

Layer-by-Layer Surface Freezing of Freely Suspended Liquid-Crystal Films

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Computer-enhanced polarized video microscopy has been used to study the discrete layer-by-layer surface ordering transitions of freely suspended films of 4-(*n*-nonyloxy)benzylidene-4-(*n*-butyl)aniline (9O.4). Stable tilted hexatic smectic-*I* surface layers form on both free surfaces of the 2D-liquid smectic-*A* interior in a monolayer, bilayer, trilayer, . . . sequence as $T \rightarrow T_c$. The appearance of the first ten surface layers is described very well by the simple power-law form, $L = L_0 t^{-1/3}$, predicted for the surface freezing transition in a system with van der Waals forces.

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There has been considerable recent experimental¹⁻⁶ and theoretical⁷⁻¹⁰ interest in surface melting. One of the fascinating features of surface melting is that even though an infinite bulk system undergoes a first-order melting transition, in the semi-infinite system the change in phase can start at the surface and proceed inwards, resulting in a universal first-order critical surface transition.⁷ Thus, surface melting is a special case of surface-induced disorder.^{7,8} Liquid crystals, on the other hand, are prime examples of systems with surface-induced order.¹¹⁻¹⁵ In this Letter, we report a new class of surface-induced ordering transitions in freely suspended liquid-crystal films which are the exact freezing analog of surface melting: layer-by-layer surface freezing with power-law growth of the thickness of the frozen surface region as $T \rightarrow T_c$.

Surface freezing and surface melting are predicted to have identical universal critical behavior which depends only on the range of the interactions and whether the interface between the surface phase and the interior is rough or smooth.⁷⁻⁹ If the dominant interactions are from long-range van der Waals forces, the thickness L of the surface region is predicted to follow a power-law divergence, $L \sim t^{-1/3}$, where $t = |T - T_c|/T_c$ is the reduced temperature.^{1,8} For systems dominated by short-range exponential interactions, the predicted divergence is logarithmic,^{7,8} $L \sim \ln(1/t)$. When the interface between the surface phase and the interior phase is smooth (e.g., below the roughening temperature), the growth of the thickness of the surface region is predicted to follow the power-law or logarithmic form in a layer-by-layer fashion; for rough interfaces the power-law or logarithmic growth is predicted to occur continuously.⁹

Of the four possible classes of universal surface freezing-melting behavior, (1) continuous power law, (2) continuous logarithmic, (3) layer-by-layer logarithmic, and (4) layer-by-layer power law, examples of classes (1), (2), and (3) have been reported previously by different groups. The system we report here, 4-(*n*-nonyloxy)benzylidene-4-(*n*-butyl)aniline (9O.4), is the first example of the fourth class, power-law layer-by-

layer growth. Previous experimental studies of the surface melting of thick² and thin³ physisorbed films and of bulk^{4,5} and thin-film⁶ lead have shown that these systems all have continuous surface-melting transitions (no hint of layer-by-layer behavior) indicating rough interfaces. Both power-law and logarithmic continuous growth [classes (1) and (2)] was observed; for example, thick physisorbed Ar films² have $L \sim t^{-1/3}$ and the original work⁴ on bulk Pb found $L \sim \ln(1/t)$. (Note, however, that evidence for the opposite functional form of the growth has also been reported^{2,3,5} for both systems.) Logarithmic layer-by-layer growth [class (3)] of smectic-*A* layers at the isotropic liquid-crystal-vapor interface has also been studied.¹²

Surface melting and surface freezing are also special cases of interfacial wetting: Surface melting occurs when the melt liquid wets its own solid-vapor interface and surface freezing occurs when a more-ordered surface phase wets the less-ordered interior phase-vapor interface.⁹ The generic surface freezing-melting scenarios follow the corresponding wetting behavior: nonwetting, incomplete wetting, and complete wetting. The freezing transitions of most freely suspended liquid-crystal films fall in the nonwetting category; the entire interior of the film freezes abruptly. However, many freely suspended liquid-crystal films exhibit incomplete (monolayer) wetting; the two surface monolayers freeze about 10° above the bulk-freezing transition temperature, where the rest of the interior freezes abruptly. This incomplete wetting has been studied in detail for crystalline smectic-*B* monolayers on 2D-liquid smectic-*A* films¹⁴ and for tilted hexatic smectic-*I* monolayers on tilted 2D-liquid smectic-*C* films.¹⁵ The new feature of the system described here (9O.4) is that the wetting is complete. The transition starts in the same way—with surface-induced ordered monolayers on each film-vapor interface—but the interior does not freeze abruptly and instead the entire film converts to the ordered surface phase in a layer-by-layer fashion.

The experimental arrangement is shown in Fig. 1. A freely suspended liquid-crystal film is prepared in a

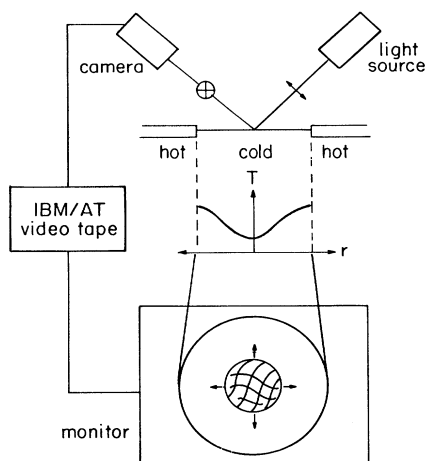


FIG. 1. Schematic diagram of the experimental arrangement. Computer-enhanced polarized video microscopy was used to observe the texture of the freely suspended liquid-crystal films. The film oven produced a radial temperature gradient which allowed the layer-by-layer surface-freezing transitions to be observed as circular regions which nucleated at the cold center of the film and propagated outwards as the oven temperature was decreased.

computer-controlled temperature-regulated oven. The oven provides a radial temperature gradient with the center of the film being the coldest and the edge of the film being the hottest; the radial gradient near the center of the film, where the measurements are made, is about 10 mK/mm. In the experiment, the temperature of the oven is lowered linearly in time and the freezing transitions are observed optically. Because the tilted liquid-crystal phases are very birefringent, singly-monolayer freezing transitions can be observed by illuminating the film with polarized white light and viewing the specularly reflected light through a crossed polarizer.¹⁶ The observed transitions start at the center of the film and proceed radially outwards. Since the initial transition is from an untilted smectic *A* to a tilted smectic *I*, the first surface-freezing transition is observed when a textured region (corresponding to the different smectic-*I* tilt domains) appears on the untilted smectic-*A* background. Subsequent layer transitions appear as waves of slightly increasing contrast spreading radially outwards. The experiments consist of recording the transition temperature as each layer freezes. Typical cooling rates were 5–10 mK/min. Faster and slower cooling rates did not produce any measurable change in the layer freezing temperatures. Since the optical contrast change corresponding to a single-layer transition is very small, the video images were computer-contrast enhanced to increase the visibility. The contrast-enhanced images were recorded on video tape and the temperature was simultaneously recorded on the audio channel using a 1200 baud modem. This allowed subsequent reanalysis of the

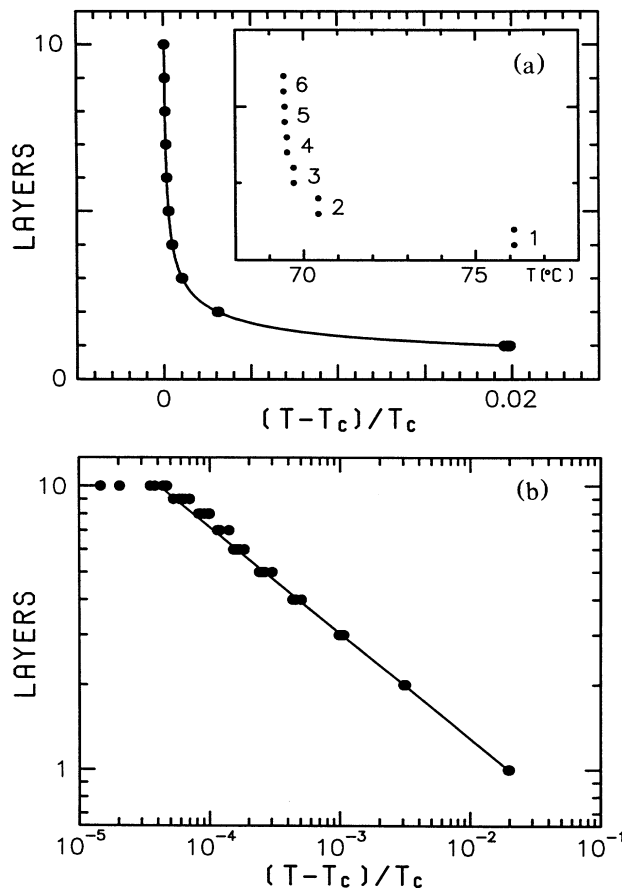


FIG. 2. Linear and log-log plots of the number of frozen surface layers on each film-vapor interface vs reduced temperature t for six different films. Only the first ten-layer transitions (on each interface) are shown. The layer-by-layer freezing continues until the entire film is frozen. The first ten transitions are fitted very well by the power-law form $L = L_0 t^{-\nu}$. The solid line indicates the corresponding power-law fit. The data from the six films agree very well; most of the points are indistinguishable in the linear plot. The inset in the linear plot shows both the top and the bottom freezing-transition temperatures for the first six pairs of transitions in a single film. The first four frozen surface layers on each surface occur as clearly resolved pairs indicating that the top and the bottom layers freeze at very nearly the same temperature.

freezing transitions from the video tapes.

The observed layer freezing transitions are shown in Fig. 2. Above about 76.1 °C the entire film is smectic *A*. At ~76.1 °C, the two outside layers freeze and the film becomes stratified: from about 76.1 °C there are tilted hexatic smectic-*I* monolayers on the two exterior surfaces, and the interior layers are smectic *A*.¹⁷ There is a small time separation between the freezing transition for the top and bottom surfaces; this corresponds to an apparent transition-temperature difference of about 5 mK. The second, third, and fourth freezing transitions also

appear as well resolved top and bottom pairs with similar transition-temperature separations. After about the fourth pair, the temperature separation between adjacent pairs becomes comparable to the separation within pairs. The layer-by-layer freezing continues until the entire film is smectic *I*. The entire film remains smectic *I* from about 69.2 to 68.8 °C where there is an abrupt first-order transition to the smectic-*F* phase.

The first ten-layer freezing transitions are well described by a power-law form for the number of surface layers L versus reduced temperature $L \sim t^{-\nu}$. This is illustrated in Fig. 2 for six different 67-layer films with slightly different transition temperatures. It is well established for these liquid crystals that the transition temperatures slowly degrade with time due to the spontaneous decomposition of the liquid-crystal molecules. The resulting impurities lower the transition temperature, but typically do not affect the critical behavior aside from the shift in T_c . To test for the possible effects of impurities, we deliberately produced large T_c shifts by keeping some samples for weeks; no change in the critical behavior was observed. However, the data for the six films reported here were taken with fresh samples. Each data set shown in Fig. 2 was fitted separately by $L = L_0(|T - T_c|/T_c)^{-\nu}$ to determine L_0 , T_c , and ν . The figure shows that the data sets agree very well once they are corrected for their T_c shifts; the transition-temperature variations shown in the figure are random (there is no systematic variation for different films) and correspond to about ± 8 mK per point. The log-log plot shows that the data are well described by the power-law form over about three decades in reduced temperature. The solid line indicates the best-fit power law to the combined data set; the corresponding parameters are $L_0 = 0.24 \pm 0.01$ and $\nu = 0.373 \pm 0.015$. The critical exponent determined from the power-law fit is consistent with the exponent predicted, $\nu = \frac{1}{3}$, for simple van der Waals forces at the 3-standard-deviation level. Our data cannot be described by the logarithmic form predicted for short-range forces.

After about the first ten surface layers have frozen, the freezing of additional surface layers deviates from the power-law form. This is shown in Fig. 3. The dashed line indicates the power-law form which fits the first ten-layer freezing transitions, but progressively deviates from the data as the freezing continues inward. The solid line indicates a crossover form, $t = \alpha L^{-n} - \beta L^3$ with $\alpha = 6.79 \pm 0.46$, $n = 2.68 \pm 0.17$, and $\beta = 9.0 \pm 3.5 \times 10^{-6}$, which fits all the layer-by-layer freezing transitions. The critical exponent determined from the crossover form fit, $\nu = n^{-1} = 0.373 \pm 0.024$, is in good agreement with the predicted van der Waals exponent at the 2-standard-deviation level.

The observed deviation from the pure power-law divergence predicted for van der Waals forces is probably produced by a small shift in the interior transition tempera-

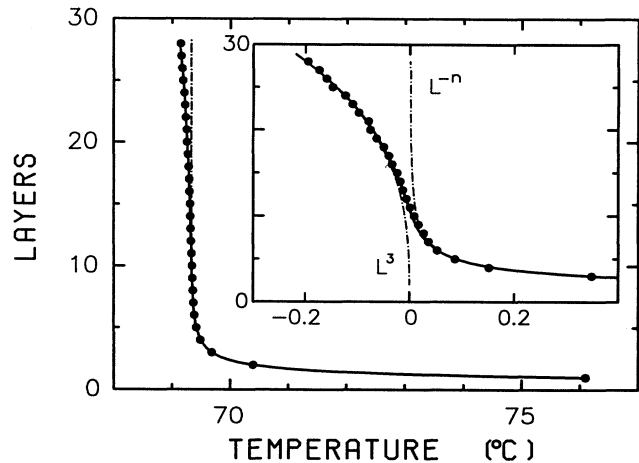


FIG. 3. Plot of the number of frozen surface layers (on each interface) vs temperature T in the crossover region. The dashed line indicates the power-law form $L = L_0 t^{-\nu}$, which fits the transitions near the surface, but progressively deviates from the data as the freezing continues inward. The solid line indicates the phenomenological crossover form $t = \alpha L^{-n} - \beta L^3$, which fits all the freezing transitions. Inset: The contributions of the two terms close to T_c ; the dashed lines indicate the power law L^{-n} and cubic L^3 contributions. The solid line indicates the combined crossover form.

tures with the thickness of the frozen surface layer. Much larger shifts in the phase boundary versus film thickness have been observed in surface stabilized smectic-*B*, smectic-*I*, and smectic-*F* phases; the smectic-*B* boundary shifts ~ 2 K (Ref. 14) and the smectic-*F* and -*I* boundaries shift ~ 10 K.¹⁶ The smectic-*I* phase produced in our system is a surface stabilized phase—it does not occur in bulk 9O.4. The total shift produced in 9O.4 by the cubic term $-\beta L^3$, for thirty frozen surface layers is only ~ 0.2 K. The crossover form for large L predicted¹⁸ for surface-induced disorder in a system dominated by short-range forces with a two-phase coexistence region (produced by defects) is $t = \alpha \exp(-L/\xi) - \beta L$. This would translate to $t = \alpha L^{-n} - \beta L$ for systems dominated by long-range forces. A linear shift at large L is also consistent with our data, but the data then require the crossover from a constant shift at small L to a linear shift at large L .

In conclusion, near the surface (within ten layers), the layer-by-layer surface freezing transitions of freely suspended films of 9O.4 have the power-law form expected for surface freezing governed by van der Waals interactions. For thick films the layer-by-layer freezing continues until the entire film is frozen, but there is a crossover to a nonpower-law form once the frozen-surface region becomes thicker than about ten layers (300 Å).

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¹⁷The current experimental evidence for the freezing from the surface inwards consists of the observation (optically) of overlapping tilt domains; adjacent frozen layers at the center of the film would not have overlapping domains. Freezing from the surface inwards is also consistent with both the behavior expected theoretically and with recent direct interlayer x-ray observations of frozen smectic-*I* surface layers in films of the homolog, 7O.7 by D. J. Tweet, B. D. Swanson, H. Stragier, and L. B. Sorensen (unpublished). A direct x-ray determination for 9O.4 is now in progress. The present identification of the surface phase as a smectic *I* is based on the observed texture which indicates either a smectic-*I* or -*F* phase. Since the "smectic-*I*"-to-smectic-*F* transition is observed in the film at the temperature corresponding to the bulk phase transition, the interface is that the surface phase is a surface-induced smectic *I*. In-plane x-ray measurements to verify this assignment are also in progress.

¹⁸D. M. Kroll and G. Gompper (to be published).