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Temperature variation of film tension above the bulk smectic-*A*–isotropic transition in freestanding liquid-crystal films

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We have measured the temperature variation of film tension above the bulk smectic-*A*–isotropic transition in freestanding films of two liquid-crystal compounds. Above the transition, the tension increases sharply with temperature, and the slope is proportional to the film's thickness regardless of whether or not the compound exhibits regular layer-by-layer thinning. The data can be interpreted in the context of theoretical models for layer thinning.

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In 1994 Stoebe *et al.* experimentally observed melting phenomenon in which, upon heating, the freestanding liquid-crystal film (FSLCF) melts one layer at a time [1]. Since then, a considerable amount of experimental and theoretical studies have been performed to shed light on the nature of this intriguing layer-thinning transition [2–11]. Our current understanding of the phenomenon is incomplete in part because it is difficult to perform comprehensive experimental studies to yield critical checks of the theoretical predictions. For one thing, the thinning transitions that are only found in a handful of compounds are strongly first order. The stable temperature window above the bulk melting point for an individual film thicker than 10 layers is usually very small (<0.5 K). Another problem is that there are few probes that enable us to conveniently and effectively study this unusual melting transition. Optical reflectance has been the primary means of experimental study because of its convenience and relatively high resolution, but optical reflectance data alone have not proven sufficient to provide physical insight toward the theoretical advances. We recently have developed a pressure-curvature tensiometer [11] that allows convenient and high-resolution study of film tension as the film is heated through the layer-by-layer melting process. With the probe, we have begun to collect important information crucial to advancing the understanding of the thinning process. In this paper, we make critical comparisons between our data and theoretical advances.

Employing our tensiometer, we measured the temperature variation of film tension in the FSLCFs of two similar compounds, F3MOCPF6H5OB (F compound) and H5OCPH11OB (H compound), as the films were heated above the bulk smectic-*A* (Sm*A*) to isotropic (*I*) transition temperature, T_{AI}. The molecular structures are given at the tops of Figs. 1 and 3. Their transition sequences are *I* (104.0 °C) Sm*A* (92 °C) Sm*C* and *I* (76 °C) Sm*A*, respectively, for the F and H compounds. These two compounds were chosen for their similar chemical structure but significantly different melting behavior at temperatures greater than T_{AI}. The cores of the molecules are identical. The flexible tails are the same "length" in that each molecule consists of one five-carbon tail and one 11-carbon tail. The only difference chemically is the fluorinated groups at the ends of the tails in the F compound. Using an optical reflectance probe, Pankratz *et al.* showed that freestanding films of the F compound exhibit regular layer-thinning transitions when heated above T_{AI}, while the H compound displays highly irregular thinning transitions [7].

The details of our tensiometer are given in Ref. [11], but the technique will be summarized in order to describe an additional modification that was crucial to this study. The

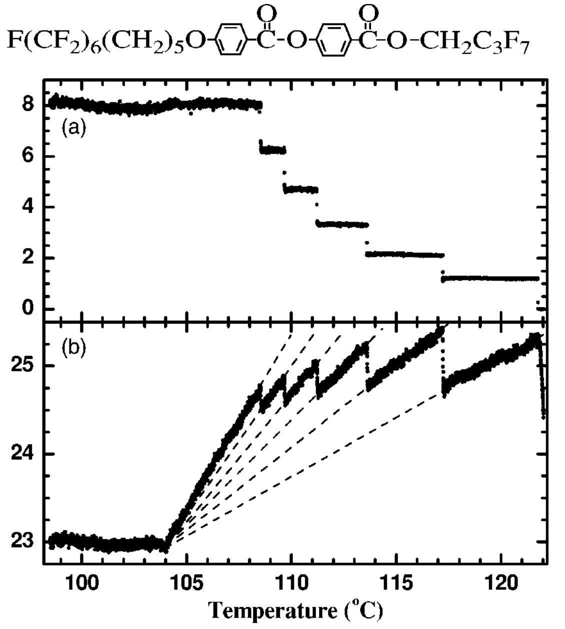

FIG. 1. Optical reflectance (a) and film tension (b) vs temperature upon heating an eight-layer F compound film above T_{AI}. The plateaus followed by abrupt drops indicate that the film undergoes a layer-thinning transition. At each thinning, the film tension abruptly jumps to a lower value and then continues to increase with a smaller slope.

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FSLCFs were prepared in a 1-cm-diameter hole, and the film acted to diffusively seal off two separate chambers. By applying a pressure difference in argon gas between the two chambers, the film was inflated to some radius of curvature [12]. A laser beam was reflected from the inflated film to a position sensitive detector. A feedback loop monitored the detector signal and adjusted the applied pressure difference to hold the beam position, and thus the film's radius of curvature, constant while the temperature was varied. By recording the pressure difference as a function of temperature we obtained the temperature variation of film tension. The system was modified by splitting the reflected laser beam, sending a fraction of the beam's intensity to a photodiode that was used to monitor the reflected beam's intensity. The simultaneous optical reflectance probe was crucial for interpreting our data because the behavior of optical reflectance through a thinning transition is well-understood experimentally.

Figure 1 shows the simultaneous optical reflectance, R, and film tension, γ, data obtained from an eight-layer F-compound film as it was heated above T_{AI}. The optical reflectance has been previously studied and characterized for this compound [7]. This probe established what happened to the film upon heating. In Fig. 1(a), the plateaus followed by abrupt drops in the reflectance curve are a well-established indication of the layer-thinning transitions [1,5–7]. Furthermore, the reflectance values clearly indicate that upon heating the film thinned by single layers from eight to three layers before rupturing at around 121.8 °C. It should be noted that although it is more common for a three-layer film to thin to two-layers in the flat FSLCFs before rupturing in this F compound, these data are still representative of a film's tension during a thinning run. The premature film rupture at three layers of this film is most likely due to the finite curvature of the film which required different anchoring condition in the meniscus region. Incidentally, there is a small bump in the eight-layer plateau at ~104.0 °C, which is suspiciously near T_{AI}. This feature is often observed in layer-thinning transitions, but to our knowledge is not understood.

Although the optical reflectance is a crucial part, the film tension is the main focus of our study. Figure 1(b) shows the film tension data that was acquired simultaneously with the optical reflectance of Fig. 1(a). At ~104.0 °C, the tension-temperature curve abruptly changes from a small negative slope to a noticeably larger positive slope. Recall that this is concurrent with the small bump in the optical reflectance near T_{AI}. The sharp upturn is consistent with what we previously observed in the thick films of the compound MHPBC over a small temperature window (~0.5 °C) just before film rupture [11]. In contrast to MHPBC, however, the film of the F compound thins layer by layer rather than simply rupturing. At each thinning, the film tension abruptly jumps to a lower value and then continues to increase with a smaller slope. Above 121.8 °C, the point of film rupture, the film tension values shown are meaningless because there is no reflected beam to hold in position. In Fig. 1(b), we have included dashed lines showing that the film tension curves for each thickness can be extrapolated approximately to a common point at the initial upturn in film tension at ~104.0 °C. We have performed numerous measurements showing that these dashed lines are not merely hypothetical extrapolations. A film of a given thickness will display a film tension-temperature curve approximately along the dashed lines. To demonstrate, Fig. 2 shows the data from Fig. 1(b) merged with a completely different set of data obtained from the heating of a five-layer film. Both data sets have been scaled to absolute units by the same factor, and there has been no shifting of temperatures in either data set. Notice that below 104.0 °C, the five-layer and eight-layer data overlap within experimental resolution. Above 104.0 °C, the five-layer film tension increases with a smaller slope, intersecting with the five-layer data obtained from the layer-by-layer thinning of the eight-layer film. Although there is no space to show all of the experimental permutations, our measurements show that the film tension-temperature curves are robust. Multiple heating and cooling runs on films from two to over 20 layers show that the curves are reproducible with temperature (provided the film is not heated to the point of thinning). The film tension-temperature curves also do not depend upon how a particular film thickness is achieved. A film that thins to five layers, for instance, shows the same curve as a film that is prepared as a five-layer film. These tension data will be discussed further later in this paper.

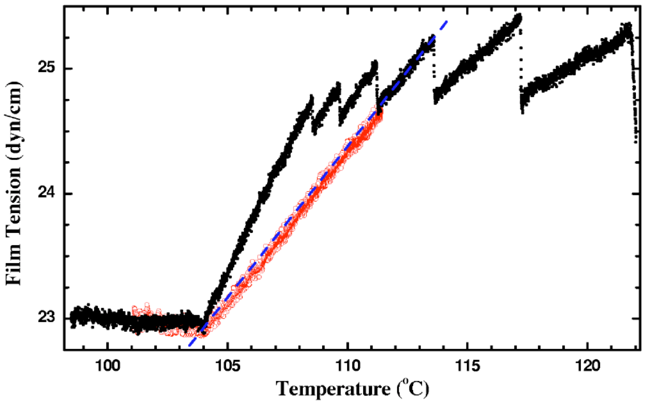

FIG. 2. (Color online) Film tension vs temperature of the F compound upon heating an eight-layer film (smaller, solid black circles) and a five-layer film (larger, open red circles) above T_{AI}. The eight-layer film thinned layer by layer so that at ~111 °C, the film thinned to five layers. The two data sets overlap again at this point.

For comparison, we have made similar measurements with the H compound. In the roughly one dozen experimental runs we performed, no thinning transitions were observed through the optical reflectance probe in our system. Again the inflated films seem to disrupt the irregular thinning transitions found previously in the flat films. Despite this, our tension probe still detected an upturn in tension just before film rupture. Figure 3 shows the data acquired while heating a six-layer film. Notice that the tension increases by less than 1% before rupturing at ~75.4 °C. Just before the clear upturn at ~75.1 °C, the film tension shows a "zigzag" pattern. This film had a noticeably thick meniscus that was visually observed to thin between 74.9 and 75.1 °C. This effect tends to show up in data from both compounds studied, but it is much more difficult to see in Fig. 1(b) due to the larger scale of the graph. Our measurements show that the meniscus ef-

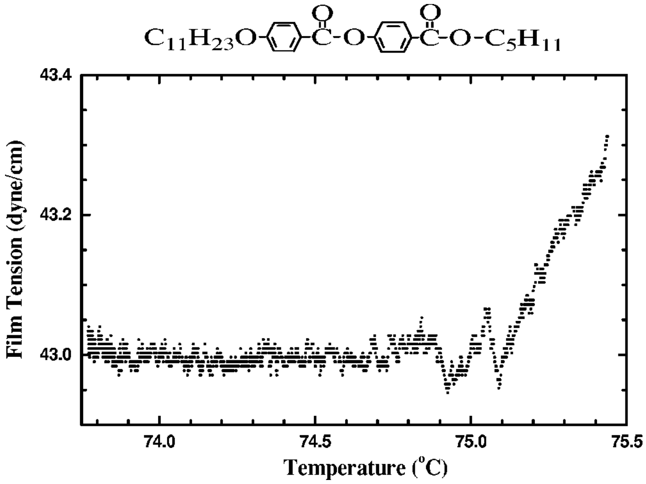

FIG. 3. Film tension vs temperature upon heating a six-layer H-compound film above T_{AI}. Even though the film did not undergo a thinning transition, there is still a resolvable upturn in tension near T_{AI}.

fect is greatly reduced, if not removed, when a film is heated past bulk melting temperature and then cooled back to the bulk Sm*A* range. It is interesting to note that the upturn in film tension is observed even for a material that does not exhibit regular thinning. This also has been an indication of the commonly accepted idea that surface-enhanced smectic ordering is a universal behavior. Further studies will hopefully shed more light on this idea.

As previously seen in Figs. 1 and 2, the film tension-temperature curves above T_{AI} depend on film thickness. We have performed detailed studies of this film tension-temperature slope in the F-compound films. It should be noted that the experimental film tension-temperature curves are only approximately linear. It is difficult to observe in Figs. 1 and 2, but the curves do show a slight curvature downward as the temperature increases. For this reason, we have restricted our comparison to a small range of temperatures just above 104.0 °C. For films between two and ten layers in thickness, we repeated the following procedure. A film was prepared below 104.0 °C, and the temperature was ramped back and forth between roughly 99 and 107 °C. Linear fits between 104.3 and 106.7 °C determined the average slope over that temperature range. For films thicker than ten layers, the procedure was essentially the same but with temperatures lower than 106.7 °C because the films thin before reaching that temperature. Figure 4 shows the extracted slopes as a function of the film thickness. Each data point for the F compound is the average of anywhere between two and ten values. We attempted to acquire data for films thicker than 24 layers, but the mechanical response of our pressure-control system was not sufficiently fast to track the rapidly changing tension, even at slow ramping rates ($\sim$0.01 °C/min). There is some scatter in the measured slope values. The error bars are slightly smaller than the size of the data point. We attribute the scatter to uncertainty of the film's anchoring to the meniscus. Nonetheless, there is an unmistakable trend indicating that the slope is proportional to the film's thickness. At this moment, we do not know if the slope will continue to increase in proportion to the film thickness or if it will saturate. Currently, our ability to address this question is hindered by the experimental limitations. We have also included slopes extracted from three films of the H compound in Fig. 4 for comparison. The H compound shows a similar trend, except with a larger slope $(d\gamma/dT)$. Here γ is the film tension. Perhaps this difference in slopes between the two compounds is in some way related to the likelihood that the compounds will display regular thinning transitions. We are currently pursuing that question in a wider range of compounds.

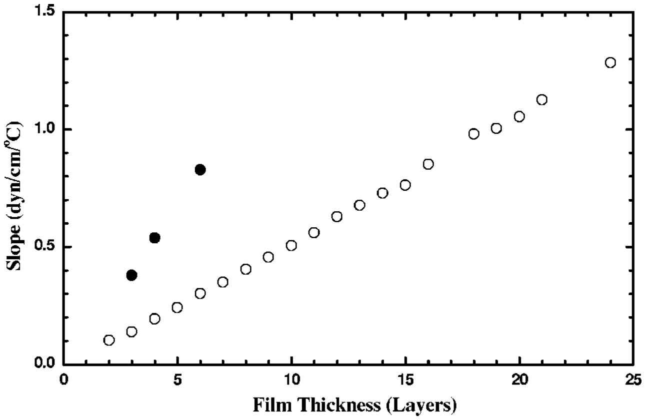

FIG. 4. The slope $(d\gamma/dT)$ of film tension vs film thickness obtained just above T_{AI} from the F compound (open circles) and H compound (solid circles), respectively.

We can interpret Fig. 4 in terms of the macroscopic law

$$\gamma \approx 2\sigma - \Delta PL, \tag{1}$$

where σ is the film-vapor interfacial tension, L is the film thickness, and ΔP is the pressure difference between the film and surrounding vapor. Below T_{AI}, the bulk Sm*A* phase is stable, so that $\Delta P \approx 0$ and γ will have only a weak dependence on film thickness. This is consistent with Fig. 2. Above T_{AI}, $\Delta P < 0$ because the Sm*A* phase is unstable relative to the vapor. Thus, the film tension should show an increase. This is certainly consistent qualitatively with the data in Fig. 2. If we assume that, over a sufficiently restricted temperature range above T_{AI}, the average smectic layer spacing and σ are both constant and that ΔP is simply proportional to $T_{AI} - T$, then Eq. (1) predicts that γ will increase linearly with the temperature and that the slope will be proportional to the number of smectic layers. This is quantitatively what we observe in Fig. 4. We can use the slopes extracted from the data sets in Fig. 4 with layer-spacing values from ellipsometry [13] of 31.8 and 32.8 Å for the F and H compounds, respectively, to get approximate expressions for ΔP near T_{AI}. $\Delta P \approx (1.7 \times 10^5 \text{ dyn/cm}^2\ {}^\circ\text{C})(T_{AI} - T)$ for the F compound and $\Delta P \approx (4.1 \times 10^5 \text{ dyn/cm}^2\ {}^\circ\text{C})(T_{AI} - T)$ for the H compound.

It is important to consider our results in the context of the theoretical work. The improved resolution of our experimental apparatus has allowed a critical test of the existing theories. Two mean-field models have been proposed to explain the layer-thinning transitions in smectic films [8–10].

Mirantsev and Martínez-Ratón *et al.* proposed a density functional mean-field model including a term to promote surface-enhanced smectic ordering. By varying the range of interaction for the various terms, Martínez-Ratón *et al.* identify two regimes in which smectic films are stable above the bulk melting temperature. They designate these two regimes as "type 1" and "type 2". The main difference between the two regimes is that the type 1 regime has a Sm*A*-*I* phase sequence, whereas the type 2 regime has a Sm*A* to nematic (*N*) transition that is very near a Sm*A*-*N*-*I* triple point. The F compound exhibits a Sm*A*-*I* transition, consistent with the type 1 behavior. Our tension data, however, are quantitatively more consistent with the type 2 behavior. For both regimes, the authors predict the film tension to be approximately consistent with Eq. (1). The scale of the effect, however, is markedly different for the two types. An eight-layer film showing the type 1 behavior is predicted to have a roughly threefold increase in tension from T_{AI} to the point of thinning to seven layers. The tension of a type 2, eight-layer film increases by only ~15%. Recall that Fig. 1(b) showed that the film tension from eight-layer F-compound films increases by ~7.5%, making it more consistent with type 2. So it seems that the F compound does not neatly fit into either regime identified. It should be noted that Martínez-Ratón *et al.* admittedly have not performed an exhaustive study of all the available parameter spaces. It remains possible that the experimentally observed behavior in the F compound can be satisfactorily explained by their model if the parameters are appropriately varied. Our experimental results should stimulate additional theoretical advances.

Mirantsev has also proposed a mean-field model to explain layer thinning transitions [9,10]. The model predicts layer thinning in compounds that exhibit a bulk Sm*A*-*I* transition as well as compounds that show the Sm*A*-*N*-*I* transition. Although the film tension is not specifically predicted by Mirantsev, the average smectic layer spacing and the "disjoining pressure" (i.e., the additional pressure exerted on the film from the free surfaces) are predicted in order to explain an unusual layer compression observed through optical reflectance in another perfluorinated compound H8F(4,2,1)MOPP [4]. Mirantsev's model predicts an appreciable, monotonic increase in the disjoining pressure with respect to temperature above T_{AI}. The model also predicts a weak monotonic decrease in the average smectic layer spacing. Recall that earlier we used Eq. (1) to generate approximate expressions for ΔP in the F compound and H compound assuming a linear increase in ΔP with temperature, constant L, and constant σ. Over a restricted range just above T_{AI}, Mirantsev shows a nearly linear increase in disjoining pressure with respect to temperature, just as we assumed in interpreting Fig. 4. For that reason, it warrants a numerical comparison. In the range from T_{AI} to $T_{AI}+2.6\,°\mathrm{C}$, Mirantsev's results give $\Delta P \approx (3.8\times10^5\ \mathrm{dyn/cm^2\,°C})(T_{AI}-T)$, comparable to what we extracted from our data in Fig. 4. In the near future, further study of a wider range of compounds will be conducted to determine whether or not the comparable numbers between our experiments and Mirantsev's model are real or just coincidental. Despite the promising similarities between our experimental results and the theoretical predictions of Martínez-Ratón *et al.* and Mirantsev, many questions and challenges still remain.

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