Layer-by-Layer Surface Ordering near a Continuous Transition in Free-Standing Liquid-Crystal Films

T. Stoebe,(1) R. Geer,(1),(a) C. C. Huang,(1) and J. W. Goodby(2)

(1)*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*
(2)*School of Chemistry, The University, Hull HU6 7RX, England*

(Received 11 June 1992)

High-resolution heat-capacity experiments on free-standing films of the liquid-crystal compound 3(10)OBC near the smectic-*A*-hexatic-*B* phase transition have been conducted. The hexatic-*B* phase has been found to propagate into the smectic-*A* phase through a series of layer transitions, each appearing to be continuous. Furthermore, the evolution of the layer-by-layer transitions is shown to be inconsistent with recent theory regarding the fluctuation-induced forces of the highly anisotropic smectic phases.

PACS numbers: 64.70.Md, 61.30.−v, 64.60.Kw

Surface melting has been of increased interest to both experimentalists and theorists over the past ten years [1-3]. More recently, surface ordering in liquid-crystal films has also generated numerous research projects and interesting papers [4-7]. The two phenomena are closely related and are predicted to exhibit the same universal behavior depending on the range of the relevant interaction and the relative roughness of the interfaces of the system in question. In both surface freezing and surface melting, the penetration length L of the surface phase is predicted to diverge logarithmically, $L(t) \sim \log(1/t)$ as a function of reduced temperature ($t = |T - T_c|/T_c$) near the bulk transition temperature (T_c) for systems dominated by short-ranged (decaying exponentially) forces. In systems dominated by long-ranged forces (decaying algebraically), the surface region should diverge as a power of the reduced temperature, $L(t) \sim t^{-\nu}$, where $p = 1/\nu$ is related to the order of algebraic decay of the long-range force. Rough interfaces cause the surface region to grow continuously, whereas smooth interfaces favor layer-by-layer growth [8]. The reports, to date, on each of the four possible combinations of smoothness and range of interaction have been on systems undergoing first-order transitions exclusively. In this Letter we present the first data that exhibit layer-by-layer, power-law growth of the surface region near a continuous transition and discuss the results in light of recent theoretical predictions regarding the form of the interaction between the smectic layers in our system.

The experiments were performed on free-standing films of the liquid-crystal compound 3(10)OBC (a member of the *n*-alkyl-4′-*n*-alkoxybiphenyl-4-carboxylate, *nm*OBC, homologous series). The films were prepared in the oven of our recently constructed ac calorimeter (described in Ref. [9]) and the heat capacity was measured as a function of temperature for films 60, 30, and 6 molecular layers in thickness (scanning rates ∼15 mK/min). The data are shown in Figs. 1(a)-1(c) [10]. The thicknesses of the two thicker films were determined by examining the chromaticity of reflected white light and have estimated errors of ±3 and ±2 layers, respectively [11]. Since, for films thinner than 12 layers, the reflectivity (measured using a 0.63-μm HeNe laser as the light source) scales as N^2, where N is the number of smectic layers, the thickness of the 6-layer film could be determined exactly [12].

Heat-capacity studies on bulk samples of 3(10)OBC have been completed previously; the data exhibit large, relatively symmetric anomalies near 66 °C corresponding to the smectic-*A*-hexatic-*B* (Sm*A*-Hex*B*) phase transition [13]. The Sm*A* phase is the higher-temperature, disordered, phase and can be thought of as a stack of two-dimensional liquid layers. The Hex*B* phase is often characterized as a stack of layers in which there is order

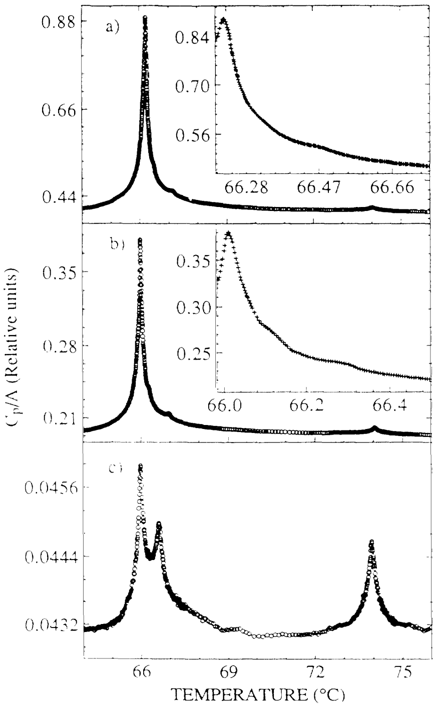

FIG. 1. (a)-(c) Heat capacity as a function of temperature for 60-, 30-, and 6-layer free-standing films of the liquid-crystal compound 3(10)OBC near the Sm*A*-Hex*B* phase transition. The temperature axis is expanded in the insets to make the layer transitions more apparent near the large interior anomaly.

among local lattice orientations (bond orientational order) but no long-range positional order. Because there was no detectable thermal hysteresis (down to the 3-mK resolution of the bulk calorimeter) and the data were independent of the direction of the temperature scan, the bulk Sm*A*-Hex*B* transition in 3(10)OBC was determined to be continuous.

The heat-capacity signature of 3(10)OBC in the free-standing film geometry is considerably richer than the aforementioned bulk samples since the films undergo a series of transitions due to the ordering effects of the film-vapor interfaces (see Fig. 1). By examining *e*-beam diffraction data on thin films [14] and the evolution of the heat-capacity data as a function of film thickness, it is clear that the anomaly near 74 °C corresponds to the Sm*A*-Hex*B* transition in only the two outermost surface layers of the film [15]. The anomaly near 67 °C is due to the Sm*A*-Hex*B* transition of the two layers adjacent to the two outermost layers. The next two layers become Hex*B* near 66.3 °C and the transition temperatures of the subsequent layers converge near the bulk Sm*A*-Hex*B* transition temperature yielding a large anomaly [16]. 3(10)OBC appears to be unique among the other *nm*OBC compounds that exhibit the Sm*A*-Hex*B* transition, in that four (as opposed to three) individual layer transitions can be resolved above the bulk transition temperature. This is presumably due to the fact that 3(10)OBC has the longest total alkyl chain length, and therefore the weakest interlayer coupling. As in the bulk samples, the data on the 3(10)OBC films are independent of the direction of the temperature scan and none of the peaks exhibited any thermal hysteresis (down to the 7-mK resolution of the film calorimeter). In fact, films only two layers thick have been studied extensively; the heat-capacity anomaly, similar to the surface transitions of the thicker films, was successfully fitted by a simple power-law form, $C_p \sim t^{-\alpha}$ [17]. The transitions appear, therefore, to be continuous and the surface region grows in a layer-by-layer fashion consistent with the smooth nature of the smectic interfaces.

This is an intriguing result since such behavior would be predicted to be impossible for an ordinary system undergoing a continuous phase transition. Unlike the case of a first-order transition, where the fluctuations may be abruptly terminated when the system changes phase, the correlation length for the fluctuations of a critical transition should diverge. A conventional continuous transition that establishes hexatic order over a macroscopic area in the *X*-*Y* plane should therefore also establish hexatic order over a macroscopic distance along the *Z* axis. Since even the 60-layer film is less than 180 nm thick (far less than the characteristic lateral dimension for the hexatic order ≈ 1 mm [18]), any continuous transition should penetrate the entire film at the transition temperature and no individual layer ordering would be possible. The fact that it does occur in our system can be understood to be a consequence of the extreme anisotropy inherent in the smectic phases and the ordering effects of the film-vapor interfaces. The intermolecular interactions are much stronger within the planes of the layers than along the layer normals (the *Z* axis). In fact, the layers must be so weakly coupled that the layer boundaries act as barriers to the fluctuations in the *Z* direction, confining each surface transition to a single smectic layer. It is only when the boundary conditions of the interior layers become similar (i.e., near the bulk transition temperature) that they undergo the phase transition at the same temperature, resulting in the large interior anomaly. An interesting result of such strong anisotropy is that the separate layer transitions can all be regarded as effectively two dimensional.

As mentioned in the introduction, the temperature dependence of the penetration depth of the surface region, *L*, is dependent on the form of the dominant intermolecular interaction. The calculation is straightforward [19]. Since the surface Hex*B* phase appears at a temperature higher than the bulk Sm*A*-Hex*B* transition temperature, the system free energy must be reduced by replacing the Sm*A*-vapor interfacial coefficient (γ_{AV}) with the sum of the Sm*A*-Hex*B* and Hex*B*-vapor interfacial coefficients ($\gamma_{AB}+\gamma_{BV}$). If the surface region is not macroscopically large, the mean-field free energy reduction per unit area (denoted here as δF_1) will be a function of *L* due to the truncation of the interactions across the interfaces. For power-law forces between interfaces varying as $(1/\text{distance})^p$, it is given by

$$\delta F_1 = \Delta\gamma(1 - \alpha L^{1-p}) \, ,$$

where $\Delta\gamma = \gamma_{AV} - \gamma_{AB} - \gamma_{BV}$ and α is a constant of order unity. This effect competes with the increase, proportional to *L*, in the system free energy per unit area due to the lower entropy of the surface Hex*B* phase (denoted here as δF_2). At the bulk transition temperature (T_c), $\delta F_2 = 0$ and, for $T > T_c$, δF_2 can be expanded in terms of $t = (T - T_c)/T_c$. To lowest order, δF_2 can be expressed as $\delta F_2 = \beta L t$ and, therefore,

$$\delta F_{\text{tot}} = \delta F_1 + \delta F_2 = \Delta\gamma(1 - \alpha L^{1-p}) + \beta L t \, ,$$

where β is also a constant of order unity. Minimizing δF_{tot} with respect to *L* yields the desired result: $L \approx t^{-1/p}$. In a typical system dominated by van der Waals type forces, $p = 3$ so one would expect *L* to diverge algebraically with exponent $\nu = 1/p = 1/3$.

The smectic films are not typical systems, however, and they may not be dominated by simple van der Waals type forces. The fluctuations of the smectic phase are altered by the imposition of the boundary conditions arising from the film-vapor interfaces. This change in the fluctuation free energy induces an interaction between the interfaces. This is an example of a fluctuation-induced force, often referred to as a Casimir force. By examining the effect of boundaries on the orientational fluctuations in the highly anisotropic smectic phase, Ajdari, Peliti, and Prost [20] recently determined that this force should decay as (dis-

TABLE I. Transition temperatures (°C) of the transitions from Fig. 1.

Thickness (layers)	T_c (bulk) (± 0.01)	T_c ($L=4$) (± 0.015)	T_c ($L=3$) (± 0.01)	T_c ($L=2$) (± 0.01)	T_c ($L=1$) (± 0.07)
60	66.231	66.34	66.493	67.136	74.03
30	66.015	66.12	66.283	66.953	74.04
6	65.751[a]		65.982	66.613	73.94

[a]See Ref. [26].

tance)$^{-2}$ ($p=2$) instead of the inverse cubic van der Waals type force ($p=3$) predicted between the interfaces of an isotropic fluid [21]. Moreover, they determined that the excess free energy density due to this force for symmetric boundary conditions, such as those in free standing films, is given by

$$\delta F_s = -\frac{k_b T \zeta(2)}{L 16\pi}\left(\frac{B}{k_1}\right)^{1/2},$$

where ζ is the Riemann zeta function, L is the film thickness, k_1 is a Frank constant, and B is the bulk modulus. This free energy form infers a penetration length $\lambda = (k_1/B)^{1/2}$ that can be used to compare the strength of this interaction to the van der Waals type interaction. Using nominal values for k_1 ($k_1 = 5\times 10^{-7}$ dynes) [22] and B ($B = 1\times 10^{8}$ dynes/cm^2) [23] λ is found to be $\lambda \approx 7$ Å. Because λ is smaller than the 30-Å separation between the smectic layers and this interaction decreases much more slowly than the van der Waals type interaction, it should dominate over length scales as small as the interlayer spacing. Because the dominant force decays as (distance)$^{-2}$ ($p=2$) the calculation from the preceding paragraph gives $\nu_{\text{th}} = 1/2$ and the surface Hex$B$ region should grow as $L(t) \approx t^{-1/2}$ in the 3(10)OBC films.

This discussion is motivated by the fact that the exponent $\nu = 1/p$ is an experimentally accessible quantity since the temperatures of the individual layer transitions can be used to follow the propagation of the Hex$B$ phase into the SmA phase [24]. The transition temperatures of each anomaly shown in Fig. 1 were determined with high resolution [25] and are shown in Table I ($L=1$ corresponds to the outermost layer). These data were then used to construct the plots of L vs $t = [T_c(L) - T_c]/T_c$ exhibited in Fig. 2. The three data sets were fitted by the expression $L = L_0 t^{-\nu}$ and the fitted curves are superimposed on the data in Fig. 2 [26]. The agreement between the data and the fits is clearly quite good but, to more closely examine this point, the 60-, 30-, and 6-layer data, as well as their respective fits (and fitting parameters), were replotted as log(L) vs log(t) in Figs. 3(a), 3(b), and 3(c), respectively. The linearity of these plots confirms the long-range nature of the dominant intermolecular interaction and the consistency of the fitting parameters, L_0 and ν, strongly supports this analysis. These results, therefore, appear to be highly reproducible and the excellent agreement in ν for the three film thicknesses ($\nu_{60} = \nu_{30} = 0.32 \pm 0.01$, $\nu_6 = 0.31 \pm 0.02$) implies that the form of the interaction does not change in this range of film thickness [27]. Furthermore, these exponents are clearly incompatible with the exponent, $\nu_{\text{th}} = 1/2$, resulting from the theory proposed by Ajdari, Peliti, and Prost.

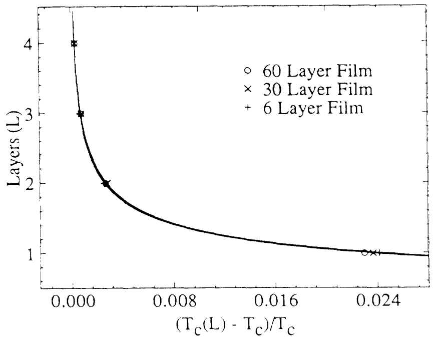

FIG. 2. Plot of L vs $[T_c(L) - T_c]/T_c$ and the respective fitted curves from the three data sets listed in Table I (after converting the transition temperatures into K). The agreement is clearly quite good.

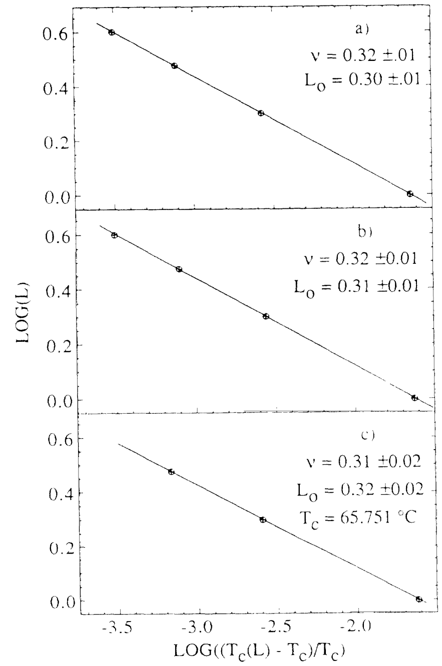

FIG. 3. (a)-(c) Plot of log(L) vs log[$(T_c(L) - T_c)/T_c$] for the 60-, 30-, and 6-layer films, respectively. The linearity of these plots establishes the power-law form of the dominant intermolecular interaction, while the slope ν determines the exponent of the power-law decay. The consistency of the L_0 fitting parameter supports the fit results (see text).

They are, however, consistent with the exponent $\nu = 1/3$ expected for systems dominated by van der Waals type forces.

In conclusion, we have accurately measured the heat capacity of a series of continuous surface SmA-Hex$B$ transitions preceding a continuous bulk SmA-Hex$B$ transition in a number of free-standing 3(10)OBC liquid-crystal films. To the best of our knowledge, this is the first report of a system in which, due to the highly anisotropic nature of its layer structure, the surface region grows in a layer-by-layer fashion near a continuous transition. The transition temperatures were obtained with high resolution and the surface region was found to diverge algebraically $[L(t) \sim t^{-\nu}]$, consistent with the long-ranged nature of the intermolecular forces of the smectic phases for the entire range of film thicknesses studied. The experimentally determined exponents ($\nu_{\mathrm{expt}} \approx 1/3$) are not consistent with recent theory on the nature of fluctuation-induced forces in the smectic phases ($\nu_{\mathrm{th}} = 1/2$). It should be noted, however, that the experimental exponents are consistent with forces having the same distance dependence as van der Waals forces, suggesting that the dominant interaction in these films decays algebraically as (distance)$^{-3}$.

We are grateful to Professor M. Shick for numerous valuable discussions. This work was supported by the National Science Foundation, Solid State Chemistry Program, Grants No. DMR89019334 and No. DMR9024-992. Fellowship support from the Department of Education (T.S.) and IBM (R.G.) is acknowledged.

---

[a] Current address: Naval Research Laboratory, Washington, DC 20375-5000.

[1] J. W. M. Frenken and J. F. van der Veen, Phys. Rev. Lett. **54**, 134 (1985).

[2] D. M. Zhu and J. G. Dash, Phys. Rev. Lett. **57**, 2959 (1986).

[3] J. Krim, J. P. Coulomb, and J. Bouzidi, Phys. Rev. Lett. **58**, 583 (1987).

[4] B. C. Swanson, H. Straigler, D. J. Tweet, and L. B. Sorensen, Phys. Rev. Lett. **62**, 909 (1989).

[5] E. B. Sirota, P. S. Pershan, S. Amador, and L. B. Sorensen, Phys. Rev. A **35**, 2283 (1987).

[6] R. Geer. T. Stoebe, C. C. Huang, R. Pindak, J. W. Goodby, M. Cheng, J. T. Ho, and S. W. Hui, Nature (London) **355**, 152 (1992).

[7] H. Li, M. Paczuski, M. Kardar, and K. Huang, Phys. Rev. B **44**, 8274 (1991).

[8] G. An and M. Shick, Phys. Rev. B **37**, 7534 (1988).

[9] R. Geer, T. Stoebe, T. Pitchford, and C. C. Huang, Rev. Sci. Instrum. **62**, 415 (1991).

[10] The calibration of the absolute heat-capacity scale in these plots requires more data on different film thicknesses. Because rescaling to the absolute values of the heat capacity would not affect the results of this Letter, the data are simply plotted in terms of relative units.

[11] E. B. Sirota, P. S. Pershan, L. B. Sorensen, and J. Collet, Phys. Rev. A **36**, 2890 (1987).

[12] C. Rosenblatt and N. Amer, Appl. Phys. Lett. **36**, 432 (1980).

[13] C. C. Huang, G. Nounesis, R. Geer, J. W. Goodby, and D. Guillon, Phys. Rev. A **39**, 3741 (1989).

[14] J. T. Ho (private communication).

[15] Similar surface ordering has been observed in a number of experiments employing the free-standing film geometry (Refs. [4] and [5], among others). Reference [6] discusses this issue more explicitly.

[16] As the individual layer transitions begin to overlap near the bulk T_c, they become progressively more difficult to resolve. It is therefore not clear whether this system exhibits true complete wetting (as observed in Ref. [4]) or incomplete wetting.

[17] T. Stoebe, C. C. Huang, and J. W. Goodby, Phys. Rev. Lett. **68**, 2944 (1992).

[18] R. Pindak, D. E. Moncton, S. C. Davey, and J. W. Goodby, Phys. Rev. Lett. **46**, 1135 (1981).

[19] The calculation appears (among other places) in a review article by J. G. Dash, in *Proceedings of the Nineteenth Solvay Conference*, edited by F. W. Dewitte (Springer-Verlag, New York, 1988).

[20] A. Ajdari, L. Peliti, and J. Prost, Phys. Rev. Lett. **66**, 1481, (1991). This result has been recently reproduced in Ref. [21].

[21] H. Li and M. Kardar, Phys. Rev. Lett. **67**, 3275 (1991).

[22] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1979).

[23] M. Benzekri, T. Claverie, J. P. Marcerou, and J. C. Roullon, Phys. Rev. Lett. **68**, 2480 (1992); M. R. Fisch, P. S. Pershan, and L. B. Sorensen, Phys. Rev. A **29**, 2741 (1984).

[24] This analysis is similar to that done in Ref. [4]. There are some important differences to be noted, however. The phase transition discussed in Ref. [4] is a strongly first-order SmA-surface-stabilized-SmI transition of the liquid-crystal compound 90.4. The smectic-I phase is not thermodynamically stable in bulk samples of 90.4 and exists in only a limited range of film thicknesses. This fact, coupled with the presence of the coexistence region inherent in any strongly first-order phase transition, may explain why their value for ν ($\nu = 0.373 \pm 0.015$) is in only marginal agreement with the exponent expected for a system dominated by van der Waals type forces.

[25] Unfortunately the system is not as stable over the long data runs (13 K over 14 h) exhibited in Figs. 1(a), 1(b), and 1(c) as it is over the short hysteresis runs (± 1.5 K over 3 h) and the relative temperature resolution decreases with increasing separation. Therefore, even though the lack of any hysteresis can be determined to better than 10 mK, an examination of repeated runs on films of similar thickness yields the estimated errors: ± 70, ± 10, ± 10, and ± 15 mK for the $L = 1$, 2, 3, and 4 transitions, respectively.

[26] Because no anomaly associated with the bulk transition could be detected for the 6-layer film, the bulk T_c was allowed to be a fitting parameter in this case. This fit effectively solves three equations for the three unknowns: L_0, T_c, and ν. The agreement between these results and the results from the thicker films supports this approach.

[27] Since the layer transitions near the interior transition become more difficult to resolve for films thicker than 60 layers, these film thicknesses roughly span the experimentally accessible range.