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# Critical heat capacity at the smectic A–smectic C transition in a partially fluorinated liquid crystal

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A high resolution a.c. calorimetric study of a phenyl pyrimidine derivative with one alkyl and one perfluorinated end group shows that the excess heat capacity associated with the smectic A–smectic C transition exhibits critical fluctuation behaviour that is consistent with the three-dimensional XY universality class. This is in contrast to the usual mean-field SmA–SmC behaviour and the near tricritical fluctuation behaviour reported recently in several other compounds. It is speculated that smaller than usual correlation lengths are the cause for the wide fluctuation region in this compound.

## 1. Introduction

In the vicinity of the smectic A (SmA)–smectic C (SmC) transition, the SmC order parameter can be written as  $\theta \exp(i\phi)$ , where  $\theta$  is the tilt angle of the director with respect to the smectic layer normal and  $\phi$  is an azimuthal angle. De Gennes [1] showed 25 years ago that as a result the SmA–SmC transition should belong to the three-dimensional (3D) XY universality class. However, extensive experimental studies [2–7] of a wide variety of SmA–SmC transitions in nonchiral systems and SmA–SmC\* transitions in several chiral systems reveal mean-field behaviour that is well modelled by the so-called extended Landau theory [2]. In the extended Landau model, the sixth-order term in the tilt order parameter plays an important role in the free energy and, indeed, most systems show evidence of being close to a mean-field tricritical point at which the coefficient of the fourth-order term is zero [5, 6].

The explanation for the absence of critical fluctuation effects at most SmA–SmC transitions lies in the Ginzburg criterion, since true critical behaviour is expected only when  $|t| < t_G$ , where  $t$  is the reduced temperature  $(T - T_c)/T_c$  and  $t_G$  is the Ginzburg temperature. The large bare correlation lengths typically obtained from scattering studies yield  $t_G \approx 10^{-5}$  [8, 9]. This  $t_G$  value implies that the SmA–SmC critical region is experimentally inaccessible. There is, however, no universal

reason for such a narrow SmA–SmC critical region nor the proximity to a tricritical point. Thus vigorous efforts have been made to discover liquid crystal systems that exhibit critical SmA–SmC fluctuation effects.

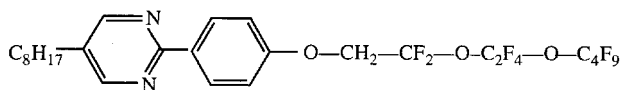
Non-Landau behaviour has been reported recently for the heat capacity near the SmA–SmC transition in 5-*n*-decyl-2-[4-*n*-(perfluoropentylmetheleneoxy)phenyl]-pyrimidine (H10F5MOPP) [10] and the SmA–SmC $^*$  $_{\alpha}$  transition in 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC) and three related compounds [11]. The latter are chiral compounds, and the SmC $^*$  $_{\alpha}$  phase is an antiferroelectric version of the familiar SmC\* ferroelectric phase. As discussed in §3, all of these fluctuation  $C_p$  data indicate the important influence of a Gaussian tricritical point. The present study involves a high resolution investigation of the SmA–SmC heat capacity in a new partially fluorinated liquid crystal. This compound exhibits much stronger energy fluctuations in the disordered (SmA) phase than seen previously. Furthermore, in spite of anomalies observed very close to the transition, which are presumably due to trace impurities, the  $C_p$  data can be well described by the 3D-XY model over a wide temperature range.

## 2. Experimental results and analysis

High resolution a.c. calorimetric measurements have been made at MIT on 2-{4-[1,1-dihydro-2-(2-perfluorobutoxyperfluoroethoxy)perfluoroethoxy]}phenyl-5-octylpyrimidine, denoted as H8F(4,2,1)MOPP and having a

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molecular weight  $M = 674.5 \text{ g mol}^{-1}$  †. The structural formula is



This compound was synthesized and purified at 3M Corporation in St. Paul, MN and was used without further treatment. Samples from the same batch are being used for thin film optical studies of the SmA–Isotropic (I) transition at the University of Minnesota. The phase transition sequence is



On cooling, the SmC phase does not freeze into a crystal but forms a room temperature smectic glass.

Heat capacity data for a small mass ( $\sim 20 \text{ mg}$ ) of the liquid crystal, cold-weld sealed into a thin silver cell, were obtained as a function of temperature at an a.c. frequency  $\omega_0 = 2\pi f = 0.196 \text{ s}^{-1}$ . Some measurements made at  $\omega_0/2$  confirmed that these data correspond to the static limit. The calorimeter and appropriate equations for analysing the observed  $T_{ac}$  response to the  $P_0 \exp(i\omega t)$  heat input are described elsewhere [12]. The temperature range from 300 to 350 K was investigated with emphasis on a 30 K-wide region centered around the SmA–SmC transition. A very strongly first order SmA–I transition (not shown) was observed with a 1.1 K-wide two-phase coexistence region centered at 344.67 K. The observed pretransitional heat capacity wings were typical of other SmA–I transitions.

Shown in figure 1 is the  $C_p$  peak associated with the SmA–SmC transition after taking into account the heat capacity of the addenda (silver cell, heater, and leads). These data, which were obtained on cooling at a slow scan rate of  $-67 \text{ mK h}^{-1}$ , are in good agreement with the data from two other scans—a heating run made at a  $+134 \text{ mK h}^{-1}$  scan rate and a second cooling run made at  $-293 \text{ mK h}^{-1}$ . No appreciable drift in the SmA–SmC transition temperature was observed over a period of 37 days, and the  $C_p$  wings superimposed very well for all three runs except for a region about 0.4 K wide near the transition. The presence of anomalously large (and history dependent)  $C_p$  values in this region is

† Attempts were made to analyse the SmA–SmC transition for the compound H8F(4,2,1)MOPP using high resolution calorimetry at the University of Minnesota. While preliminary results were very similar to those presented in this paper, a thorough study of the compound was impeded by technical difficulties. Due to its particularly low surface tension, this compound has a tendency to leak out of an unsealed glass calorimetry cell. Various surface treatments of the cell have thus far not resolved these difficulties.

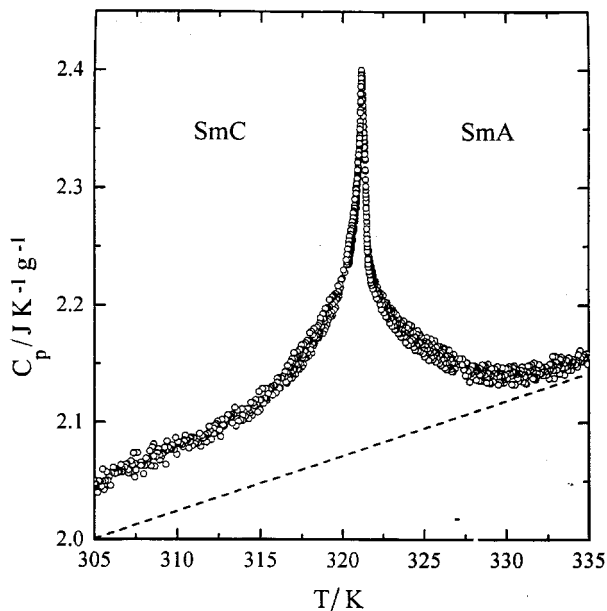


Figure 1. Heat capacity of H8F(4,2,1)MOPP near the SmA–SmC transition. The dashed line represents the  $B_r + Et$  background heat capacity variation that would occur in the absence of the SmA–SmC transition. The slope  $E = 1.51$  is the least-squares value from fit 2 in the table.

most obvious on the high temperature side of the transition, as shown in figure 2. It seems likely that anomalous  $C_p$  behaviour close to  $T_c$  is an impurity effect since it slowly becomes more pronounced with the length of time the sample is held at temperatures near  $T_{AC}$ . It should be noted that the first-order SmA–I transition, which is more sensitive to impurity effects, shows a slow downward drift in  $T_{AI}$  of about  $-0.007 \text{ K day}^{-1}$  but the width of the SmA+I two-phase coexistence region remains constant.

In spite of the anomalous behaviour close to the transition, it is possible to carry out a power-law analysis of the excess heat capacity  $\Delta C_p$  associated with the SmA–SmC transition. The observed heat capacity  $C_p$  is given by

$$C_p = \Delta C_p + C_p(\text{background}) \quad (1)$$

$$= A^\pm |t|^{-\alpha} (1 + D^\pm |t|^{0.5}) + B_c + B_r + Et \quad (2)$$

where  $C_p(\text{background})$  represents the underlying low- $T$  tail of the SmA–I heat capacity. Since the SmA–I and SmA–SmC transitions are well separated (by  $\sim 23.6 \text{ K}$ ) and the SmA  $C_p$  wing of the SmA–I feature is not very large or rapidly varying, this background can be well approximated by the linear expression  $B_r + Et$ . The quantity  $\alpha$  is the critical heat capacity exponent that characterizes the singular  $\Delta C_p$  behaviour, and  $B_c$  is a critical contribution to the nonsingular behaviour. In a

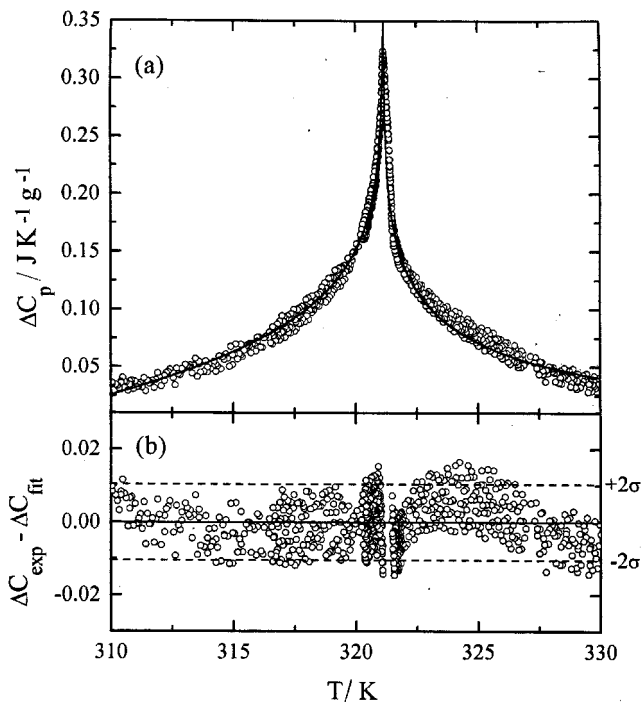


Figure 2. (a) Excess heat capacity  $\Delta C_p$  associated with the SmA–SmC transition. The data points represent  $C_p$  values minus the background  $C_p$  line  $B_r + Et$  shown in figure 1. The solid line represents fit 2 in the table. (b) A deviation plot of the points used for fit 2 with  $\pm 2\sigma$  limits, where  $\sigma$  is the standard deviation.

fit of  $C_p$  data with equation (2), one obtains only the sum  $B \equiv B_c + B_r$ , but  $B_r$  can be estimated as described below, which allows an evaluation of  $B_c$ .

The  $C_p$  data in figure 1 were least-squares fit with equation (2) without corrections-to-scaling terms (i.e.  $D^\pm \equiv 0$ ) over two temperature ranges: range A with  $|t|_{\max} = 1.5 \times 10^{-2}$  (316.25–326.03 K) and a broader range B with  $-3.5 \times 10^{-2} < t < 2.8 \times 10^{-2}$  (310–330 K). In both cases, anomalous data in the range 321.097–321.470 K ( $t_{\min} \approx -1.6 \times 10^{-4}$  and  $+1.0 \times 10^{-3}$ ) were omitted from the fits. Due to this relatively large gap near  $T_c$ , the  $\chi^2_{\nu}$  minimum is quite broad, and 40 fits were carried out for each range with the critical exponent  $\alpha$  fixed at values 0.02 apart between  $-0.3$  and  $+0.5$ . On the basis of the F test, the best least-squares values of  $\alpha$  with 90% confidence limits are  $\alpha = 0 \pm 0.08$  for range A and  $\alpha = 0 \pm 0.10$  for range B. Not only is the  $\chi^2_{\nu}$  value significantly worse for  $\alpha$  equal to  $+0.1$  or  $-0.1$ , but the systematic deviations also support an  $\alpha$  value close to zero. For both  $\alpha = +0.1$  and  $-0.1$ , the deviations below  $T_c$  are clearly worse than those for  $\alpha \approx 0$ . Above  $T_c$ , the deviations are worse ( $\alpha = +0.1$ ) or comparable ( $\alpha = -0.1$ ) to those for  $\alpha \approx 0$ . The best least-squares exponent values are consistent with the 3D-XY exponent  $\alpha_{XY} = -0.007$ , and fits were made with  $\alpha$  held fixed

at this value. The resulting values of the adjustable parameters are given in the table for both fitting ranges.

Although the  $\chi^2_{\nu}$  value is smaller for fit 1 (range A) than for fit 2 (range B), the slope  $E = 2.23 \text{ J K}^{-1} \text{ g}^{-1}$  obtained for fit 1 is too large to be physically reasonable for the background  $C_p$  slope. Thus fit 2 is more realistic. However, the important point is that both fits yield the same critical exponent value when  $\alpha$  is allowed to be a freely adjustable variable. The quality of fit 2 is shown in figure 2, where the excess SmA–SmC heat capacity  $\Delta C_p$  is given, together with a deviation plot of  $\Delta C_p(\text{exp}) - \Delta C_p(\text{fit})$ . In order to obtain  $\Delta C_p$  from equation (1),  $C_p(\text{background})$  was taken to be  $2.076 + 1.51t$ , where the  $E = 1.51 \text{ J K}^{-1} \text{ g}^{-1}$  value is taken directly from fit 2 and  $B_r = 2.076 \text{ J K}^{-1} \text{ g}^{-1}$  is obtained by matching  $C_p(\text{background})$  to the high-temperature  $C_p$  data in figure 1. This  $B_r$  estimate yields  $B_c = B - B_r = 6.854 \text{ J K}^{-1} \text{ g}^{-1}$  for the representation of  $\Delta C_p$  with fit 2 parameters. Inspection of figure 1 shows that the choice of the fit 1 slope  $E = 2.23$  will result in  $\Delta C_p$  values in the SmC phase that decrease on cooling from  $T_c$  to  $\sim 312 \text{ K}$  and then increase on further cooling. This is inconsistent with the overall behaviour required for excess pretransitional heat capacities.

The region of anomalous  $C_p$  values that deviate from power-law behaviour in the region just above  $T_c$  is clearly shown in figure 2, and similar anomalies were observed on other runs. The deviation plot indicates an excellent fit for  $T < T_c$  and the presence of a slight systematic character for the differences when  $T > T_c$ . Additional fits were also tried with the inclusion of the correction terms in equation (2), i.e.  $D^\pm$  allowed to be freely adjustable parameters. The quality of these fits was not significantly better than those of fits 1 and 2 and the effective  $\alpha$  values were still  $\alpha \approx 0$ . Furthermore, the  $D^\pm$  values are strongly coupled with the  $E$  value, and physically appropriate  $E$  values imply quite small  $D^\pm$  values. Thus there is no evidence that corrections-to-scaling terms play a major role or alter the  $\alpha$  values.

Finally, one can inspect the consistency of the fit parameters in the table with expectations based on 3D-XY theory and experiments on N–SmA transitions with XY character. For the XY universality class, the

Table. Adjustable parameter values from least-squares fitting of  $C_p$  with equation (2). In these fits,  $\alpha$  was held fixed at  $\alpha_{XY} = -0.007$  and  $D^\pm \equiv 0$ . The units of  $A^\pm$ ,  $E$  and  $B \equiv B_c + B_r$  are  $\text{J K}^{-1} \text{ g}^{-1}$ . The values of  $|t|_{\max}$  are  $1.5 \times 10^{-2}$  for range A and  $\sim 3 \times 10^{-2}$  for range B.

Fit	Range	$T_c/\text{K}$	$A^+$	$A^-/A^+$	$B$	$E$	$\chi^2_{\nu}$
1	A	321.141	-6.83	0.994	8.763	2.23	1.22
2	B	321.135	-7.00	0.995	8.930	1.51	1.52

amplitude ratio has the universal theoretical value  $A^-/A^+ = 0.9714 \pm 0.0126$  [13] and N-SmA liquid crystal experimental values are  $A^-/A^+ = 0.99 \pm 0.005$  [14]. These values agree well with the  $A^-/A^+$  values in the table. The ratio  $A^+/B_c$  is not truly universal, but five N-SmA liquid crystals with XY character yield  $A^+/B_c$  values in the narrow range  $-1.038$  to  $-1.053$  [13]. This compares fairly well with the ratio  $A^+/B_c = -7.00/6.85 = -1.02$  for fit 2. Thus, the present data are fully consistent with 3D-XY behaviour.

### 3. Discussion

It is clear from figures 1 and 2 that the excess heat capacity associated with the SmA-SmC transition in H8F(4,2,1)MOPP exhibits substantial critical fluctuation effects.  $\Delta C_p(\text{SmA-SmC})$  for this compound is almost the same above and below  $T_c$ , in contrast to a mean-field SmA-SmC transition for which  $\Delta C_p = 0$  for  $T > T_c$ . This fluctuation behaviour is qualitatively confirmed by the substantial temperature dependence of the thermal expansion coefficient for the smectic layer thickness over a wide temperature range *above*  $T_c$  [15].

Due to the anomalous behaviour of  $C_p$  close to  $T_c$ , which led to a gap in the fitting range from  $T_c - 0.04$  K to  $T_c + 0.33$  K, there is a fairly large uncertainty of  $\pm 0.10$  in the least-squares exponent value  $\alpha = 0.0$ . However, as discussed in §2, the data are consistent with 3D-XY behaviour over a 20 K range. The present results differ from earlier reports of SmA-SmC fluctuation behaviour, where  $\Delta C_p$  above  $T_c$  was much smaller than  $\Delta C_p$  below  $T_c$  [10, 11]. In the case of  $C_p$  data for H10F5MOPP, Reed *et al.* [10] analysed their  $\Delta C_p$  variation with an additive combination of a mean-field model plus Gaussian fluctuation terms that gave rise to a very small  $\Delta C_p$  contribution above  $T_c$ . The calorimetric studies of Ema and coworkers show that racemic MHPOBC exhibits a Gaussian tricritical  $\Delta C_p(\text{SmA-SmC})$  behaviour [16] whereas  $\Delta C_p(\text{SmA-SmC}_\alpha^*)$  for chiral MHPOBC and related compounds crosses over from 3D-XY critical behaviour close to  $T_c$  ( $t_{\max} \approx 10^{-3}$ ) to Gaussian tricritical in the wings ( $t_{\max} \approx 10^{-2}$ ) [11].

Presumably critical fluctuations seen at the SmA-SmC transition in H8F(4,2,1)MOPP and the other compounds cited above are due to a small value for the bare correlation length  $\xi_0$  relative to the usual value of  $\sim 20$  Å [8, 9]. Since the Ginzburg temperature  $t_G \sim \Delta C_{MF}^2 \xi_0^{-6}$  [17], where  $\Delta C_{MF}$  is the mean-field jump at  $T_c$ , the value of  $t_G$  is very sensitive to  $\xi_0$ . As a hypothetical example, a change in  $\xi_0$  from 20 to 5 Å with a constant  $\Delta C_{MF}$  value would increase  $t_G$  from  $\sim 1 \times 10^{-5}$  to  $\sim 4 \times 10^{-2}$ . The latter would mean that critical behaviour should dominate over the entire temperature range investigated.

X-ray studies of H10F5MOPP and its homologues [18], in which one tail is perfluorinated and the other protonated, show evidence of a statistically antiparallel alignment of neighbouring molecules in both the SmA and SmC phases. The thermal expansion coefficient for the layer spacing exhibits typical SmC behaviour for  $T < T_c$ , but within the resolution of these experiments a small negative expansion coefficient with no temperature dependence is observed for  $T > T_c$ . This is consistent with the very narrow range of excess heat capacity observed in H10F5MOPP above  $T_c$  [10]. For the case of H8F(4,2,1)MOPP, not only is the perfluorinated tail bulkier than the alkyl tail but the presence of two ether linkages should produce greater flexibility and thus more complex conformations (i.e. a cone shape rather than an ellipsoid). A complex molecular packing in the smectic layer is thought to cause the anomalous layer compression observed in H8F(4,2,1)MOPP films [19], and such complex packing is consistent with the fact that bulk H8F(4,2,1)MOPP forms a smectic glass rather than freezing into a crystal. Any such complex and varied molecular configurations and smectic packing could cause a marked decrease in the correlation lengths. High-resolution X-ray and optical studies of H8F(4,2,1)MOPP would be of great value in completing the characterization of the critical fluctuations near this SmA-SmC transition.

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### References

- [1] DE GENNES, P. G., 1973, *Mol. Cryst. liq. Cryst.*, **21**, 49.
- [2] HUANG, C. C., and VINER, J. M., 1982, *Phys. Rev. A*, **25**, 3385.
- [3] HUANG, C. C., and DUMRONGRATTANA, S., 1986, *Phys. Rev. A*, **34**, 5020 and references therein.
- [4] GARLAND, C. W., 1992, *Phase Transitions in Liquid Crystals*, edited by S. Martellucci and A. N. Chester (New York: Plenum Press), NATO ASI Ser. B290, Chap. 11 and references therein.
- [5] LIU, H. Y., HUANG, C. C., BAHR, CH., and HEPPKE, G., 1988, *Phys. Rev. Lett.*, **61**, 345.
- [6] CHAN, T., BAHR, CH., HEPPKE, G., and GARLAND, C. W., 1993, *Liq. Cryst.*, **13**, 667.
- [7] THOEN, J., 1995, *Int. J. mod. Phys. B*, **9**, 2157.
- [8] SAFINYA, C. R., KAPLAN, M., ALS-NIELSEN, J., BIRGENEAU, R. J., DAVIDOV, D., LITSTER, J. D., JOHNSON, D. L., and NEUBERT, M. E., 1980, *Phys. Rev. B*, **21**, 4149.

- [9] BIRGENEAU, R. J., GARLAND, C. W., KORTAN, A. R., LITSTER, J. D., MEICHLE, M., OCKO, B. M., ROSENBLATT, C., YU, L. J., and GOODBY, J., 1983, *Phys. Rev. A*, **27**, 1251.
- [10] REED, L., STOEBE, T., and HUANG, C. C., 1995, *Phys. Rev. E*, **52**, R2157.
- [11] EMA, K., and YAO, H., 1998, *Phys. Rev. E*, **57**, 6677, and references therein.
- [12] GARLAND, C. W., 1985, *Thermochim. Acta*, **88**, 127; YAO, H., CHAN, T., and GARLAND, C. W., 1995, *Phys. Rev. E*, **51**, 4585.
- [13] BERVILLIER, C., 1986, *Phys. Rev. B*, **34**, 8141.
- [14] GARLAND, C. W., NOUNESIS, G., and STINE, K. J., 1989, *Phys. Rev. A*, **39**, 4919; GARLAND, C. W., NOUNESIS, G., YOUNG, M. J., and BIRGENEAU, R. J., 1993, *Phys. Rev. E*, **47**, 1918.
- [15] RADCLIFFE, M. D., private communication; EPSTEIN, K. A., RADCLIFFE, M. D., BROSTROM, M. L., RAPPAPORT, A. G., THOMAS, B. N., and CLARK, N. A., 1993, abstract, 4th International Conference on Ferroelectric Liquid Crystals.
- [16] EMA, K., TAKAGI, A., and YAO, H., 1996, *Phys. Rev. E*, **53**, R3036; EMA, K., TAKAGI, A., and YAO, H., 1997, *Phys. Rev. E*, **55**, 508.
- [17] GINSBURG, V. L., 1960, *Sov. Phys. Solid State*, **2**, 1824.
- [18] RIEKER, T. P., and JANULIS, E. P., 1994, *Liq. Cryst.*, **17**, 681; RIEKER, T. P., and JANULIS, E. P., 1995, *Phys. Rev. E*, **52**, 2688.
- [19] MACH, P., JOHNSON, P. M., WEDELL, E. D., LINTGEN, F., and HUANG, C. C., 1997, *Europhys. Lett.*, **40**, 399.