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# Experimental Studies of Liquid Crystal Phase Transitions

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Some recent experiments that have been carried out at M.I.T. provide results that illustrate the effect of thermal fluctuations on order-disorder phase transitions.

## INTRODUCTION

Recent experimental and theoretical work in statistical mechanics has elucidated the important role of spatial dimensionality on the types and properties of condensed phases in which matter can exist. We now have some understanding how the symmetry and dimension of a system determines the effect of thermally excited fluctuations. There is an upper marginal dimension $d^*$; when $d > d^*$ the effect of thermal fluctuations is weak and can be ignored. Consequently a mean-field of Landau approximation is adequate for statistical mechanical calculations and most such problems can be easily solved. There is also a lower marginal $d^\circ$; when $d < d^\circ$ the fluctuations are strong enough to prevent the establishment of long range order which interactions between the molecules or atoms would otherwise favor. The region $d^\circ < d < d^*$, which we shall call the moderate fluctuations region, is where one observes behavior commonly known as critical phenomena. Here, the fluctuations do not prevent long range order but they cause the properties near the phase transition to differ quantitatively from mean-field behavior. Renormalization group methods have provided very good approximate calculations of the statistical mechanics of systems in the moderate fluctuation régime. At this conference we should like to discuss the results

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of some recent experiments at M.I.T. on the properties of smectic liquid crystals; the experiments we have chosen will illustrate cases of weak, moderate, and strong fluctuations.

## NEMATIC TO SMECTIC A TRANSITIONS

The smectic A (SmA) phase of liquid crystals[1] results from the establishment of a one-dimensional density wave in a three-dimensional liquid; the wave vector is parallel to the nematic (N) director ($z$ axis). The SmA order parameter $\psi = |\psi|e^{i\phi}$ may be defined by writing the density as

$$\rho = \rho_0[1 + \mathrm{Re}(\psi e^{iq_0 z})] \tag{1}$$

where $q_0$ is the wave vector of the density wave. A central focus for understanding the N to SmA transition has been the analogy to a charged superfluid proposed by de Gennes[2] and McMillan.[3] The order parameter associated with such a transition has two degrees of freedom (in the case of an $n$-vector model this corresponds to $n = 2$, i.e., an $X$-$Y$ model). Since $d^* = 4$ it is an example of the moderate fluctuation case and one expects pretransition critical behavior analogous to that seen in $^4$He near its lambda point. Fluctuations in the short range smectic order in the nematic phase will be characterized by correlation lengths $\xi_{\|} = \xi_{\|}^0 t^{-\nu_{\|}}$ and $\xi_{\perp} = \xi_{\perp}^0 t^{-\nu_{\perp}}$ along and normal to the nematic director, respectively. Here $t = T/T_c - 1$ is the reduced temperature, and the exponents $\nu_{\|}$ and $\nu_{\perp}$ should both have the value 0.67 if the $^4$He analogy is valid. The nematic bend elastic constant should have a divergence proportional to $\xi_{\|}$, in analogy with fluctuation diamagnetism in superconductors.[2] A divergence in the heat capacity of the form $At^{-\alpha}$ with $\alpha \simeq 0$ (almost logarithmic divergence) should also be observed if the $^4$He analogy holds. These predictions have been extensively tested in experiments carried out at M.I.T. and elsewhere.

The picture of the N-SmA transition which has emerged from these experiments is that the $^4$He analogy provides a very close description of short-range-order effects in the N phase, but that it may not be quite exact. Measurements of the correlation length $\xi_{\|}$ by x-ray and light scattering[4,5] show $\nu_{\|}$ to be close to the $^4$He result, but x-ray scattering (for technical reasons,[4] $\nu_{\perp}$ cannot reliably be determined by light scattering) suggests $\nu_{\perp}$ is somewhat smaller than 0.67 ($\nu_{\perp} = 0.51 \pm 0.04$ in octylcyanobiphenyl or 8CB). The first heat capacity measurements[6] in biphenyl compounds seemed to confirm the $^4$He value $\alpha \simeq 0$, but recent experiments on higher purity samples[7–9] indicate that $\alpha > 0$, being as large as $\sim 0.25$. The reason for these departures from the $^4$He analogy are not yet understood, but it seems likely that in some liquid crystal compounds the experiments may be determining effective exponents

that result from the influence of a fixed point other than the helium ($n = 2$, $d = 3$) one. In the thiol-alkoxybenzoate series of compounds[10] this may be a tricritical point, and Lubensky and Chen[11] have proposed the influence of an anisotropic fixed point caused by coupling to nematic director fluctuations. This leads to a hyperscaling relation $\nu_{\|} + 2\nu_{\perp} = 2 - \alpha$ which appears to hold with experimental error.[7,9] However, calculations also predict[12] the director fluctuations will cause the N-SmA transition to be first order (in four dimensions, at least) while experiments[7] show any discontinuity must occur on a temperature scale $t < 10^{-5}$. Thus detailed numerical calculations using known material parameters are required to see if Lubensky's ideas can explain the apparent failure of the helium analogy in the biphenyl SmA compounds. We should also point out that the elastic constants B (for Sm layer compression) and D (for molecular tilt) in the SmA phase, which are the analogue of superfluid density, show behavior[4,13] at variance with any theoretical understanding.

Having summarized the present N-SmA situation we should like to discuss recent results on materials that exhibit reentrant SmA-N transitions on cooling. Pure 80CB has a N-SmA transition at 67.1°C, while 60CB has no smectic phase. Cladis and her collaborators first showed[14] that adding 60CB to 80CB lowered the N-SmA transition and gave rise to a reentrant N phase at lower temperatures, resulting in the phase diagram shown in Figure 1. We felt that a detailed study of this phase diagram might give insight into the effect of molecular interactions on the properties of SmA phases, and have carried out a high resolution ac calorimetric study[15] of the N-SmA phase transition in pure 80CB and mixtures containing 12, 20, and 25 weight % 60CB. The results of these measurements are shown in Figure 2. The interesting result is that increasing 60CB concentration results in a greatly reduced heat capacity peak for the N-SmA transition. In fact for the 27% mixture both the normal and reentrant transitions are seen visually but are undetectable calorimetrically. (Crystallization prevented observation of the reentrant transition in lower concentrations of 60CB.) A more detailed analysis[15] shows that the observed N-SmA peaks $\Delta\tilde{C}_p = \tilde{C}_p(\text{obs}) - \tilde{C}_p(\text{background})$ have the same shape and may be plotted on top of one another by a simple scaling of the amplitude of $\Delta\tilde{C}_p$. Thus it seems as if the amplitude A is reduced while the exponent $\alpha$ remains unchanged as 60CB is added. By light scattering from the director modes with $\mathbf{q} = q_z$, we were able to determine the behavior of the bend elastic constant $K_3$. The divergent part of $K_3$ has been shown theoretically[16] to follow the expression

$$\tilde{K}_3 = \frac{kTq_0^2}{8qz}\left[\left(1 + \frac{1}{X^2}\right)\tan^{-1} X - \frac{1}{X}\right] \tag{2}$$

where $X = (1/2)q_z\xi_{\|}$. This expression has been verified experimentally[17]

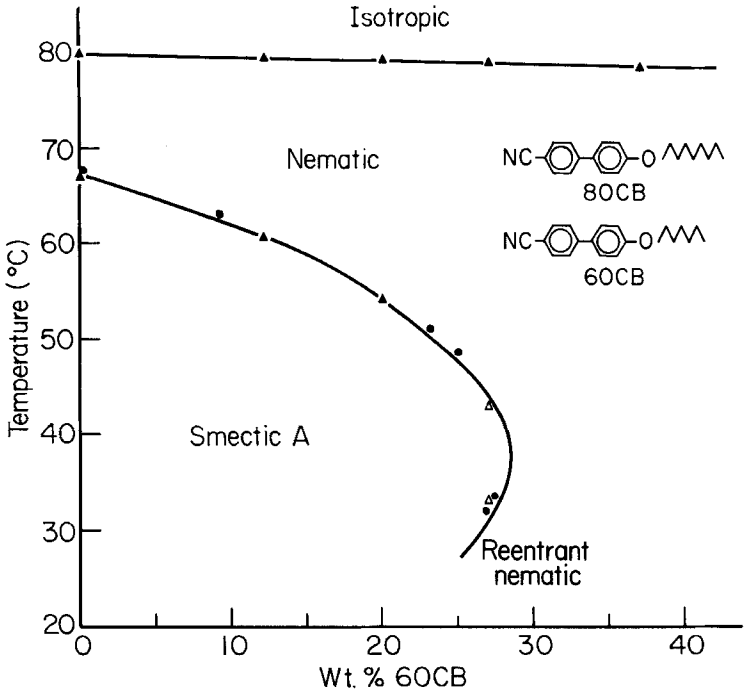


FIGURE 1 The nematic-smectic-reentrant nematic phase diagram of 60CB/80CB mixtures. Solid triangles indicate the transitions observed calorimetrically and open triangles transitions observed visually but not detectable calorimetrically. Solid circles indicate the transitions studied by light scattering.

and if $\tilde{K}_3$ can be measured at large enough values of $X$ it enables one to determine both the exponent $\nu_{\|}$ and the amplitude $\xi_{\|}^0$ for the longitudinal correlation length. We have carried out measurements[1] in pure 80CB and mixtures containing 9.1, 23.1, 25.2, 25.3 weight % of 60CB. All quantities in Eq. (2) except $\xi_{\|}^0$ and $\nu_{\|}$ were independently measured; these two were used as adjustable parameters to fit the data. We found $\nu_{\|} = 0.67 \pm 0.04$ at all concentrations and in both the normal and reentrant nematic phases. Our value of $\xi_{\|}^0 = 4 \pm 4$ Å in pure 80CB compares well with the x-ray value[4] of 4.5 Å. As the amount of 60CB increased, so did the amplitude $\xi_{\|}^0$. The values are shown in Figure 3 as a function of the McMillan parameter[3] $T_{NA}/T_{NI}$ which is a measure of the degree of nematic order at the N-SmA phase transition. A more detailed analysis of these results will be published elsewhere.

It is interesting to examine these results in terms of the hypothesis of two-scale-factor universality,[19] which in this system would require $A\xi_{\|}^0(\xi_{\perp}^0)^2$ to be a constant. On the basis of our data for $\tilde{C}_p$ and $\xi_{\|}^0$, this hypothesis indicates

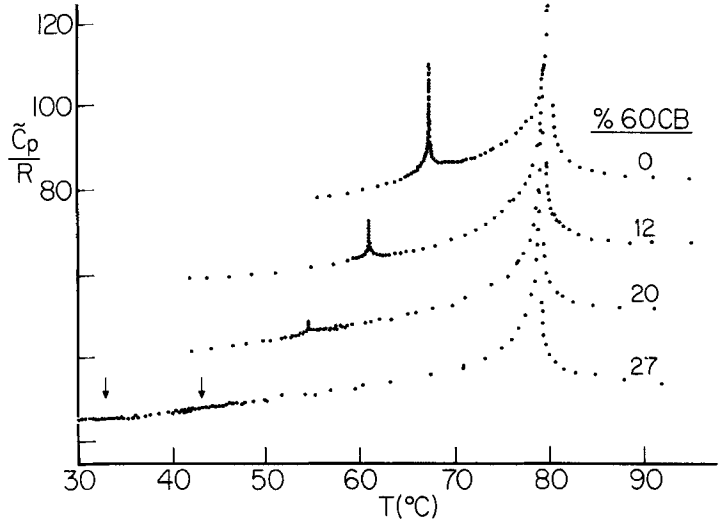


FIGURE 2 Measurements of $C_p$ in 80CB/60CB mixtures. The different mixtures correspond to the triangles of Figure 1, and the arrows for the 27% mixture indicate where the transitions were observed optically.

that $\xi_\perp^0$ is independent of 60CB concentration. X-ray measurements of $\xi_\perp^0$ for 80CB 60CB mixtures are now in progress to test the two-scale-factor universality hypothesis.

## LANDAU-PEIERLS STATE IN SMECTICS

We turn now to discuss an experiment[20] which demonstrates the effect of strong fluctuations. In the 1930's Landau[21] and Peierls[22] predicted that fluctuations of the Goldstone modes arising from an ordered state would destroy that order if the space dimensionality were low enough ($d < d^\circ$, where $d^\circ = 2$ for solids). Quite analogous effects can occur in three dimensions in smectic A liquid crystals, as we shall now explain.

The Goldstone mode arising from smectic A ordering corresponds to fluctuations in the layer displacement $u(\mathbf{r})$ (the phase of the order parameter can be written $\phi = q_0 u$). Using the Landau-de Gennes free energy it is quite straightforward to show that the dispersion relation for these fluctuations is[1]

$$\hbar\omega(\mathbf{q}) = \tfrac{1}{2}[K_1 q_\perp^4 + \mathrm{B} q_\parallel^2] \tag{3}$$

where $K_1$ is the splay elastic constant and B is the compressibility of the smectic layers. The unusual anisotropy in Eq. (3) arises from the fact that the layers are quite free to slide on one another; thus the wave vector $\mathbf{q}$ is normal

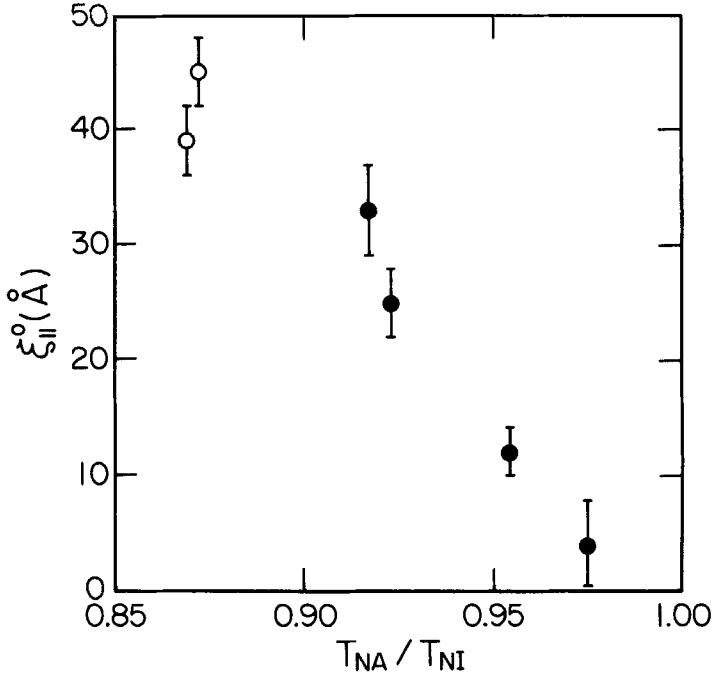


FIGURE 3 The amplitude $\xi_{\parallel}^{0}$ for the diverging longitudinal correlation length of smectic A short range order in 80CB/60CB mixtures. The abscissa is the McMillan parameter $T_{NA}/T_{NI}$. Solid points are values on the upper phase boundary, open circles on the lower (reentrant) boundary.

to the director ($q_{\parallel} = 0$) the only restoring force arises from curvature of the layers or splay of the director. This has a profound effect on the properties of smectic A (and also C) phases, for if we calculate the mean squared fluctuations in $u$ the result is

$$\langle u^2 r(\mathbf{r})\rangle = \frac{kT}{(2\pi)^3}\int \frac{d^3q}{Bq_{\parallel}^2 + K_1 q_{\perp}^4}. \tag{4}$$

For a sample of dimension $L$ we obtain an approximate answer by integrating over the region $(2\pi/L) < q < q_0$ and readily obtain

$$\langle u^2(r)\rangle \simeq \frac{kT}{4(B/K_1)^{1/2}} \ln(q_0 L) \tag{5}$$

Thus in three dimensions this simple calculation gives the same logarithmic singularity from long wavelength Goldstone modes as one expects for solids in two dimensions.[21,22]

If we study this effect by means of x-ray scattering what we observe is not

$\langle u^2(\mathbf{r})\rangle$ but the Fourier transform $S(\mathbf{q})$ of the correlation function

$$G(\mathbf{r}) = \langle e^{iq_0[u(\mathbf{r})-u(0)]}\rangle. \tag{6}$$

Then the momentum transfer $\mathbf{q}$ is measured relative to the SmA density wave value $\mathbf{q}_0 = q_0\hat{z}$. The form of $G(\mathbf{r})$ has been calculated by Caillé[23] in the harmonic approximation to be

$$G(\mathbf{r}) \sim \frac{1}{(x^2+y^2)^{\eta}} e^{-\eta E_1(x^2+y^2/4\lambda z)} \tag{7}$$

where $\lambda_2 = K_1/B$ is the analogue of the penetration depth in a superconductor, $\eta = (kTq_0^2/8\pi\lambda B)$, and $E_1$ is the exponential integral. From the properties of $E_1$, it is apparent that $G(\mathbf{r})$ does not extend to infinity (as it would for long range order) but decays algebraically with distance:

$$G(r) \sim \frac{1}{r_\perp^{2\eta}} \qquad (r_\perp \gg r_\parallel) \tag{8a}$$

$$\sim \frac{1}{r^{\eta}} \qquad (r_\parallel \gg r_\perp). \tag{8b}$$

This means the scattering from the SmA density wave is not a Bragg peak but a power law singularity of the form $q_\parallel^{-2+\eta}$ (for $q_\perp = 0$) and $q_\perp^{-4+2\eta}$ (for $q_\parallel = 0$). To observe this in an experiment is rather delicate because even perfect crystals have scattering tails that fall off as $q^{-2}$; since $\eta$ will be small it would be difficult to distinguish the expected scattering from that due to a Bragg peak. To circumvent this problem, channel-cut crystals with three Bragg reflections (and therefore $q^{-6}$ tails) were used for collimation. The resolution function of the spectrometer was carefully measured, its real space transform multiplied by $G(r)$ in the form given in Eq. (7) and the result numerically transformed into reciprocal space and fit to the data by a nonlinear least squares method. It should be possible to describe the normalized data in terms of two parameters, $\lambda$ and $\eta$ of Eq. (7). Since we know $\lambda$ from light scattering measurements,[4] only $\eta$ was allowed to vary as a freely adjustable parameter. In Figure 4 we show the spectrometer resolution function and the resulting fits for data at two different reduced temperatures. In Table I we give the results for 80CB from our analysis. Knowing these parameters it

TABLE I

Parameters obtained from analysis of Landau–Peierls scattering in 80CB

| $t$ | $\lambda q_0$ | $\eta$ | $K_1$(dynes) | $B$ (erg/cm$^3$) |
|---|---|---|---|---|
| $-9.0 \times 10^{-4}$ | 3.9 | $0.17 \pm 0.02$ | $(8.4 \pm 1) \times 10^{-7}$ | $(2.2 \pm 0.3) \times 10^7$ |
| $-5.9 \times 10^{-4}$ | 4.2 | $0.23 \pm 0.02$ | $(7.1 \pm 0.6) \times 10^{-7}$ | $(1.5 \pm 0.2) \times 10^7$ |
| $-4 \times 10^{-6}$ | 8 | $0.38 \pm 0.06$ | $(7.7 \pm 2) \times 10^{-7}$ | $(4.7 \pm 0.8) \times 10^6$ |

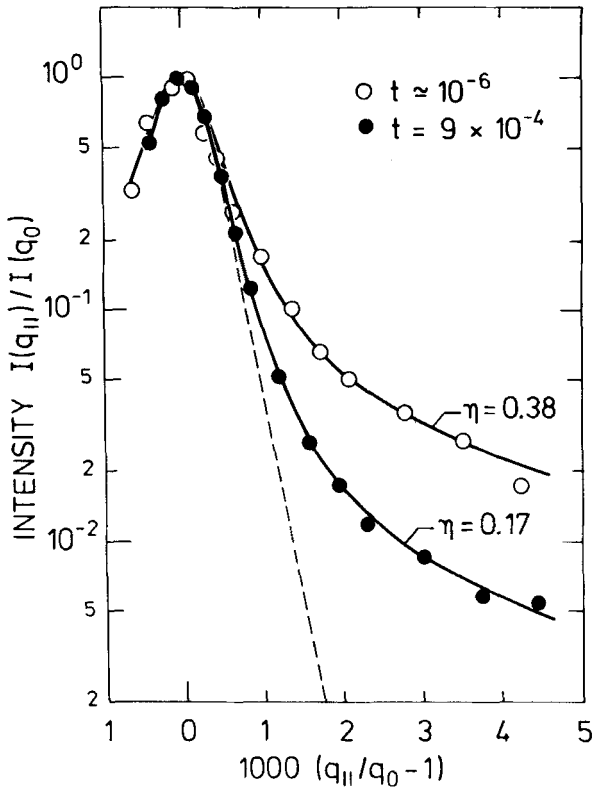


FIGURE 4 The intensity profile for x-ray scattering from the SmA density wave in 8OCB at two different reduced temperatures. The dashed curve is the measured spectrometer resolution function, as would be seen for true Bragg scattering. The solid curves are a convolution of the resolution function with the Fourier transform of Eq. (6) in the text.

is possible to determine the elastic constants B and $K_1$ which are also given in the table. The results are in excellent agreement with the value $K_1 = (6.8 \pm 0.7) \times 10^{-7}$ dynes obtained by Karat and Madhusudana.[24]

This experiment represents the first observation of the algebraically decaying correlation functions predicted to occur in the case of strong fluctuations. However the situation in the SmA phase is rather complex and we should not conclude, as one would from the simple Landau-Peierls arguments, that $d^\circ = 3$ for the SmA phase. Halperin and Lubensky can mathematically transform[12] to a gauge in which the order parameter, although not the one experimentally observed, does have true long range order. This cannot be done for two-dimensional solids. Also, for systems with $d^\circ = 2$ theory does not predict observable singularities in the heat capacity such as are clearly present for the N-SmA transition. We conclude that the SmA phase

does have algebraically decaying correlations in the physically observable density wave, but that a completely satisfactory theoretical understanding of this interesting phase still eludes us.

## SMECTIC A TO SMECTIC C TRANSITION

This is a transition of the $n = 2$ type and should therefore have $d^* = 4$; it has been studied in various materials by several different laboratories with reports of both critical (moderate fluctuation) and mean-field (weak fluctuation) behavior. We should like to discuss briefly some experiments carried out at M.I.T. on pentylphenylthiol-octyloxybenzoate, $\overline{8}S5$, by means of x-ray[25] and light[26] scattering.

In the SmA-SmC transition, the smectic density wave acquires a tilt with respect to the nematic director; this is a second order transition in $\overline{8}S5$ with a jump in the specific heat[27] of $\Delta C \simeq 10^6$ erg/cm$^3$ K. The x-ray scattering measurements were carried out with the director held fixed in a field of 6 KOe; thus it was possible to measure simultaneously the tilt angle of the SmC density wave (which is the order parameter) and the layer spacing. Over the range $-5 \times 10^{-3} < t < -3 \times 10^{-5}$, the order parameter followed a power law $(-t)^{\beta}$ with $\beta = 0.47 \pm 0.04$. This effective exponent is very close to the value ($\beta = 0.50$) expected for mean-field behavior. Thus the SmA-SmC transition in $\overline{8}S5$ appears to be one in which fluctuations are unimportant. This can be understood in terms of an argument originally given by Ginsburg.[28] Even though critical behavior must obtain as $t \to 0$, Ginsburg's criterion would argue that mean-field behavior will be observed if the magnitude of $t$ is greater than

$$t_c = k_B^2/[32\pi^2(\xi_{\parallel}^0)^2(\xi_{\perp}^0)^4(\Delta C)^2] \tag{9}$$

where $\xi_{\parallel}^0$ and $\xi_{\perp}^0$ are the amplitudes for the diverging correlation lengths for fluctuations in smectic C order. These correlation lengths are given in terms of the SmA phase elastic constants as $\xi_{\parallel} = (K_3/D)^{1/2}$ and $\xi_{\perp} \simeq [(K_1 + K_2)/2D]^{1/2}$. The phase transition is driven by $D$ going to zero in the SmA phase; $D \sim t$ in the mean-field situation. By light scattering from director modes we were able to measure $D \sim t^{\gamma}$ with $\gamma = 1.1 \pm 0.12$, $\xi_{\parallel}^0 = 13.5 \pm 2$ Å, and $\xi_{\perp}^0 = 21 \pm 9$ Å. The pretransitional effects in the SmA phase also seem quite close to mean-field behavior (over the range $2 \times 10^{-5} < t < 3 < 10^{-3}$). Substituting these values into Eq. (9) we estimate $t_c$ to lie in the range $2 \times 10^{-5}$ to $2 \times 10^{-6}$ so that our observation of mean-field exponents is consistent with the Ginsberg criterion. In other compounds[29] the experiments suggest critical behavior, but also smaller values of $\xi_0$ so that the results appear to be consistent with the Ginsburg criterion. It thus appears that truly asymptotic behavior at the SmA-SmC transition would show thermodynamic

divergences consistent with moderate fluctuations but, for reasons we understand quantitatively, the experimentally accessible region in many materials gives effective exponents quite close to the weak fluctuation (mean-field) limit. It would be useful to have a quantitative theory for behavior near Ginsburg's crossover value of $t_c$.

## CONCLUSIONS

We have presented data to illustrate current ideas about the importance of thermal fluctuations in order-disorder phase transitions and also the fact that the rich variety of phases that occur in liquid crystals can be used to elucidate modern concepts in statistical mechanics.

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### References

1. P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford University Press, 1974, London.
2. P. G. de Gennes, *Sol. St. Comm.*, **10**, 753 (1972).
3. W. McMillan, *Phys. Rev.*, **A4**, 1238 (1971).
4. J. D. Litster, J. Als-Nielsen, R. J. Birgeneau, S. S. Dana, D. Davidov, F. Garcia-Golding, M. Kaplan, C. R. Safinya, and R. Schaetzing, *J. de Phys.*, **40**, C3–339 (1979).
5. D. Davidov, C. R. Safinya, M. Kaplan, S. S. Dana, R. Schaetzing, R. J. Birgeneau, and J. D. Litster, *Phys. Rev.*, **B19**, 1657 (1979).
6. D. L. Johnson, C. F. Hayes, R. J. deHoff, and C. A. Schantz, *Phys. Rev.* **B18**, 4902 (1978).
7. C. W. Garland, G. B. Kasting, and K. J. Lushington, *Phys. Rev. Lett.*, **43**, 1420 (1979) and G. B. Kasting, K. J. Lushington, and C. W. Garland, *Phys. Rev. B*, in press for June 1980.
8. L. D. LeGrange and J. M. Mochell, *Phys. Rev. Lett.*, **45**, 35 (1980).
9. Ichiro Hatta and Takao Nakayama, Paper presented at 8th International Conference on Liquid Crystals, Kyoto, 1980 (to be published in Molecular Crystals and Liquid Crystals).
10. D. Brisbin, R. DeHoff, T. E. Lockhart, and D. L. Johnson, *Phys. Rev. Lett.*, **43**, 1171 (1979).
11. T. C. Lubensky and J.-H. Chen, *Phys. Rev.*, **B17**, 366 (1978).
12. B. I. Halperin and T. C. Lubensky, *Sol. St. Comm.*, **14**, 997 (1974).
13. H. Birecki, R. Schaetzing, F. Rondelez, and J. D. Litster, *Phys. Rev. Lett.*, **36**, 1376 (1976).
14. D. Guillon, P. E. Cladis, and J. Stamatoff, *Phys. Rev. Lett.*, **41**, 1598 (1978).
15. K. J. Lushington, G. B. Kasting, and C. W. Garland, *Phys. Rev.* **B22**, 2569 (1980) **B**, in press.
16. F. Jähnig and F. Brochard, *J. de Phys.*, **35**, 301 (1974).
17. H. Birecki and J. D. Litster, *Mol. Cryst. Liq. Cryst.*, **42**, 33 (1977).
18. R. Schaetzing, D. Davidov, and J. D. Litster, unpublished.
19. P. C. Hohenberg, A. Aharony, B. I. Halperin, and E. D. Siggia, *Phys. Rev.*, **B13**, 2986 (1976).
20. J. Als-Nielsen, J. D. Litster, R. J. Birgeneau, M. Kaplan, and C. R. Safinya, in *Ordering in Strongly Fluctuating Condensed Matter Systems*, T. Riste, ed. (Plenum, New York 1980), p. 57.
21. L. D. Landau, in *Collected Papers of L. D. Landau*, D. ter Haar, ed. (Gordon and Breach, New York 1965), p. 209.

22. R. E. Peierls, *Helv. Phys. Acta*, 7, Suppl. No. 11, 81 (1934).
23. A. Caille, *Comptes Rendus Acad. Sci. (Paris)*, **274B**, 891 (1972).
24. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **47**, 21 (1978). These authors used an incorrect value for $\chi_a$, the diamagnetic anisotropy of the 80CB molecule; the correct value is $44 \times 10^{-6}$ cm$^3$/mole.
25. C. R. Safinya, M. Kaplan, J. Als-Nielsen, R. J. Birgeneau, D. Davidov, J. D. Litster, D. L. Johnson, and M. E. Neubert, *Phys. Rev.*, **B21**, 4149 (1980).
26. R. Schaetzing, Ph.D. Thesis, M.I.T. 1980 (unpublished).
27. C. A. Schantz and D. L. Johnson, *Phys. Rev.*, **A17**, 1504 (1978). These authors interpret their data as a cusp at the A–C transition, however data for $|t| < 5 \times 10^{-4}$ are consistent with a mean field jump $\Delta C = 10^6$ erg/cm$^3$ K.
28. V. L. Ginsburg, *Sov. Phys. Sol. State*, **2**, 1824 (1960).
29. M. Delaye, *J. de Phys.*, **40**, C3–350 (1979). Also Y. Galerne and G. Durand, private communication.