitude of all three peaks combined, which shows an almost quadratic dependence on N up to $N = 6$, and an essentially linear dependence beyond that. It is interesting to point out that the linear portion of the total integrated magnitude vs N extrapolates to the origin. The behavior below the extrapolated linear dependence for $N \leq 6$ suggests a surface-induced suppression of the critical fluctuations manifested in the thinner films. To see whether our results in 64COOBC are somewhat unique, we have made a preliminary analysis of the published data in its homolog n -pentyl-4'- n -pentanoyloxy-biphenyl-4-carboxylate (54COOBC) [7,18]. We find that the 54COOBC data show similar but less pronounced dependence of the magnitude of the C_p anomalies on N . Our results suggest that, unlike the nm OBC compounds which exhibit completely uncoupled layer-by-layer Sm-A-Hex-B transitions, the surface transitions in 64COOBC (and to a lesser extent in 54COOBC) already contain entropy contributions from the interior layers.

To obtain additional evidence about the interlayer correlations, we have examined the temperatures $T_c(1, N)$, $T_c(2, N)$, and $T_c(3, N)$ at which the first, second, and third C_p anomalies occur in films with N layers shown in Figs. 1 and 2, as summarized in Table I. Also displayed in Table I are the differences $\Delta T_c(N)_{12} = T_c(1, N) - T_c(2, N)$ and $\Delta T_c(N)_{23} = T_c(2, N) - T_c(3, N)$, both of which increase with N , with $\Delta T_c(N)_{12}$ reaching an asymptotic value near $N = 6$ and $\Delta T_c(N)_{23}$ saturating near $N = 15$. It has been demonstrated that the dependence of the temperature difference on N can be used to determine the effective penetration depth of the surface ordering field [6]. Following this procedure, we first fit the values of $\Delta T_c(N)_{12}$ in Table I to the expression $\Delta T_c(N)_{12} = \Delta T_{01} - \delta T_1 \exp(-N/\xi_1)$, where ξ_1 is the effective penetration depth of the ordering

TABLE I. Temperatures $T_c(1, N)$, $T_c(2, N)$, and $T_c(3, N)$ (in $^\circ\text{C}$) of the first, second, and third (if present) heat-capacity peaks in Figs. 1 and 2 for various film thicknesses N . The differences $\Delta T_c(N)_{12} = T_c(1, N) - T_c(2, N)$ and $\Delta T_c(N)_{23} = T_c(2, N) - T_c(3, N)$ are also listed.

N	$T_c(1, N)$ (± 0.06)	$T_c(2, N)$ (± 0.01)	$T_c(3, N)$ (± 0.01)	$\Delta T_c(N)_{12}$ (± 0.07)	$\Delta T_c(N)_{23}$ (± 0.02)
3	63.58	58.27	...	5.31	...
4	63.47	57.45	...	6.02	...
5	63.46	57.19	57.04	6.27	0.15
6	63.43	57.09	56.85	6.34	0.24
7	63.40	57.06	56.71	6.34	0.34
8	63.32	56.99	56.60	6.33	0.39
9	63.21	56.90	56.46	6.31	0.44
10	63.17	56.89	56.42	6.28	0.47
11	63.16	56.89	56.39	6.27	0.50
15	63.14	56.84	56.29	6.30	0.55
17	63.14	56.84	56.29	6.30	0.55

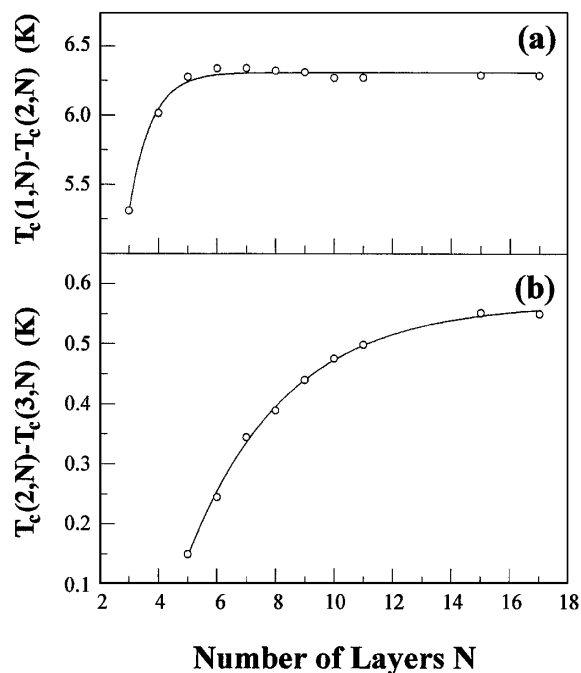


FIG. 5. Temperature difference (a) $\Delta T_c(N)_{12}$ and (b) $\Delta T_c(N)_{23}$ as a function of 64COOBC film thickness N . The solid lines are best fits to the exponential form $\Delta T_c(N) = \Delta T_0 - \delta T \exp(-N/\xi)$.

from the surface layer, as shown in Fig. 5(a). The fitting yields $\xi_1 = 0.75$, suggesting that the effective penetration depth of the surface ordering is slightly less than one molecular layer. This result is similar to that reported previously in the surface freezing of N -(4- n -butyloxybenzylidene)-4- n -octylaniline (4O.8) [6].

While the behavior of $\Delta T_c(N)_{12}$ in 64COOBC appears to be rather common, the pronounced N dependence of $\Delta T_c(N)_{23}$ for $5 \leq N \leq 15$ as displayed in Table I is quite unusual. Previous C_p measurements on the surface freezing near the Sm-A–Hex-B transition in 3(10)OBC show that $\Delta T_c(N)_{23}$ is essentially independent of N [5]. In 64COOBC, it appears that $T_c(2,N)$ and $T_c(3,N)$ decrease with different rates as N is increased, leading to a systematic and significant variation of $\Delta T_c(N)_{23}$ with N . Following the analysis of $\Delta T_c(N)_{12}$, we find that, to a good approximation, the experimental dependence of $\Delta T_c(N)_{23}$ on N can be described by the expression $\Delta T_c(N)_{23} = \Delta T_{02} - \delta T_2 \exp(-N/\xi_2)$, with $\Delta T_{02} = 0.568$ K, $\xi_2 = 3.35$, and $\delta T_2 = 1.876$ K. The fitting is shown in Fig. 5(b). Since a reasonable interpretation of the meaning of ξ_2 is the effective penetration depth of the ordering from the next-to-surface layer, its unusually large value in 64COOBC could be a key factor that accounts for the highly correlated C_p anomalies reported here. The difference in the values of ξ_1 and ξ_2 may be a result of the different asymmetric environment of the first two layers. The apparent crossover behavior in the total integrated magnitude of the C_p anomalies at about $N = 6$

likely signifies the suppression of interior fluctuations by the outer layers when the film thickness is below, say, twice ξ_2 .

In summary, we report highly correlated thermal behavior associated with the layer-to-layer Sm-A–Hex-B transitions in 64COOBC films of different thickness. While the physics behind this unusual phenomenon is not fully understood, it suggests a hitherto unanticipated manifestation of surface-induced phase transitions and wetting behavior that warrants further studies.

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*Email address: cychao@phy.ncu.edu.tw

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