## Unusual Layer-Thinning Transition Observed near the Smectic-A–Isotropic Transition in Free-Standing Liquid-Crystal Films

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Calorimetric and optical reflectivity studies on free-standing partially fluorinated liquid-crystal films have revealed novel melting phenomena. The smectic-A-isotropic transition occurs through a series of layer-*thinning* transitions, causing the films to thin in a stepwise manner as the temperature is increased. The temperature dependence of the film thickness has been found to be well fitted by a simple power law. These results are discussed in the context of present theory and the effects of fluorination are addressed.

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Melting phenomena have long been of great interest and the investigation of bulk phase transitions has generated an immense amount of literature. More recently, however, the importance of melting at interfaces has become increasingly appreciated. It is now believed that most conventional solids coexist with a surface liquid layer even well below the bulk melting temperature. As the temperature is increased, the liquid layer penetrates deeper into the sample until it entirely replaces the solid phase just above the transition temperature. This is an example of an ordinary melting transition; the melting originates at the surface and penetrates inwards. These transitions can be described in terms of the liquid layer wetting the solid-vapor interface. The theory of wetting is very powerful because it predicts universal behavior based primarily on the form of the dominant intermolecular interaction and the roughness of the respective interfaces [1]. For example, the penetration length L of the surface phase is expected to diverge algebraically,  $L \approx t^{-\nu}$ , as a function of reduced temperature,  $t = |T - T_c| / T_c$ , near the bulk transition temperature  $T_c$  in systems dominated by an algebraically decaying long-range force. Moreover, the exponent  $\nu (= 1/p)$  is related to the order of the algebraic decay of the dominant intermolecular interaction (p = 3 for nonretarded van der Waals forces) [2]. Rough interfaces cause the surface region to grow continuously, whereas smooth interfaces favor layer-by-layer transitions [3].

Unlike conventional solids, the surface tension associated with the sample-vapor interface has been shown to promote order at the surface of many thermotropic liquidcrystal systems. For example, through their low angle xray diffraction experiments, Ocko *et al.* [4] observed the formation of smectic-A (SmA) bilayers at the free surface of an isotropic liquid-crystal sample well above the bulk SmA-isotropic transition temperature. As its name suggests, the liquid-crystal isotropic phase possesses neither translational nor orientational order. However, the rodlike liquid-crystal molecules ( $\approx 25$  Å long  $\times 5$  Å diameter) aggregate into layers in the SmA phase so that the long axes of the molecules are normal to the planes containing the layers [5]. One of the most interesting aspects of many smectic liquid crystals is that, under the appropriate conditions, they can be spread across an opening to form freestanding films (much like a soap film on a ring). Because the smectic layer normal is parallel to the film normal, film thickness is quantized in units of layers. Even films only 2 molecular layers thick can be readily prepared and remain stable for days. Single layer films appear to be unstable and quickly rupture [6]. Because of the lack of order, isotropic films are also unstable and cannot be prepared. Despite these inconveniences, the free-standing liquid-crystal film experimental geometry has proven to be immensely rich.

As in the case of the free surfaces of bulk liquid-crystal samples, the surface tension appears to promote order at the film-vapor interfaces [4,7,8] and the wetting aspects of the resultant surface freezing transitions have been the focus of a number of recent studies [4,8]. In this Letter we report our observation of unusual melting phenomena above the bulk SmA-isotropic transition temperature. Our calorimetric and optical reflectivity data indicate that the free-standing films undergo the layer-by-layer *thinning* transition as an intriguing function of temperature. These results provide a unique insight into the physics of highly anisotropic layered systems and interfacial ordering effects. To the best of our knowledge, such *layer-thinning* behavior has never before been observed.

The 1 cm square films were prepared in the oven of our ac calorimeter described in Ref. [9]. Our present experimental system allows simultaneous high-resolution measurement of both heat capacity and optical reflectivity as a continuous function of temperature [10]. The temperature of the oven is computer controlled and uniform ramping rates ( $\approx 50 \text{ mK/min}$ ) were used for this study. Because of the anisotropy inherent in the liquid-crystal molecules, the SmA phase is not optically isotropic. However, to an excellent approximation, the films can be treated as uniform uniaxial dielectric slabs. The reflectivity for radiation at near normal incidence (our experimental geometry)

is given by [11]

$$R = \frac{(n_0^2 - 1)^2 \sin^2(n_0 hk)}{4n_0^2 + (n_0^2 - 1)^2 \sin^2(n_0 hk)}.$$
 (1)

Here,  $n_0$  is the ordinary component of the index of refraction, k is the wave vector of the incident radiation, and h is the thickness of the slab. Because of the layered nature of the films,  $h = N\varepsilon$  where N is the number of layers and  $\varepsilon$  is the layer spacing ( $\varepsilon \approx 25$  Å). Since a red HeNe laser ( $\lambda = 638$  nm) was used as the light source, and  $n_0$  is of order unity ( $n_0 \approx 1.5$ ), the factor  $n_0hk \ll 1$  for thin films (N < 15) and Eq. (1) reduces to

$$R = \frac{(1 - n_0^2)^2 N^2 \varepsilon^2 k^2}{4} = c N^2, \qquad (2)$$

where  $c = [(1 - n_0^2)\epsilon k]^2/4$  is a constant. Therefore, by measuring the relative reflectivity of a number of thin films, c can be obtained and the film thickness (in units of layers) can be easily determined [12]. Furthermore, because our ac calorimeter is sensitive to the heat capacity per unit area, it provides another means by which the film thickness can be determined. As expected, the measured heat capacity has been found to increase linearly with film thickness N [13].

In our previous work on hydro-alkyl terminated liquidcrystal compounds, to ensure that no interesting phase behavior was overlooked, the films were heated until they spontaneously ruptured, invariably at or below the bulk SmA-isotropic transition temperature. It was therefore quite surprising when significantly different behavior was exhibited by members of the partially perfluorinated 5*n*-alkyl-2-[4-*n*-(*perfluoroalkyl*-metheleneoxy)phenyl] pyrimidine homologous series [denoted here simply as HmFnMOPP where m(n) gives the number of carbons in the hydrocarbon (fluorocarbon) tail]. For example, the reflectivity and heat capacity data shown in Figs. 1 and 2, respectively, represent a typical heating run through the bulk SmA-isotropic transition  $(T_c \approx 85 \,^{\circ}\text{C})$  of the partially fluorinated compound H10F5MOPP. The film was initially 25 layers thick below ≈85 °C. From the figures, it is obvious that these films do not rupture at the bulk  $T_c$ ; rather both the reflectivity and heat capacity decrease in a series of sharp steps separated by wide plateaus as the temperature is increased. The steps are very sharp (< 10 mK in width) and perfectly correlated between the two probes. Moreover, the plateau values have been found to obey the  $R = cN^2$  (N < 15) and  $C_p = bN$  relations introduced in the preceding paragraph. It is therefore clear that the steps correspond to discrete reductions of the film thickness, demonstrating the unique nature of this melting transition. It should be noted that the effect is monotropic so that the film thickness does not increase upon cooling. Furthermore, since no spontaneous thinning is observed when the temperature is held constant, the effect is primarily a function of tem-



FIG. 1. Optical reflectivity data associated with the SmAisotropic transition of an initially 25 layer thick H10F5MOPP film. The melting occurs as a series of discrete transitions in which interior layers become progressively disordered and drain out of the film. The resultant thinning continues until the films become only 2 layers thick and eventually rupture near 112 °C. The inset allows the reflectivity plateaus corresponding to 8, 7, 6, 5, 4, 3, and 2 layers to be more easily distinguished.

perature. As mentioned above, surface enhanced order is common in free-standing liquid-crystal film systems. It is therefore probable that these films thin as the interior layers undergo the SmA-isotropic transition and the van der Waals interaction between the free surfaces squeezes the isotropic phase out of the interior and into the surrounding reservoir of sample at the edges of the film plate. The fact that the films do not rupture during these transitions is truly remarkable. Because the phenomenon was observed to be independent of the orientation of the film, the effects of the Earth's gravitational field are minimal and the thinning is therefore fundamentally related to the elastic properties of these thin films.

The experiment was repeated starting with films of various thicknesses. Thick films generally exhibited transitions involving a number of interior layers near the



FIG. 2. Plot of heat capacity data measured simultaneously with the optical reflectivity data exhibited in Fig. 1. The inset demonstrates that the plateau values are consistent with the expected linear dependence on film thickness, confirming our hypothesis that the melting occurs as a series of layer-thinning transitions.

bulk SmA-isotropic transition temperature. However. once the films had thinned to roughly 10 molecular layers, the transitions progressed in basically a layer-by-layer fashion. This is also apparent in Figs. 1 and 2 as the initially 25 layer film thinned to 15, 11, 9, 8, 7, 6, 5, 4, 3, and 2 layers before it finally ruptured near 112 °C. Again, the fact that 2 layer SmA films remain stable more than 25 K above the bulk isotropic transition is somewhat surprising. It is also interesting to note that single layers are removed even though the two interior layers of the even numbered films are seemingly equivalent. The temperatures of the layer transitions are reproducible and an intriguing functional dependence is revealed when the film thickness is plotted versus these transition temperatures (see Fig. 3). The data can be fitted with a simple power law of the form  $h(t) = l_0 t^{-\nu}$  where h is the film thickness (in units of layers),  $t = [T_c(N) - T_0]/T_0$ , and  $T_c(N)$  is the maximum temperature at which the N layer film exists. Both Figs. 3 and 4 clearly demonstrate the success of this approach. The fit yields the following values for the adjustable parameters:  $l_0 = 0.34 \pm 0.02$ layer,  $\nu = 0.74 \pm 0.02$ , and  $T_0 = 84.84 \pm 0.04$  °C which is very close to the bulk SmA-isotropic transition temperature.

If  $\xi$  is taken to be the penetration length of the smectic order generated by the film-vapor interfaces, the interior layers of films more than  $2\xi$  layers in thickness would not be stabilized above the bulk SmA-isotropic transition and could be expected to be expelled from the film. Moreover, since the surface penetration length is expected to be the same as the bulk correlation length [4], the fitting expression can be written more suggestively as  $\xi = \xi_0 t^{-\nu}$ . The resultant film thickness would therefore be directly related to the decay of the smectic correlation length. While this interpretation is appealing, it is very difficult to reconcile with the fact that the SmA-isotropic transition in H10F5MOPP is strongly first order and therefore an algebraically divergent smectic correlation length over such a large temperature window ( $\approx 25$  K) is not expected.



FIG. 3. Plot of film thickness (given in terms of number of layers N) versus the highest temperature at which N layer films appear to be stable (circles). The line represents the best fit with a simple power law (see text).



FIG. 4. Log-log plot of the data and fit result exhibited in Fig. 3 to more conclusively demonstrate the success of the simple fitting expression.

As discussed in the introduction, wetting theory can also predict an algebraically divergent penetration length of the surface phase. Unfortunately, however, such calculations require a competition between interfacial coefficients due to the coexistence of three phases and only two phases (SmA and vapor) are readily identified in this system. This observation raises an interesting point related to the contact between the film and the stainless-steel film plate. It is unlikely that the smectic layer structure is strictly maintained near the edge of the film plate. Above 85 °C, the film must then be somehow supported by the surrounding reservoir of (isotropic) bulk sample along the plate edge and in this region coexistence of the surface SmA and interior isotropic phase is clear but difficult to model. Moreover, the fitted exponent  $\nu$  ( $\approx 0.75$ ) is considerably larger than the standard wetting calculation predicts for van der Waals forces ( $\nu_{\rm th} = \frac{1}{3}$ ) [2]. Therefore, although the power-law behavior is highly suggestive, an adequate account for the observed phenomena is not yet apparent.

As mentioned above, the behavior exhibited in Figs. 1 and 2 presently appears to be unique to the partially fluorinated compounds. While both H10F5MOPP and H8F7MOPP revealed qualitatively similar results, hydroalkyl terminated compounds simply ruptured at or below the bulk SmA-isotropic transition temperature. In particular, members of the nmOBC (n-alkyl-4'-nalkyloxybiphenyl-4-carboxylate), nCB (n-alkyl-cyanobiphenyl), and nOSI [4-(2'-methylbutyl)-phenyl-4'-nalkyloxybiphenyl-4-carboxylate] homologous series, as well as DOBAMBC (p-decyloxybenzylidene-p-amino-2-methylbutylcinnamate) were tried without success. The fluorination, therefore, appears to have a profound effect on the physics exhibited by these samples. This observation is supported by the obvious enhancement, relative to their nonfluorinated analogs, of the smectic phase ranges of these compounds [14]. Moreover, recent x-ray work has been performed in which higher order (001), l = 1, 2, 3, peaks were readily observed in the SmA phase of both H10F5MOPP and H8F7MOPP [15].

Similarly, higher order x-ray diffraction peaks have been observed in another highly perfluorinated compound [16]. The l = 2 and l = 3 peaks have proven to be very difficult to resolve in the hydro-alkyl SmA phase, presumably due to large fluctuations in the layer order associated with the one-dimensional density wave [17]. The fluorinated SmA phase therefore appears to exhibit a much more well defined layer structure. In fact, since enhanced layer order allows the intralayer interaction to become more dominant, it is most likely this property that causes the *thinning* transition to occur in a layer-by-layer fashion and prevents rupture as the interior layers are progressively drained out of the film.

In conclusion, we have observed novel melting phenomena associated with the SmA-isotropic transition in free-standing liquid-crystal films. The unique thinning behavior has been simultaneously characterized by both heat capacity and optical reflectivity experimental probes. The data indicate that the free-standing films thin through a reproducible series of layer-by-layer transitions as the temperature is increased above the bulk transition temperature. Such behavior has never before been reported and it constitutes a highly unusual melting transition. The temperature dependence of the film thickness h was found to obey a simple power law so that  $h = l_0 t^{-\nu}$ . To the best of our knowledge, no existing theory can adequately account for these results. Moreover, the phenomena presently appear to be unique to partially fluorinated liquid-crystal compounds and the effects of fluorination have been discussed with respect to the more common hydro-alkyl terminated compounds. Further study, experimental as well as theoretical, is clearly necessary to fully understand this novel layer-thinning transition and the intriguing properties of highly perfluorinated compounds.

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