Comparison between experiment and theory in the temperature variation of film tension above the bulk isotropic transition in free-standing liquid-crystal films

M. Veum,[1,*] L. Duelge,[1] J. Droske,[2] H. T. Nguyen,[3] C. C. Huang,[4] and L. V. Mirantsev[5]

[1]*Department of Physics and Astronomy, University of Wisconsin–Stevens Point, Stevens Point, Wisconsin 55481, USA*

[2]*Department of Chemistry, University of Wisconsin–Stevens Point, Stevens Point, Wisconsin 55481, USA*

[3]*Centre de Recherche Paul Pascal, CNRS, Universite Bordeaux I, Avenue A, Schweitzer, F-33600 Pessac, France*

[4]*School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA*

[5]*Institute of the Problems of Mechanical Engineering, Academy of Sciences of Russia, St. Petersburg 199178, Russia*

Using differential scanning calorimetry, the transition enthalpies and temperatures for the bulk smectic-isotropic phase transition have been measured for a series of liquid-crystal compounds. For five compounds, those values were used as parameters in a microscopic mean-field model to predict the temperature dependence of the difference in free-energy density between a sample of material in a free-standing smectic film and that in the bulk. The model predicts a weak temperature dependence below the bulk clearing point and a pronounced monotonic increase with temperature above the transition temperature. The compounds used in this study were chosen specifically because they were also the subject of a previous independent experimental study [M. Veum *et al.*, Phys. Rev. E **74**, 011703 (2006)] that demonstrated a sudden monotonic increase in the free-standing film tension with temperature, which is qualitatively consistent with the predictions of the above-mentioned mean-field model. This study presents a direct and quantitative comparison between the predictions of the mean-field model and the results from previous tension experiments.

PACS number(s): 61.30.−v, 64.70.M−

I. INTRODUCTION

In 1994 Stoebe *et al.* experimentally observed a novel phenomenon in which a free-standing liquid-crystal film will remain stable above the bulk melting temperature and will melt one layer at a time as temperature is increased [1]. Although there have been a number of experimental [1–9] and theoretical [10–13] studies of this intriguing phenomenon, it has proven difficult to perform thorough comparative studies that involve both the fundamental theoretical predictions and the experimental results for specific liquid-crystal compounds. One reason is that these thinning transitions are only found in a handful of compounds. While this clearly indicates that the effect is quite sensitive to chemical structure, it does limit the experimenter's ability to study the nature of the thinning transition while systematically varying the chemical structure of the molecule. The dearth of available compounds also decreases the likelihood that a particular compound has been thoroughly studied experimentally through the range of available probes such as optics, calorimetry, x ray, etc. This can limit the theorist's ability to make predictions specific to a given compound if necessary model parameters or data for comparison are not available. Furthermore, the thinning transitions are observed to be strongly first order and films thicker than ten layers are typically stable only over a small temperature window above the bulk melting point (<0.5 K). There are a limited number of probes that allow convenient and effective study under these limitations.

Despite the practical challenges, there have been significant advances. Of particular relevance to this paper are the studies summarized in Refs. [9,11–13]. References [11–13] are theoretical studies that used a particular microscopic mean-field model to calculate the free-energy density of a free-standing smectic film. For reasonable sets of parameters, the free-energy density of the film was compared to that of the bulk at the same temperature and pressure in order to predict that a free-standing film in the smectic-*A* (Sm*A*) phase can remain stable when heated to temperatures above the bulk clearing point.

In Ref. [9], a recently developed experimental probe [14] was employed to measure the film tension versus temperature in free-standing films in a series of smectic compounds. Those compounds, which are also the subject of this paper, were of interest because previous optical reflectivity studies showed varying degrees of regularity between the compounds in their layer-by-layer melting behavior above the bulk clearing point [7]. It was observed that, when heated through the bulk clearing point, there was a significant monotonic increase in the tension of a free-standing film beginning near the bulk melting temperature. In qualitative accordance with the predictions of the mean-field model, the observed increase in tension was interpreted as an indication of a monotonically increasing difference in free-energy density between the free-standing film and the bulk. In [9], it was suggested that bulk measurements of enthalpy could provide further insight into the validity of that interpretation. This paper follows up on that suggestion in order to make a more quantitative and compelling comparison between the predictions of the theoretical model and the experimental results. The relevant transition temperature and enthalpy values were measured for the compounds used in the previous experimental film tension studies. Those values will be discussed in the context of the tension measurements and the theoretical predictions. The values were also used to deter-

---

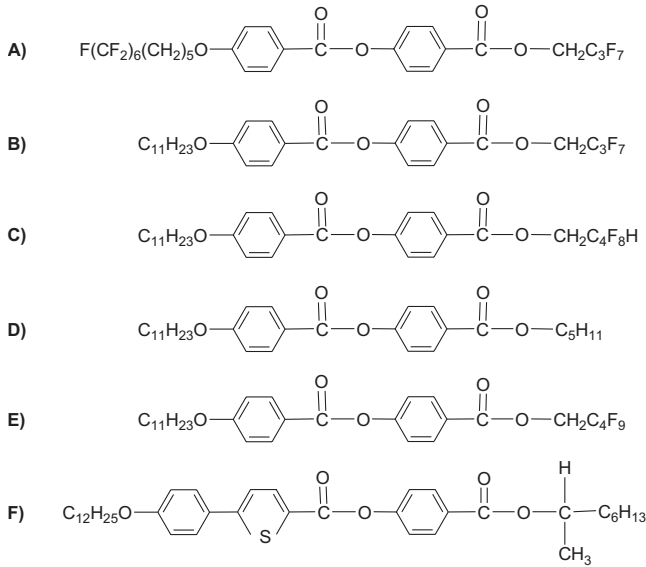*Author to whom correspondence should be addressed. mveum@uwsp.edu

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*.

mine compound-specific model parameters with which to simulate the tension experiments using the mean-field model and thus directly compare the two studies. These results will be presented and discussed.

II. OVERVIEW OF RELEVANT PREVIOUS ADVANCES

The chemical structures of the six compounds used in this study are depicted in Fig. 1. Five of the compounds (A through E) have the same molecular core but differ in the degree of fluorination in the tails of the molecules. Compound F differs significantly in structure from the other five and was included for comparison. Compounds A, B, C, D, and F exhibit a bulk smectic-*A*-to-isotropic (Sm*A-I*) transition and compound E exhibits a bulk smectic-*C*-to-isotropic (Sm*C-I*) transition. The relevant previous experimental results [9] can be summarized as follows. For free-standing films in all six compounds, an abrupt change in the tension-temperature slope, $d\gamma/dT$, was observed near the bulk Sm*A-I* (Sm*C-I*) transition temperature, T_{AI} (T_{CI}). $d\gamma/dT$ is a small negative value below T_{AI} (T_{CI}) and is a larger positive value above T_{AI} (T_{CI}). For a given compound, the larger positive slope is proportional to the film's thickness, while the smaller negative slope shows no resolvable thickness dependence. A compound-specific parameter resulted by taking the ratio of the larger positive slope to the film's thickness in layers, N. This ratio, $(d\gamma/dT)/N$, correlated inversely with the molecular weight of the material for the five compounds exhibiting the Sm*A-I* transition. For compound E, which exhibits a Sm*C-I* transition, $(d\gamma/dT)/N$ was markedly larger than for the other compounds with similar molecular weight.

These experimental observations and the meaning of the parameter $(d\gamma/dT)/N$ can be interpreted by considering two contributions to the film tension, such that

$$\gamma = 2\sigma + f_N, \tag{1}$$

where σ is the surface tension and f_N is the film's excess free energy per area (relative to the bulk reservoir to which the film is anchored). Since the surface tension has been shown to be localized to the molecular groups exposed at the free surface [15], σ is *not* expected to show dependence on film thickness, N. In accordance with the density of molecular groups at the free surface, σ is expected to show a weak and negative temperature dependence, both below and above the bulk transition temperature. f_N results from the finite thickness of the film and will have a more complicated temperature and thickness dependence than σ. Below the bulk transition temperature when both the reservoir and the film are in the same state, the surface enhanced ordering is localized to the layers "near" the free surfaces. Interior layers that "far" from the surfaces will not differ significantly in free-energy density from the bulk and will not contribute to f_N and the temperature variation of f_N should show no thickness dependence below T_{AI} (T_{CI}). Furthermore, if the surface enhanced ordering is independent of or weakly dependent on temperature, then f_N will also be so. When the film-reservoir system is heated above T_{AI} (T_{CI}), all layers of the film are in a different state than the reservoir and this difference in state will result in a temperature-dependent contribution to f_N from each of the layers including the interior layers. At the transition temperature, the bulk smectic and isotropic phases coexist with the same free-energy density, but, as temperature is increased, the isotropic phase becomes more favorable; i.e., it has a lower free-energy density. Furthermore, the difference in free-energy density between the bulk smectic and isotropic phases will increase monotonically with temperature. The increase will be approximately linear over a sufficiently small temperature range just above T_{AI} (T_{CI}). By applying this reasoning to each of the layers in a free-standing smectic film of N layers, it is reasonable to predict a linear increase in f_N with temperature just above T_{AI} (T_{CI}) such that the slope is proportional to N. And so, from Eq. (1), it is also reasonable to predict that, just below T_{AI} (T_{CI}), γ will be independent of N and only weakly dependent on temperature. Just above T_{AI} (T_{CI}), γ will increase linearly with temperature and the slope will be proportional to N.

Qualitatively, this provides a reasonable explanation for what was observed experimentally. The explanation also provides a physical meaning for the experimentally measured parameter $(d\gamma/dT)/N$. By taking the temperature derivative, dividing by N, and neglecting any temperature dependence of σ in Eq. (1), one obtains

$$(d\gamma/dT)/N \approx (df_N/dT)/N. \tag{2}$$

Notice that the left side of Eq. (2) is the final physical parameter that was extracted from the previous tension data for each compound. The value of f_N can be determined from the model in [11–13] for any N-layer free-standing film at any temperature for which the film is in the Sm*A* phase. Thus, the right-hand side of Eq. (2) can be determined from the mean-field model. Over a small temperature range just above T_{AI}, the model predicts an approximately linear increase in f_N that is proportional to N, in qualitative agreement with the physi-

TABLE I. For the six compounds of this study, the transition temperature and enthalpy values, $T_{AI}(T_{CI})$ and ΔH, measured from DSC, the molar entropy discontinuity values, ΔS, calculated from the DSC data, the average temperature slopes per layer of the tension, $(d\gamma/dT)/N$, from Ref. [9], and the average temperature slopes per layer of the excess free energy per area, $(df_N/dT)/N$, as determined by the microscopic mean-field model. ΔS is given in units of the ideal gas constant, R, for easy comparison with Ref. [18]. Since compound E exhibits a SmC-I transition, a value for (df_N/dT) could not be determined from the model.

	Compound	T_{AI}, T_{CI} (K)	ΔH (kJ/mol)	ΔS (R)	$(d\gamma/dT)/N$ (dyn/cm/K)	$(df_N/dT)/N$ (dyn/cm/K)
A	F3MOCPF6H5OB	377.7	3.79	1.21	0.049	0.053
B	F3MOCPH11OB	351.1	6.12	2.10	0.103	0.095
C	F4hMOCPH11OB	328.4	5.28	1.93	0.102	0.084
D	H5OCPH11OB	348.3	8.01	2.76	0.136	0.131
E	F4MOCPH11OB	360.7	8.40	2.80	0.120	
F	MHDDOPTCOB	370.1	5.60	1.82	0.094	0.079

cal arguments made above. In order to make a direct and quantitative comparison between theoretical predications and experimental observations, compound-specific parameters are required for the model, which can be obtained from differential scanning calorimeter (DSC) measurements.

III. DSC MEASUREMENTS

Using a Perkin-Elmer Pyrus 1 DSC, we measured the SmA-I (SmC-I) transition temperatures and enthalpies for the six compounds in Fig. 1. Prior to scanning, each sample of ~ 2 mg was annealed for several minutes at roughly 10 K above T_{AI} (T_{CI}) and then quenched to the crystalline phase. Multiple heating and cooling runs were performed at a scanning rate of 10 K/min at temperatures between the crystalline phase and the annealing temperature. Each set of scans involved an initial dummy temperature ramp that was systematically excluded from the data in order to avoid any possible problem with thermal memory. The heating (cooling) scans produced well-defined endothermic (exothermic) peaks that were reproducible. The peak maxima (minima) gave the measured transition temperatures and integration of the peaks gave the measured transition enthalpy, ΔH. These DSC techniques have been shown to be reliable for determining the transition temperatures and enthalpies for other smectic compounds [16].

Table I displays the average value of transition temperature and enthalpy from the multiple scans for each compound. The transition temperatures for these compounds are consistent with other studies [7,9]. ΔH values of ~ 4 to ~ 6 kJ/mol are typical for the SmA-I transition and it is reasonable for ΔH to be larger but on the same order for the SmC-I transition [17]. Our values span a bit more than this typical range, which will be an important consideration later. The transition discontinuity in entropy, ΔS, was calculated simply as the ratio of ΔH to T_{AI} (T_{CI}). Table I displays those values in units of the ideal gas constant for reasons that will be explained in the next section. From Eq. (2), it makes conceptual sense that the measured values of $(d\gamma/dT)/N$ will quantitatively correlate with ΔS. Recall that f_N is the *excess free energy per area* of the film (relative to the bulk reser-

voir). Since the entropy directly influences the temperature variation of the free energy, it is reasonable to speculate that the entropy difference between the bulk smectic and isotropic structures at T_{AI} (T_{CI}) will quantitatively correlate with the temperature variation of f_N just above T_{AI} (T_{CI}). As temperature is increased above the bulk clearing point, f_N will change more rapidly with temperature for a material with a larger bulk value of ΔS. As shown in Table I, the ΔS values do show qualitative consistency with the values of $(d\gamma/dT)/N$. Both sets of values can be categorized into three groups. The first group contains only compound A with the lowest value of ΔS and $(d\gamma/dT)/N$. The second group contains compounds B, C, and F with moderate values. Compounds D and E have higher values. It should be noted that grouping D and E together is dubious because compound E is unique here in that it displays a SmC-I transition. Nonetheless, for these compounds there is a consistent trend between ΔS and $(d\gamma/dT)/N$ lending credibility to the validity of using Eq. (2) to interpret the results of the tension measurements. In the next section, an even more direct comparison will be made.

IV. MEAN-FIELD CALCULATIONS

As mentioned above, the value of f_N can be determined from the mean-field model for any N-layer free-standing film at any temperature T for which the film is in the SmA phase. The transition temperature and enthalpy values from DSC were used to determine parameters in the model to make predictions specific to the compounds in Fig. 1. Because the model is not applicable to the SmC-I transition, compound E was excluded from the analysis presented in this section. There are four model parameters necessary to make the calculation. The first three parameters, N_i, V_0, and α, appear in McMillan's model for the bulk SmA phase [18]. N_i is the density of molecules. V_0 is the intermolecular interaction constant associated with orientational ordering and it sets the temperature scale of the model. α is the dimensionless interaction strength for the SmA phase. It can vary from 0 to 2, but $\alpha \geq 0.98$ is required for a first-order SmA-I transition. In the theory, α determines both the first order SmA-I transition

entropy discontinuity, ΔS, and also the strength of V_0 relative to the transition temperature, T_{AI}. Using Table I of [18], one can work backward and use a value of ΔS to determine α and the relative strength of V_0. As mentioned in the previous section, $\Delta S = \Delta H / T_{AI}$ was calculated for each compound using the DSC data. Table I displays ΔS in units of the ideal gas constant, R, for easy comparison with Ref. [18].

Using this approach to determine α and the relative strength of V_0 for each compound immediately introduced a complication because the range of measured ΔS values is wider than the range given in Table I of [18]. This is not entirely unexpected since McMillan pointed out that the trends predicted for the entropy are more reliable than the magnitudes when compared to experiment. To reasonably deal with this complication, first recall that the range of ΔH values measured for these compounds is wide. Typical values range from ~ 4 to ~ 6 kJ/mol, while the ones in this paper span from 3.79 to 8.01 kJ/mol. This suggests that the range of ΔH values does approximately span the range of possible values for compounds exhibiting a first-order Sm*A*-*I* transition. For this reason, the corresponding minimum and maximum allowed values of α were assigned to compounds A and D, respectively. The measured ΔS values for the remaining three compounds do fall in the range allowed by McMillan's theory. For simplicity, each of the remaining compounds was assigned a value for α assuming the measured and theoretical ΔS values are identical. While this is likely not quite correct given the results for compounds A and D, an extrapolation based upon the end points provided by compounds A and D was not attempted. This issue will be addressed later with discussion of uncertainty. Using this approach, α equals 0.98, 1.2, 1.1, 2.0, and 1.05 for compounds A, B, C, D, and F, respectively. From the second column of Table I in [18], the reduced temperatures, $T_{AI}^* = k_B T_{AI} / V_0$, which correspond to the assigned value of α, are equal to 0.220, 0.236, 0.228, 0.308, and 0.225 for compounds A, B, C, D, and F, respectively. The values of V_0 were then set so that this model value of the reduced temperature coincides with the transition temperature as obtained from DSC.

The density of molecules, N_i, represents the number of molecules within a single smectic layer of unit area, i.e., the in-plane number density. For each of the compounds, the value was set to $N_i = N_A(\rho/M_0)\ell$, where N_A is Avogadro's number, ρ is the mass density, M_0 is the molecular weight, and ℓ is the layer thickness. Mass density values were not available, so ρ was set to 1 g/cm³ for each of the compounds. Values for ℓ were based upon available ellipsometry measurements of the average smectic layer spacing for compounds A, D, and F. Those values are 31.8, 32.8, and 35.1 Å, respectively. While the same layer-spacing data were not readily available for compounds B and C, reasonable values can be interpolated due to the similarity in chemical structures to compounds A through D. For B and C, ℓ was set to be the average of the values for A and D, 32.3 Å. Admittedly, the values of N_i could be refined by measuring the layer spacings for B and C. However, without mass density data for each of the compounds, there would be little to gain in that refinement. This will be addressed further with the discussion of uncertainty.

The fourth parameter, W/V_0, was introduced into the model in [11–13] to account for the intermolecular forces

responsible for the stability of a free-standing film at temperatures above the bulk clearing point. In the model, the temperature variation of f_N is only weakly dependent upon this ratio, which is consistent with the assumptions that were made to establish the validity of Eq. (2). For this reason, all five compounds were assigned the nominal value of 1.8 that was used in previous papers.

In order to make a direct comparison between the model predictions and the experimental tension studies for the specific compounds, f_N versus T was calculated from $\sim T_{AI}$ to $\sim (T_{AI}+1$ K) with resolution of ~ 0.1 K. For each of the five compounds, this calculation was made for eight-, nine-, and ten-layer films and the slope was extracted from the graph of f_N versus T. As expected, the extracted slopes were very nearly proportional to the number of layers, N. The slopes were then divided by N and averaged for each of the compounds. The average of the three slopes provides a theoretical value of $(df_N/dT)/N$ that can be compared directly to the experimental values of $(d\gamma/dT)/N$ in accordance with Eq. (2). Both the experimental and theoretical values are listed in Table I. As with the ΔS values, the slopes can be categorized into three groups: (i) compound A with the lowest value, (ii) compounds B, C, and F with moderate values, and (iii) compound D has the highest value.

From an order-of-magnitude point of view, there is striking agreement between the theoretical predictions and the experimental results. It is important to note that the two results were obtained independently. This agreement lends credibility to the theoretical interpretation of the film-tension data and to the validity of the mean-field model.

Reference [9] showed that $(d\gamma/dT)/N$ correlated inversely with molecular weight. Figure 2 shows a plot of both $(df_N/dT)/N$ and $(d\gamma/dT)/N$ versus molecular weight for the five compounds exhibiting the Sm*A*-*I* transition. The plot conveniently displays the deviations between these two data sets. With the exception of compound A, the results from the theoretical model produce numbers that are systematically smaller than those from the tension studies. The discrepancy falls within the uncertainty of the tension studies only for compound D and nearly so for compound A. This discrepancy is most noticeable, and is notably consistent, for the compounds of intermediate molecular weight. The theoretical values are lower than the experimental values by $\sim 15\%$. We have not included error bars for the results from the theoretical model. Reliably estimating the uncertainty is problematic due to the nature of the sources of uncertainties. For instance, one source of uncertainty in the theoretical model is the value used for the in-plane number density, N_i. Recall that the values used for each of the compounds were based upon an assumption that the mass densities of free-standing films in each compound are identically equal to 1 g/cm³. While this is a reasonable estimate for the mass density of a liquid-crystal compound near the Sm*A*-*I* transition, it is guesswork at best to speculate on the degree of uncertainty this introduces into the calculation. Having data for the bulk mass densities would certainly allow for the refinement of this model parameter, but even with the data, it is not clear that the mass density of a thin free-standing film is equal to that of the bulk.

Another, and probably more significant, source of uncertainty is the model parameter α. The calculated values of f_N,
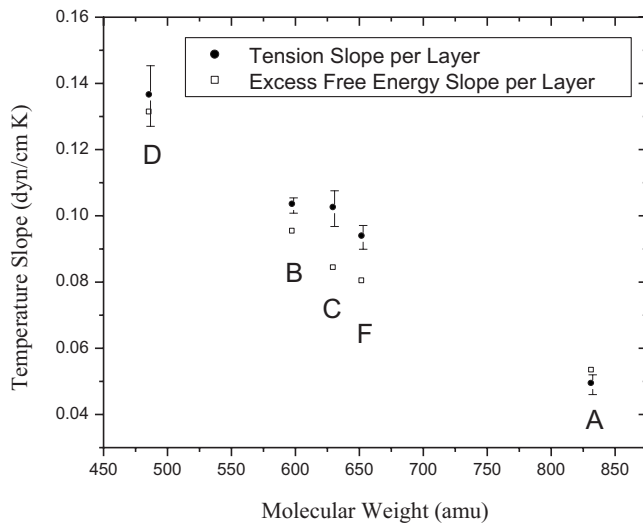
FIG. 2. Temperature slope per layer of tension, $(d\gamma/dT)/N$, from Ref. [9], and the temperature slope per layer of the excess free energy per area, $(df_N/dT)/N$, versus molecular weight for the five compounds exhibiting the Sm*A-I* transition. For all but compound A, the values of $(df_N/dT)/N$ are systematically smaller than the values of $(d\gamma/dT)/N$. With the exception of compound D, the discrepancies do not fall within the experimental uncertainties of the tension-temperature slopes. For the three compounds of intermediate molecular weight, the values differ by $\sim 15\%$.

and thus the temperature slopes, are quite sensitive to this parameter. Recall that α was determined from Table I of [18] using the entropy discontinuity values that were determined from DSC data. Recall also that for compounds A and D, the measured transition entropies were outside the range allowed by the McMillan theory for a first-order Sm*A-I* transition. For A and D, α was set at the minimum and maximum allowed, respectively. Interestingly, the smallest discrepancies between $(d\gamma/dT)/N$ and $(df_N/dT)/N$ occur for compounds A and D. The larger discrepancies for compounds B, C, and F could be removed by appropriately adjusting the values for

α. Making such adjustments is, in effect, the same as assuming the theoretical and experimental entropy discontinuities are not identical. Since McMillan pointed out that the theoretically predicted trends in transition entropy are more reliable than the magnitudes when compared to experiment, it might be reasonable to, in some way, collectively shift the values of α for B, C, and F to minimize the discrepancies between $(d\gamma/dT)/N$ and $(df_N/dT)/N$. While this would lead to a prettier graph in Fig. 2, we have not done so. It would not further the scientific knowledge disseminated in this paper and it could mislead the reader into thinking there is greater precision in the values of $(df_N/dT)/N$ than actually exists.

Future study on a wider range of compounds will be required to sort through the correlation between the measured entropy discontinuity and the temperature slopes resulting from both the mean-field model and tension measurements. In particular, it would be compelling to perform studies on a series of compounds that extends the range of the parameter α. Recall that in McMillan's model α can vary from 0 to 2, but it is required that $\alpha \gtrsim 0.98$ in order to have a first-order Sm*A-I* transition [18]. For $\alpha < 0.98$, McMillan's model predicts an intermediate nematic (N) phase between the Sm*A* and *I* phases. The model from [11–13] can be applied to the Sm*A-N* transition as it was here for the Sm*A-I*. In principle, it would be possible to perform a similar study on a series of compounds that vary in chemical structure so as to span a wider range of phase behavior that also includes the Sm*A-N* transition. The challenge is to find a series of compounds that not only exhibits this wider range of phase behavior but also one for which free-standing films will remain stable up to ~ 1 K above the bulk transition temperatures.

[1] T. Stoebe, P. Mach, and C. C. Huang, Phys. Rev. Lett. **73**, 1384 (1994).

[2] E. I. Demikhov, V. K. Dolganov, and K. P. Meletov, Phys. Rev. E **52**, R1285 (1995).

[3] V. K. Dolganov, E. I. Demikhov, R. Fouret, and C. Gors, Phys. Lett. A **220**, 242 (1996).

[4] E. A. L. Mol, G. C. L. Wong, J. M. Petit, F. Rieutord, and W. H. de Jeu, Physica B **248**, 191 (1998).

[5] P. M. Johnson, P. Mach, E. D. Wedell, F. Lintgen, M. Neubert, and C. C. Huang, Phys. Rev. E **55**, 4386 (1997).

[6] P. Mach, P. Johnson, E. D. Wedell, F. Lintgen, and C. C. Huang, Europhys. Lett. **40**, 399 (1997).

[7] S. Pankratz, P. M. Johnson, H. T. Nguyen, and C. C. Huang, Phys. Rev. E **58**, R2721 (1998).

[8] M. Veum, E. Kutschera, N. Voshell, S. T. Wang, S. L. Wang, H. T. Nguyen, and C. C. Huang, Phys. Rev. E **71**, 020701 (2005).

[9] M. Veum, M. K. Blees, N. Voshell, H. T. Nguyen, and C. C. Huang, Phys. Rev. E **74**, 011703 (2006).

[10] Y. Martínez–Ratón, A. M. Somoza, L. Mederos, and D. E. Sullivan, Faraday Discuss. **104**, 111 (1996); Phys. Rev. E **55**, 2030 (1997).

[11] L. V. Mirantsev, Phys. Lett. A **205**, 412 (1995).

[12] L. V. Mirantsev, Liq. Cryst. **20**, 417 (1996).

[13] L. V. Mirantsev, Phys. Rev. E **63**, 061701 (2001).

[14] M. Veum, P. Messman, Z. Q. Liu, C. C. Huang, N. Janarthanan, and C. S. Hsu, Rev. Sci. Instrum. **74**, 5151 (2003).

[15] P. Mach, C. C. Huang, and H. T. Nguyen, Phys. Rev. Lett. **80**, 732 (1998).

[16] D. Sharma, J. C. MacDonald, and G. S. Iannacchione, J. Phys. Chem. B **110**, 16679 (2006).

[17] P. J. Collings and M. Hird, *Introduction to Liquid Crystals* (CRC Press, Cleveland, 1997), p. 192.

[18] W. L. McMillan, Phys. Rev. A **4**, 1238 (1971).