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Role of molecular weight and phase sequence in the temperature variation of film tension above the bulk isotropic transition in freestanding liquid-crystal films

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Building upon our previous report [Veum *et al.*, Phys. Rev. E **17**, 020701(R) (2005)] involving two compounds, we have performed a systematic study of the temperature variation of film tension above the bulk isotropic transition in freestanding films to include a total of six smectic liquid-crystal compounds. Consistent with the previous results, the tension increases sharply with temperature above the transition, the tension-temperature slope is proportional to the film's thickness, and the data can be interpreted in the context of theoretical models for layer thinning. Our data suggest that both molecular weight and bulk phase appearing below its isotropic phase play important roles in the slope values.

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I. INTRODUCTION

We recently reported results of film tension versus temperature measurements in freestanding films of two liquid-crystal compounds at temperatures above the bulk smectic-*A* (Sm*A*) to isotropic (*I*) transition temperature, T_{AI} [1]. The two compounds studied are very similar in molecular structure, but differ greatly in degree of fluorination in the tails of the molecules. One compound had purely hydrogenic molecular groups in both tails of the molecule. In the other compound, more than half of the molecular groups in the tails, including the end groups, were fluorinated. Our previous report can be summarized as follows: (i) For both compounds, as a freestanding film is heated, the tension-temperature slope $d\gamma/dT$ changes abruptly from a small negative value to a markedly larger positive value at a temperature near T_{AI}. (ii) The larger positive slope is proportional to the film's thickness, while the smaller negative slope shows no resolvable thickness dependence. (iii) The larger positive slopes are nearly three times greater for the purely hydrogenic compound. (iv) The data were interpreted in the context of a density-functional mean-field model put forward by Mirantsev [2] that predicts the onset of a monotonically increasing disjoining pressure above T_{AI}. Other previous investigations have shown that the two compounds exhibit markedly different surface tensions, 21.5 dyn/cm for the purely hydrogenic compound and 11.5 dyn/cm for the perfluorinated compound [3]. Other studies have also shown that freestanding films of the perfluorinated compound are remarkably stable and undergo regular layer-by-layer thinning transitions when heated above T_{AI}, while the films are much less stable and thinning is irregular in the purely hydrogenic compound [4]. The results of our previous report are consistent with those studies.

While it is clear from our previous report that chemical structure played an important role in determining the value of $d\gamma/dT$ in a film above T_{AI}, it is not clear what specific mechanisms related to chemical structure were responsible. Was it the value of surface tension? Was it the degree of fluorination? Was it both? Or was it something else? In order to better flesh out these issues, we have expanded our studies to include four additional compounds.

II. MATERIALS AND METHODS

The six compounds relevant to this paper are: (A) F3MOCPF6H5OB, (B) F3MOCPH11OB, (C) F4hMOCPH11OB, (D) H5OCPH11OB, (E) F4MOCPH11OB, and (F) MHDDOPTCOB. The chemical structures are shown in Fig. 1. There are subtle, but key

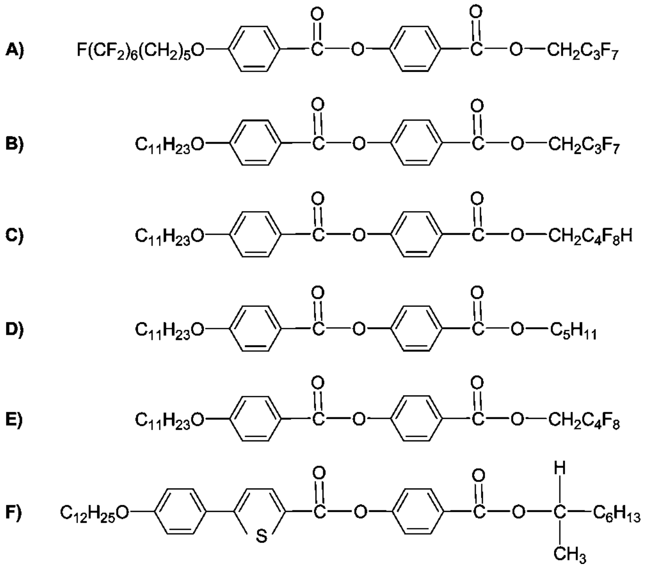

FIG. 1. The chemical structures of (A) F3MOCPF6H5OB, (B) F3MOCPH11OB, (C) F4hMOCPH11OB, (D) H5OCPH11OB, (E) F4MOCPH11OB, and (F) MHDDOPTCOB. Compounds A to E have identical molecular cores but differ in degree of fluorination in the molecular tails. Compound E differs from the others in exhibiting a bulk Sm*C*-*I* phase transition rather than Sm*A*-*I*.

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differences to note. Compounds A through E, which include the two compounds from Ref. [1], are all very similar in structure. These molecules have identical cores but differ primarily in the degree of fluorination in the tails. Compound E is distinguished from all the others by exhibiting a bulk smectic-*C* (Sm*C*)-*I* phase transition rather than Sm*A*-*I*. Compound F is structurally different from the previous five compounds and is included for comparison. The bulk clearing temperatures T_{AI} (or T_{CI} in the case of compound E), are approximately 104, 79, 58, 76, 88, and 98 °C, respectively for compounds A through F. Since the measurements described below involve heating the freestanding films above the bulk clearing temperatures and the data will be interpreted in the context of a theoretical model for layer-by-layer thinning, it is also important to mention what is known about the thinning behavior and stability against rupture for these compounds. Pankratz *et al.* [4] directly studied these characteristics in compounds A through E. Their data show that that, of this set, compound A displays the most regular layer-by-layer thinning and highest degree of stability at elevated temperature. Compounds C and D display the most irregular thinning and are most prone to rupture. Compounds B and E are somewhere in between these extremes in terms of the regularity of thinning and stability against rupture. As far as we know, these issues have not been directly studied for compound F, but the studies performed for this paper suggest irregular thinning and that the stability at elevated temperature is comparable to, or perhaps slightly higher than, compound D.

To acquire values of $d\gamma/dT$ just above T_{AI} (or T_{CI} in the case of compound E), we employed our pressure-curvature tensiometer. In the experimental apparatus, freestanding films are prepared in a 1-cm-diameter hole, and the film acts to diffusively seal off two separate chambers. By applying a pressure difference in argon gas between the two chambers, the film is inflated to some radius of curvature. A laser beam is reflected from the inflated film to a position sensitive detector. A feedback loop monitors the detector signal and adjusts the applied pressure difference to hold the beam position, and thus the film's radius of curvature, constant while the temperature is varied. By recording the pressure difference as a function of temperature we obtain the temperature variation of film tension. Further details of the apparatus are provided in Ref. [5]. For this study, our procedure was to prepare a film with a known number of layers at a temperature of ~1 °C below T_{AI} and ramp the temperature several times between $\sim(T_{AI}+1\ ^\circ\mathrm{C})$ and $\sim(T_{AI}-1\ ^\circ\mathrm{C})$ at a rate of ~0.1 °C/min while recording film tension and temperature every few seconds. Figure 2 shows single heating runs for 10-layer and 13-layer films of compound B. The slope from a linear fit to the high temperature portion of the graph produces a single value of $d\gamma/dT$. $d\gamma/dT$ for each individual temperature ramp was extracted separately. A plot of these values versus the film's layer number N for each of the compounds shows $d\gamma/dT$ to be proportional to N within experimental resolution. As an example, Fig. 3 displays the plot for compound B for film thicknesses from 4 to 16 molecular layers. We attribute the small scatter in the data to minor shifts in the anchoring position of the inflated film to the meniscus during data acquisition. A similar proportional trend is observed in all six compounds in Fig. 1. In order to produce a single number with which to compare the six compounds, we found the average value of the slope per layer, $(d\gamma/dT)/N$.

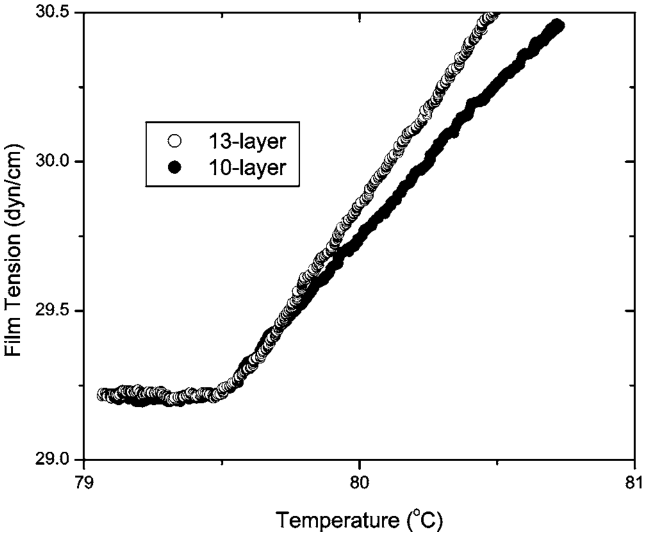

FIG. 2. Film tension versus temperature for heating runs of a 10-layer (solid circles) and a 13-layer (open circles) film of F3MOCPH11OB (compound B). At ~79.5 °C, near T_{AI}, both tension-temperature curves abruptly change from small negative slopes below ≈79.5 °C to noticeably larger positive slopes above ≈79.5 °C. The data on the low temperature side show no thickness dependence, while the graph's slope is proportional to film thickness on the high temperature side.

III. RESULTS AND DISCUSSION

A. Theoretical interpretation of the data

Since we use the quantity $(d\gamma/dT)/N$ to compare some physical properties among the six compounds, it is important

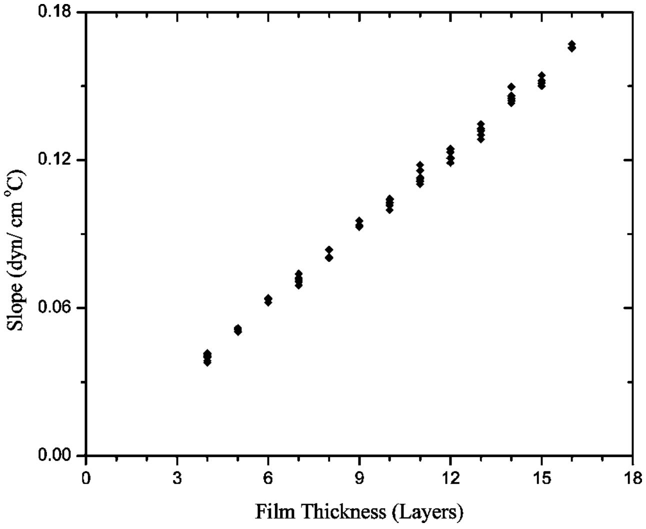

FIG. 3. Tension-temperature slope $d\gamma/dT$ versus film thickness of F3MOCPH11OB (compound B) for thicknesses from 4 to 16 molecular layers. The slopes are proportional to film thickness within the experimental resolution. A similar proportional trend was observed in all six compounds reported in this paper.

TABLE I. Measured surface tension values, molecular weights, bulk phase transitions, and average tension-temperature slopes per layer, $(d\gamma/dT)/N$, for the six compounds in this study.

	Compound	Surface tension (dyn/cm)	Molecular weight (amu)	Phase transition	$(d\gamma/dT)/N$ (dyn/cm °C)
A	F3MOCPF6H5OB	11.5	832.5	Sm*A*-*I*	0.049
B	F3MOCPH11OB	14.6	598.6	Sm*A*-*I*	0.103
C	F4hMOCPH11OB	18.4	630.6	Sm*A*-*I*	0.102
D	H5OCPH11OB	21.5	486.7	Sm*A*-*I*	0.136
E	F4MOCPH11OB	14.0	648.6	Sm*C*-*I*	0.120
F	MHDDOPTCOB	21.4	653.0	Sm*A*-*I*	0.094

to give some interpretation of the meaning behind this parameter. In our previous report [1], we interpreted the slope of $d\gamma/dT$ as an indication of a monotonically increasing disjoining pressure with temperature as predicted by Mirantsev's mean-field model [2]. In Mirantsev's model, the disjoining pressure can be understood by considering thinning a film of unit area from N to $(N-1)$ layers by removing a single smectic layer of thickness ℓ and inserting those molecules into the bulk reservoir of material on the film plate surrounding the film. If the film is in a different phase than the reservoir, the thinning will result in a nonzero change in free energy, ΔF, of the film-reservoir system. ΔF will also equal the work required to thin the film at constant temperature. The disjoining pressure, ΔP, is ratio of the work required for thinning to the film's change in thickness. Mathematically, ΔF can then be expressed as

$$\Delta F = -\Delta P \ell . \tag{1}$$

Note that since ΔF is negative above the bulk melting temperature, a positive, i.e., compressional, disjoining pressure will result. The disjoining pressure, and therefore ΔF, will contribute to the film tension γ by the macroscopic law

$$\gamma \approx 2\sigma + \Delta P L, \tag{2}$$

where σ is the surface tension and L is the film thickness [6]. The substitution of Eq. (1) and $L=N\ell$ into Eq. (2) yields

$$\gamma \approx 2\sigma - \Delta F N. \tag{3}$$

Equation (3) explains the behavior shown in Fig. 2. Below the bulk clearing temperature $\Delta F \approx 0$, resulting in no thickness dependence in γ. σ has weak temperature dependence and decreases with increasing temperature, as expected. Upon further increase in temperature past the bulk clearing temperature, the film tension increases rapidly with temperature. Over a moderate temperature range, that increase is approximately linear. Therefore, from Eq. (3), our experimental results indicate that ΔF increases roughly linearly with temperature just above the bulk clearing temperature. Within a small temperature window, a linear temperature dependence of ΔF is expected. Taking the temperature derivative and then dividing by N in Eq. (3), one obtains

$$(d\gamma/dT)/N \approx -d(\Delta F)/dT. \tag{4}$$

Notice that the left side of Eq. (4) is the final physical parameter that we have extracted from our data for each compound. In other words, we interpret our final number to represent the rate at which the free energy difference per unit area between the confined film and the bulk reservoir changes with respect to temperature. In the next sections we will discuss what mechanisms might be responsible for the differences in this quantity for the six compounds in this study. Table I lists the $(d\gamma/dT)/N$ values obtained along with each compound's surface tension, molecular weight, and phase transition.

B. Role of surface tension

As shown in Table I, the compounds A, B, and D all exhibit a bulk Sm*A*-*I* phase transition. They have similar molecular structures, but differ significantly in molecular weight due to the varying degrees of fluorination. They also exhibit a wide range of surface tension values in the Sm*A* phase due primarily to the differences in the end groups of the molecules. When the results in Table I for compounds A, B, and D are compared, one sees an overall trend of increasing $(d\gamma/dT)/N$ with increasing surface tension and decreasing molecular weight. When compound C is included and compared directly to B, something intriguing results. B and C both exhibit a bulk Sm*A*-*I* phase transition. They are very similar in molecular structure and have comparable molecular weights. They do, however, differ by ~25% in the surface tension values as measured in the Sm*A* phase. Yet the two compounds exhibit comparable $(d\gamma/dT)/N$ values. This comparison provides us with a strong indication that the surface tension is not the dominant factor in determining the values of $(d\gamma/dT)/N$. It does suggest molecular weight as a possibly crucial factor.

C. Role of molecular structure

In order to assess the role of molecular structure, the results from B, C, and F are compared. The three compounds all exhibit a bulk Sm*A*-*I* phase transition. While B and C's molecules differ in structure from F, the three compounds are comparable in molecular weight. Complicating this comparison is the wide range of surface tension values, but as seen in the previous section, there is reason to believe that

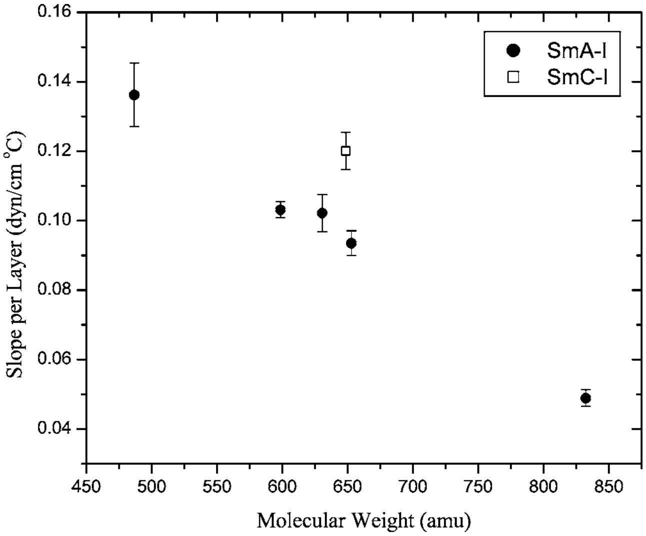

FIG. 4. Tension-temperature slope per layer, $(d\gamma/dT)/N$, versus molecular weight for the six compounds in this study. For the five compounds exhibiting a bulk Sm*A*-*I* phase transition, there is a trend showing a monotonic decrease in $(d\gamma/dT)/N$ with increasing molecular weight regardless. For F4MOCPH11OB (compound E), which displays a bulk Sm*C*-*I* sequence, $(d\gamma/dT)/N$ is ~20% larger than the compounds of similar molecular weight.

surface tension can be overlooked as a major factor in our results. All three compounds exhibit comparable $(d\gamma/dT)/N$ values, suggesting that the physical structure of the molecule in and of itself does not determine $(d\gamma/dT)/N$. The data yet again indicate that molecular weight may possibly be a crucial factor.

D. Role of molecular weight and phase transition

Figure 4 shows a plot of $(d\gamma/dT)/N$ versus molecular weight for the six compounds. For the five compounds exhibiting a Sm*A*-*I* transition, our data show $(d\gamma/dT)/N$ to monotonically decrease with weight. We plan to study a wider range of weights to test the universality of this trend. Compound E displays a $(d\gamma/dT)/N$ that is ~20% larger than what is inferred from the trend displayed by the other five compounds, indicating that molecular weight alone cannot be the only factor. Compound E is unique in this set of compounds in its Sm*C*-*I* phase transition, suggesting that the phase transition also plays a role.

The role of the phase transition can be interpreted by considering Eq. (4). Since compound E exhibits a bulk Sm*C*-*I* phase transition rather than Sm*A*-*I*, it is reasonable to assume that freestanding films remain in the Sm*C* phase above T_{CI}. Since the Sm*C* phase has a higher degree of order than the Sm*A* phase, $|\Delta F|$ as defined above will in general be larger in magnitude for films in compound E than for a compound of similar molecular weight but exhibiting a Sm*A*-*I* transition, such as B. Larger overall values of $|\Delta F|$ imply a greater rate of change of $|\Delta F|$ with respect to temperature and greater values of $(d\gamma/dT)/N$ from Eq. (3). Figure 4 is consistent with this idea, but further study in a wider variety of compounds will be required to confirm or reject our speculation. Of particular interest would also be an experimental study of the bulk enthalpies through the isotropic transition in the compounds of this paper. Such studies could provide useful information in assessing our interpretation of the role of the phase transition in the value of $(d\gamma/dT)/N$ and also in assessing our general theoretical interpretation of the meaning behind the experimental parameter $(d\gamma/dT)/N$.

Speculation about the role of molecular weight is not as straightforward but should stimulate further theoretical advances. In the discussion below, consider only the compounds exhibiting the Sm*A*-*I* transition. Notice that Fig. 4 and Eq. (3) suggest that $|\Delta F|$ increases more rapidly with temperature for less massive molecules. In Mirantsev's model [2], the free energy of the bulk reservoir is simplified to be identically zero at all temperatures above T_{AI}. In such an approximation, $|\Delta F|$ then simply represents the free energy of a single smectic layer of unit area located at the center of the film. Furthermore, the free energy in Mirantsev's model is defined in terms of a single-particle potential in analogy to the McMillan [7] theory. Thus for any given single-particle potential, the free energy per unit volume of a system will theoretically scale with the particle density of that system. Although it is a gross oversimplification, suppose that each of the compounds exhibiting a bulk Sm*A*-*I* transition in this study can be satisfactorily described by the same single-particle potential. Additionally, suppose the compounds have negligible differences in mass density. Under such circumstances, the particle density scales with the molecular weight of the material, and $|\Delta F|$ should then theoretically scale inversely with the molecular weight of the material. Although oversimplified, this analysis does point out one possible contribution to the trend shown in Fig. 4. To our knowledge, there have been no theoretical studies to predict the influence of molecular weight on the behavior of freestanding smectic films above the bulk isotropic transition temperature. Further study will be required to sort out these issues.

In summary, our measurements of temperature variation of tension for six different liquid-crystal compounds indicate that when a freestanding film is heated above the bulk isotropic transition temperature, the film tension markedly increases with temperature. The rate of increase is approximately proportional to the film's thickness, regardless of compound. Additionally, our data indicate that the specific phase transition and molecular weight play an important role in determining that rate of increase. Although the data can be interpreted in terms of theoretical models, the specific mechanisms are still not totally clear. Further studies on a wider range of compounds will be performed.

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[6] The reader should note that Eq. (2) is more often written as difference $\gamma \approx 2\sigma - \Delta P \cdot L$, rather than a sum. When written as a difference ΔP, represents the pressure difference between the film and the surrounding vapor such that a negative value of ΔP, implies compression of the film. We decided to be consistent with Mirantsev's definition of ΔP, wherein a positive value implies compression of the film.

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