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Critical fluctuations near the smectic-A–smectic-C transition of a partially perfluorinated compound

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Utilizing our high-resolution bulk and free-standing film calorimeters, we have conducted detailed heat-capacity measurements near the smectic-A–smectic-C phase transition of one partially perfluorinated liquid-crystal compound. The thin film data clearly demonstrate the importance of fluctuations due to reduced dimensionality. Moreover, the data from bulk samples and thick films cannot be adequately fit using the customary extended mean-field model. Successful fitting requires the inclusion of terms characterizing Gaussian fluctuations.

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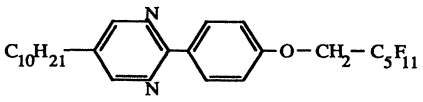
The smectic-A (Sm-A) and smectic-C (Sm-C) phases of liquid crystals can be characterized as two-dimensional (2D) orientationally ordered fluids. The smectic layers are described by a one-dimensional mass-density wave and the molecular directors are either parallel (Sm-A) or at an angle (Sm-C) to the wave vector. Proposing the order parameter associated with the Sm-A–Sm-C transition to be $\Psi = \theta \exp(i\phi)$, in 1972, de Gennes [1] argued that this transition should belong to the three-dimensional (3D) XY universality class and might be continuous. Here θ is the molecular tilt angle relative to the layer normal and ϕ the azimuthal angle of the director. Ten years later, detailed calorimetric studies [2] first revealed the novelty of this phase transition. It is mean field [3] but is in the close vicinity of a tricritical point. Thus, the extended mean-field model [2,4] is necessary to describe the physical properties associated with this transition. More recent experiments have characterized not only continuous and first order Sm-A–Sm-C transitions [5] but also identified systems in which the transition is tricritical [6]. Based on the measured mean-field heat-capacity jump and the value for the bare correlation length obtained from x-ray studies [3], the Ginzburg criterion yields $t_G \approx 10^{-5}$. This small value for t_G indicates that the reduced temperature region $|t| < t_G$ in which critical fluctuations are expected to be important for the Sm-A–Sm-C transition is virtually inaccessible in experiments. Since the Sm-C ordering is presumably not driven by long-range interactions and the Sm-A–Sm-C transition is not at or above the upper critical dimensionality ($d_u = 4$ for the XY universality class), it is very difficult to explain the observed mean-field behavior. Thus the discovery of a system showing *critical fluctuations* associated with the Sm-A–Sm-C transition is very important.

In light of numerous practical applications utilizing ferroelectric-liquid-crystals [7], many new liquid-crystal compounds exhibiting smectic phases have been synthesized. Among them, the partially perfluorinated compound is a highly intriguing example [8].

Employing our bulk and free-standing film calorimeters, we have conducted detailed heat-capacity measurements near the Sm-A–Sm-C transition of 5-n-decyl-2-(4-n-(perfluoropentyl-metheleneoxy) phenyl) pyrimidine [H10F5MOPP]. The molecular structure is



The transition sequence is

isotropic (I) $\xrightarrow[(84\ ^\circ C)]{}$ Sm-A $\xrightarrow[(73\ ^\circ C)]{}$ Sm-C $\xrightarrow[(47\ ^\circ C)]{}$ crystalline.

The heat-capacity data near the Sm-A–Sm-C transition from our bulk calorimeter are shown in Fig. 1. The data display a very sharp anomaly, indicating the proximity of this transition to a mean-field tricritical point. Any thermal hysteresis between the cooling and heating runs is less than our experi-

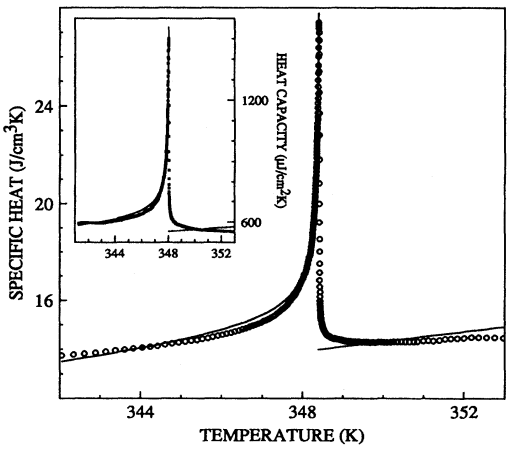


FIG. 1. Temperature dependence of the heat capacity of a bulk H10F5MOPP sample near the Sm-A–Sm-C transition. The lines are the best fitting result to Eq. (2). The inset shows similar results obtained from a 135-layer film.

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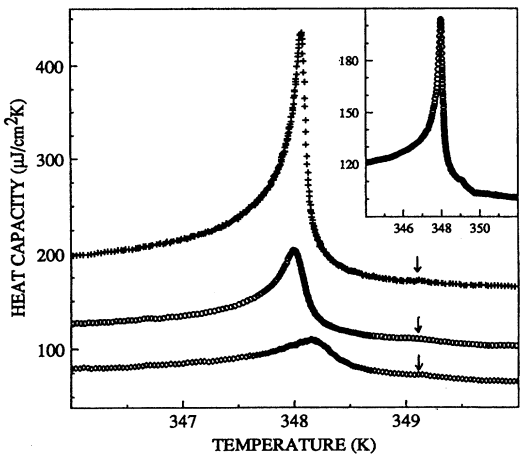

FIG. 2. Temperature variation of heat capacity of H10F5MOPP free-standing films (thicknesses are 40, 25, and 16 molecular layers). The arrows indicate the heat-capacity hump associated with the surface ordering as discussed in the text. To better show this heat-capacity hump, the inset displays the same heat-capacity data from the 25-layer film.

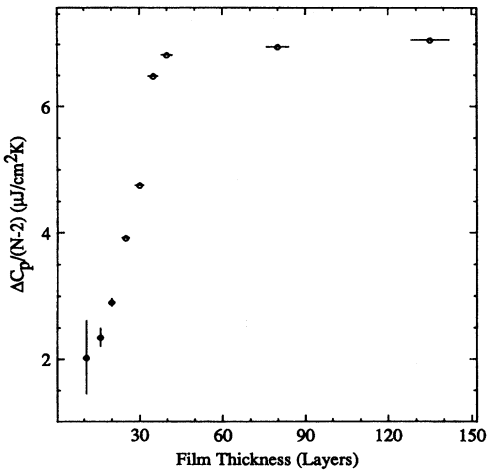

FIG. 3. $\Delta C_p/(N-2)$ versus the layer number (N). Here we assume that the main heat-capacity peak is due to the $N-2$ interior layers.

mental resolution of 3 mK. The transition therefore appears to be continuous. We have also obtained heat-capacity data from 135-, 80-, 40-, 35-, 30-, 25-, 20-, 16-, and 11-layer films. Data from the 135-layer film are presented as the inset of Fig. 1. The 135-, 80-, and 40-layer films exhibit sharp heat-capacity anomalies similar to the bulk data. Figure 2 displays the anomalies exhibited by the 40-, 25-, and 16-layer films. Significant rounding and broadening of the heat-capacity data become increasingly apparent in the thinner films. In fact, in the case of the 16- and 11-layer films, the sharp heat-capacity peak is replaced by only a broad hump. These data clearly demonstrate that further improvements in experimental resolution are required to resolve the heat-capacity anomalies of still thinner films [9].

It is important to note that a small hump is clearly discernible on the high temperature side of the main heat-capacity peak of the thinner films (see Fig. 2). We were, however, unable to detect any other features at temperatures up to (and above) the bulk Sm-A–I transition at which point the film ruptured [10]. We believe that the humps shown in Fig. 2 signal preferential Sm-C ordering at the surface of the films. This hump may represent an observation of the heat-capacity anomaly predicted by the Kosterlitz-Thouless theory of 2D defect-mediated transitions. This hump seems to decrease as the film thickness does. Further work is clearly necessary to resolve this important point and related issues [9]. Because polarized optical microscopy failed to reveal characteristic Sm-C director fluctuations, the films seem to be entirely Sm-A at temperatures just above the small hump and only the two outermost layers appear to surface order.

The magnitude of the heat-capacity jump, ΔC_p, clearly decreases with film thickness. This is illustrated in Fig. 3 where $\Delta C_p/(N-2)$ (normalized to account for the observed surface ordering) is plotted versus layer number (N). A precipitous drop in $\Delta C_p/(N-2)$ for $N<35$ demonstrates the increasing importance of fluctuations as the film thickness is reduced. This phenomenon is very different from the observed behavior of three other liquid-crystal phase transitions as a function of film thickness [11].

Based on its past success, we tried to fit the data to the following expression obtained from the extended mean-field model [2]:

$$G=G_0+at|\Psi|^2+b|\Psi|^4+c|\Psi|^6: \tag{1}$$

$$C=\begin{cases} C_0 & \text{for } T>T_c \\ C_0+AT|T_m-T|^{-1/2} & \text{for } T<T_c. \end{cases} \tag{2}$$

The nonsingular part of the free energy, G_0, contributes C_0, which can be approximated as linear in reduced temperature (i.e., $C_0=E+Dt$). The coefficients A and T_m are defined as $A=a^{3/2}/[2(3c)^{1/2}T_c^{3/2}]$ and $T_m=T_c(1+t_0/3)$. The parameter $t_0=b^2/(ac)$ is a dimensionless quantity that characterizes the crossover temperature between the mean-field tricritical point ($b=0$) and the ordinary mean-field regime ($c\approx 0$). The fitting of our bulk data to Eq. (2) with a reasonable excluded temperature region (348.6 K$>T>$348.4 K) [12] has been included in Fig. 1 as the lines. The fitting parameters are listed in Table I. The most striking difference between this fit and previous fits of other Sm-A–Sm-C heat-capacity data to the extended mean-field model is the very large background slope required. In fact, the slope necessary to provide a good fit for $T<T_c$ is so large that the fit actually crosses the data in the region $T>T_c$. Similar results have been obtained for the 135- (see the inset of Fig. 1), 80-, and 40-layer films. The simple extended mean-field model is, therefore, insufficient to describe our data. Motivated by the proximity of this transition to a tricritical point ($t_0\approx 10^{-5}$), we have tried to remedy this discrepancy by including scaling correction terms [13]. While reasonable fitting results can be obtained by adding, at least, two correction-to-scaling terms, the mean-field (MF) nature of this approach still requires a large exclusion of temperature window (348.6 K$>T>$348.4 K). The major advantage of this scheme is that it

TABLE I. List of the fitting parameters.

Sample	A ($J/cm^3K^{3/2}$)	E J/cm^3K	D J/cm^3K	T_M K	T_c K	C_+ [c] J/cm^4K
bulk [a]	5.82×10^{-3}	13.99	70.13	348.420		
bulk [b]	4.75×10^{-3}	13.73	57.13	348.423	348.416	1.58×10^5
	$\mu J/cm^2K^{3/2}$	$\mu J/cm^2K$	$\mu J/cm^2K$	K	K	J/cm^3K
135-layer [a]	0.478	553.24	1675	348.043		
40-layer [b]	0.130	156.27	219.34	348.199	348.099	4.97

[a]Fitting to the mean-field expression [Eq. (2)].
[b]Fitting to an expression including contributions from both mean-field and Gaussian fluctuations [Eq. (3)].
[c]$C_-=1.58\times10^5$ J/cm^4K (for bulk fitting) and $C_-=7.03$ J/cm^3K (for 40-layer film fitting).

allows different background slopes for $T>T_{c,\mathrm{MF}}$ and $T<T_{c,\mathrm{MF}}$. Other possible data analyses are in progress.

Because the above attempts were not adequate, and in light of our experimental data indicating the importance of fluctuations in the heat-capacity anomalies of the thin films, we refit the data to an extended mean-field model including terms characteristic of Gaussian fluctuations in finite thickness (d) [14] and bulk ($d=\infty$) [15] samples:

$$C=\begin{cases} C_0+(C_+/d)(T/T_c)^2\xi^2[1+(d/\xi)\coth(d/\xi)], & T>T_c, \\ C_0+AT|T_m-T|^{-1/2}+2(C_-/d)(T/T_c)^2\xi'^2[1+(d/\xi')\coth(d/\xi')], & T<T_c. \end{cases} \tag{3}$$

Here $\xi'=2^{-1/2}\xi=2^{-1/2}\xi_0|t|^{-1/2}$ and ξ_0 is the bare correlation length for the fluctuations. The best fitting results were obtained for very reasonable values of the bare correlation length (0.25 layer)$<\xi_0<$(0.55 layer). To reduce the number of fitting parameters, ξ_0 was thereafter fixed at $\xi_0=0.4$ layer. Since Fig. 3 indicates that the heat-capacity anomalies for films thicker than 35 layers are primarily 3D-like, we were able to further reduce the number of fitting parameters by invoking the 3D XY scaling relation between C_- and C_+ ($C_-=2^{1/2}C_+$). Under these circumstances, C_+ and T_c are the only two additional fitting parameters associated with the inclusion of Gaussian fluctuations in the analysis. The results of this approach are displayed as solid lines in Fig. 4 for the bulk sample and 40-layer film. These fits are clearly superior to those presented in Fig. 1 and the parameters are listed in Table I. It is important to note that, besides the superior fitting, this approach requires a significantly smaller region of excluded temperature [16]. In this case the Gaussian fluctuation terms are added to provide a much better description of the Sm-A–Sm-C transition. To the best of our knowledge, the fitting parameters are fairly reasonable.

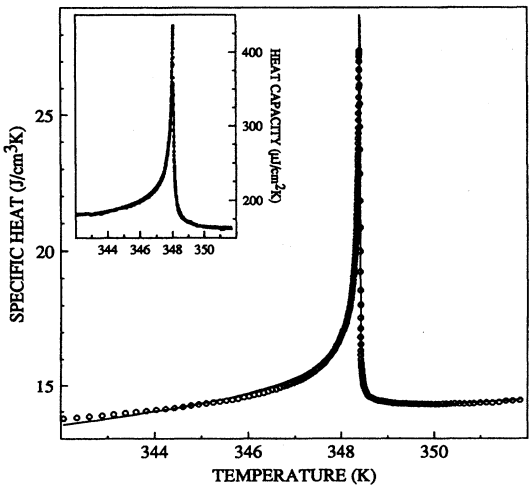

FIG. 4. The best fitting result of bulk heat-capacity data and that of the 40-layer film data (see the inset) to Eq. (3) are shown as solid lines.

A recent x-ray study [17] of free-standing films of a partially perfluorinated compound similar to H10F5MOPP determined the smectic compressional elastic modulus to be $B\approx10^9$ erg/cm. This value is more than 10 times larger than the value typically exhibited by simple alkyl terminated liquid-crystal compounds. This is consistent with the fact that the perfluoropentyl chain is bulkier and more rigid than a corresponding alkyl chain. The Ginzburg parameter t_G will increase as a result of the coupling between the molecular tilt and layer dilatation [18]. This may provide a plausible explanation for our experimental finding [19]. Moreover, we believe that the effect of the partial fluorination on the elastic properties plays an important role in the observed layer-by-layer thinning transition above the Sm-A–I transition of H10F5MOPP [10].

In conclusion, we have shown the customary extended mean-field model to be insufficient to describe the measured heat-capacity anomaly associated with the Sm-A–Sm-C transition in bulk samples and free-standing films of the H10F5MOPP compound. Other fitting

schemes have been explored. The data have proven to be consistent with a model including the effects of Gaussian fluctuations and the importance of fluorination has been discussed. Although the characterization of these intriguing partially fluorinated compounds is far from complete, a number of interesting and unusual physical phenomena have already been revealed [8,10,17]. Further studies on this remarkable group of liquid-crystal compounds are in progress.

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[9] Under the appropriate operating conditions, the amplitude of the measured ac sample temperature oscillation (T_{ac}) is proportional to (P_{ac}/C_t). Here P_{ac} is the ac input power absorbed by the film and C_t the sum of the heat-capacity contribution from the film (C_f) and the addendum contribution (C_a). By increasing the film thickness from 2 to 11 molecular layers, P_{ac} increases by roughly a factor of 5 while C_t remains about the same ($C_a > C_f$ in this range of film thickness). Therefore, although we can resolve the heat-capacity anomalies related to the surface order from moderately thick films, an additional fivefold improvement in the signal-to-noise (S/N) ratio is needed to convincingly resolve the heat-capacity anomaly associated with the Sm-A–Sm-C transition of a 2-layer H10F5MOPP film. Usually films of a moderate thickness (≈ 10 layers) yield the heat-capacity data with a much better S/N ratio. This has been the case for all the films of various liquid-crystal compounds we have studied so far. Currently, several ideas are being considered to improve our resolution of two-layer films.

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[12] In the case of a mean-field model, in principle, the heat-capacity anomaly should exhibit a vertical jump at $T_{c,MF}$. In practice, however, $T_{c,MF}$ is often determined to be at the maximum negative slope of the heat-capacity data. The data associated with the negative slope near $T_{c,MF}$ are therefore excluded from the fitting to a mean-field model.

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[16] Equation (3) was also used to fit the heat-capacity data from 35-, 30-, and 25-layer films. Meaningful fits could be obtained only if the excluded temperature window increased rapidly from 100 mK for the 35-layer-film data to 200 mK for the 25-layer-film data. To the best of our knowledge, no fitting expression has yet been developed to describe data such as ours on films of moderate thickness which display the effects of both finite size and enhanced surface ordering. Systematic variations of any coefficient, e.g., C_+ as a function of film thickness, would therefore be of considerable interest. The fitting results yield the following values of the C_+/A (in $K^{1/2}$): 62.9, 55.0, 38.2, 51.3, 50.5, and 40.2, respectively, for 135-, 80-, 40-, 35-, 30-, and 25-layer films.

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[19] Detailed discussions will be given in the future.