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Phil. Trans. R. Soc. Lond. A 1983 **309**, 145-153
doi: 10.1098/rsta.1983.0029

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Phil. Trans. R. Soc. Lond. A **309**, 145–153 (1983)
Printed in Great Britain

Structural studies of nematic and smectic phases

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The information about liquid crystal phases that can be obtained by light scattering and by high-resolution X-ray scattering is reviewed. Results for the nematic–smectic A transition suggest the de Gennes–McMillan model is correct, but adequate theoretical solutions to the model remain elusive. Recent results on the smectic A to smectic C transition are presented that show unambiguously that it exhibits classic mean-field behaviour and this is explained by a Ginzburg criterion argument. Some preliminary results of a study of a nematic–smectic A transition in a lyotropic material are given and indicate similarity to thermotropic materials.

1. Introduction

Nematic (N) phases of liquid crystals have long-range orientational order of molecules with rod-like anisotropy, but lack any positional order. The smectic A (SmA) and smectic C (SmC) phases have nematic order combined with a one-dimensional density wave along the director, or molecular orientation (SmA), or at an angle to it (SmC). The nematic–isotropic transition is rather well understood but the N–SmA transition remains one of the major unsolved problems in critical phenomena; it is also interesting as probably the simplest example of melting in three dimensions. The SmA–SmC transition is also interesting because it is expected to conform to the three-dimensional x–y model that is also thought to describe superfluid helium. This should have non-classical or non-mean-field behaviour, yet both classical and non-classical results have been reported by various investigators. In this paper I shall discuss results obtained by myself and my collaborators that elucidate these problems. I shall also mention some experiments on a lyotropic system of soap, water and ionic solute that show a neat soap to micellar transition quite analogous to a thermotropic N–SmA transition.

(*a*) *Some theoretical background*

Thanks to recent theoretical developments, largely arising from the work for which Kenneth Wilson received this year's Nobel Prize in Physics, we have an improved understanding of order–disorder-type phase changes. We believe that fundamental considerations like geometry and symmetry combine with thermally excited fluctuations to determine the nature of the phase changes. For most isotropic systems in four or more dimensions we believe that fluctuations are not important, so statistical mechanics calculations can be done by a simple mean-field approximation; we say that the upper marginality d^* is four. When the space dimension d is greater than d^*, classical behaviour occurs. If $d < d^*$ we have the region of critical phenomena; the fluctuations are importantly large and Wilson showed how to do statistical mechanics under these conditions. The physical idea is that fluctuations become correlated over long distances ξ so that behaviour is determined by the correlation length rather than the details of the interactions that produce order. In the Wilson, or renormalization group (r.g.), method the length

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scale of the problem is changed, short-wavelength fluctuations are integrated out, and thermodynamic quantities such as the free energy suitably rescaled. Frequently the problem becomes invariant under this procedure and a 'fixed point' has been reached. The result of the calculation then describes a system for which the correlation length ξ is infinite, which occurs at the phase transition point. Various approximate methods can then be used to calculate behaviour in the vicinity of the phase transition. Systems that all have the same mathematical fixed point should have identical physical behaviours and are in the same 'universality class'.

Finally, I should add that if $d < d^0$, where d^0 is the lower marginal dimensionality, the fluctuations are sufficiently important to prevent the establishment of order that interactions would otherwise favour. As an example, we believe that solids cannot exist in less than two dimensions. More pertinent to this paper, $d^0 = 3$ for SmA and SmC phases; this has been verified experimentally for the SmA phase (Als-Nielsen *et al.* 1980).

There is a rich variety of phase changes in liquid crystals and they may be studied to elucidate many of these ideas. The SmA–SmC transition has two degrees of freedom for the order parameter and should be in the 3D x–y model universality class. The de Gennes (1972)–McMillan (1971) model for an SmA is analogous to a changed superfluid and might also be thought to be in the 3D x–y class, but there are complications as we shall see presently.

2. SCATTERING FROM LIQUID CRYSTALS

Both X-rays and light can be scattered by thermal fluctuations in liquid crystals and thus used to study them. The smectic mass density waves scatter X-rays, whereas light is scattered primarily by molecular reorientations or the nematic director fluctuations; the two techniques provide different and complementary structural information about liquid crystal nematic and smectic phases.

To discuss the scattering quantitatively it is useful to have some formulae. We first consider the SmA–nematic transition. The SmA order parameter was defined by de Gennes (1972) by writing the density as

$$\rho(z) = \rho_0\{1 + \mathrm{Re}\,(\psi \mathrm{e}^{\mathrm{i}q_0 z})\}, \tag{1}$$

where the director $\hat{n}$ lies along $\hat{z}$. Then ψ has two degrees of freedom, which may be taken to be the amplitude and phase of the density wave, whose wave vector is $q_0\hat{z}$. A Landau or mean-field expansion of the free energy density may be written as

$$\phi_{\mathrm{s}} = \phi_0 + \tfrac{1}{2}a|\psi|^2 + \tfrac{1}{4}b|\psi|^4 + \frac{1}{2M_{\parallel}}|\partial_z\psi|^2 + \frac{1}{2M_{\perp}}|\{(\partial_x + \mathrm{i}q_0 n_x) + (\partial_y + \mathrm{i}q_0 n_y)\}\psi|^2 + \phi_{\mathrm{N}}, \tag{2}$$

where ϕ_{N} is the nematic free energy for small fluctuations in the director, namely

$$\phi_{\mathrm{N}} = \tfrac{1}{2}\{K_1(\nabla\cdot\hat{n})^2 + K_2(\hat{n}\cdot\mathrm{curl}\,\hat{n})^2 + K_3(\hat{n}\times\mathrm{curl}\,\hat{n})^2\}. \tag{3}$$

In (2), $\partial_z \equiv \partial/\partial_z$, etc., and the peculiar transverse gradient terms are required to make ϕ invariant under small rotations of the director and density wavevector together. The elastic constants in (3) were defined years ago by F. C. Frank (1958). As in any Landau theory, $a = a_0(T - T_{\mathrm{c}})$, whereas b is independent of temperature. In the SmA phase, bend $(\hat{n}\times\mathrm{curl}\,\hat{n})$ involves compressing the density wavelength, and twist $(\hat{n}\cdot\mathrm{curl}\,\hat{n})$ would involve a tilt angle between $\hat{n}$ and $\boldsymbol{q}_0$; thus $\mathrm{curl}\,\hat{n}$ is excluded from the SmA phase. Readers familiar with the Ginzburg–Landau (1950) model of superconductivity will recognize (2) as isomorphous with

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ϕ_N playing the role of the diamagnetic $cH^2/8\pi$ term. The exclusion of curl $\hat{n}$ from the SmA phase is analogous to the Meissner effect and the director $\hat{n}$ is the analogue to the vector potential $\boldsymbol{A}$. Analogous to fluctuation diamagnetism, the twist and bend elastic constants K_2 and K_3 diverge in the nematic phase above the N–SmA transition. This behaviour is ideally studied by light scattering from the director modes in the N and SmA phases.

More specifically, it is straightforward to show from (2) that order parameter fluctuations are described by

$$\langle\delta\psi(0)\,\delta\psi(\boldsymbol{r})\rangle = kT\chi\exp\{-\surd(x^2+y^2)/\xi_\perp - z/\xi_\parallel\}. \tag{4}$$

If we write $t = T/T_c - 1$ then the susceptibility $\chi = a^{-1}$ diverges as t^{-1} and the correlation lengths ξ as $t^{-\frac{1}{2}}$ in the mean-field calculation. More generally, $\chi = \chi_0 t^{-\gamma}$, $\xi_\parallel = \xi_\parallel^0 t^{-\nu_\parallel}$, and $\xi_\perp = \xi_\perp^0 t^{-\nu_\perp}$. These fluctuations can be studied by X-ray scattering. The intensity data for $T > T_c$ are well fitted by

$$I(\boldsymbol{q}) = kT\chi/\{1+\xi_\parallel^2(q_z-q_0)^2+\xi_\perp^2(q_x^2+q_y^2)+c\xi_\perp^4(q_x^2+q_y^2)^2\}. \tag{5}$$

Except for the $c\xi_\perp^4$ term, which is required to fit the data, (5) is just the Fourier transform of (4).

There are two director modes: $\hat{n}_1$ in the plane of $\hat{n}_0 = \hat{z}$ and $\boldsymbol{q}$, and $\hat{n}_2$ normal to $\hat{n}_0$ and $\hat{n}_1$. From (3) and (4) one may readily obtain, with $\boldsymbol{q}$ in the xz plane:

$$\langle\delta n_1^2(\boldsymbol{q})\rangle = kT\{B(q_z^2/q_x^2)+K_1q_x^2+K_3q_z^2\}^{-1} \tag{6}$$

and

$$\langle\delta n_2^2(\boldsymbol{q})\rangle = kT\{D+K_2q_x^2+K_3q_z^2\}^{-1}. \tag{7}$$

These are proportional to the intensity of scattered light; the spectrum contains useful information on the dynamical behaviour of fluctuations, but I shall not discuss that further. The elastic constants B and D give restoring forces for compression of the smectic density wave and tilt between the wavevector $\boldsymbol{q}_0$ and the director $\hat{n}$, respectively. In a mean-field calculation both B and D are proportional to the square of the mean smectic order parameter $\psi_0 = \langle\psi\rangle$, while isotropic scaling laws (Jähnig & Brochard 1974) predict that B vanishes as $\xi_\parallel^{-1}$ and D as $\xi_\perp^{-1}$ in the SmA phase. The divergences of K_2 and K_3 are (Jähnig & Brochard 1974)

$$K_2 = kTq_0^2\xi_\perp^2/24\pi\xi_\parallel \tag{8}$$

and

$$K_3 = kTq_0^2\xi_\parallel/24\pi. \tag{9}$$

These equations are for the values of K_2, K_3 at long wavelength. As the correlation length grows to exceed the wavelength of the fluctuation, the divergence levels off; these non-hydrodynamic effects for $q\xi > 1$ have also been calculated in a simple mode coupling approximation. The prediction for the divergent part of K_3 with $\boldsymbol{q} = q_z\hat{z}$ is (Jähnig & Brochard 1974)

$$\tilde{K}_3 = (kTq_0^2/8q_z)\{(1+1/X^2)\arctan X - 1/X\}, \tag{10}$$

where $X = \frac{1}{2}q_z\xi_\parallel$. The correlation length $\xi_\parallel$ becomes long enough near the phase transition that $q\xi_\parallel$ values as large as 10 are readily obtained in a light-scattering experiment; through equation (10) one may measure $\xi_\parallel$ indirectly and compare with the direct measurements by X-ray scattering.

(*a*) *The nematic–smectic A transition*

The N–SmA transition has been studied by X-ray scattering in a number of materials. In figure 1, I show the results (Birgeneau *et al.* 1981) for butoxybenzylidene octylaniline (40.8). The most striking feature for all of the materials that have been studied is that $\xi_\parallel$ and $\xi_\perp$ diverge with different exponents. This is contrary to our usual understanding of critical phenomena,

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since one length usually determines the behaviour. Light-scattering measurements of $\xi_\parallel$ (Von Känel & Litster 1981) in 40.8 analysed with (10) are in excellent agreement with the data of figure 1. In figure 2, I show $\xi_\parallel$ for butoxybenzylidene heptylaniline (40.7) obtained by X-ray and light scattering; they are also in excellent agreement. Thus it appears that the de Gennes–McMillan model and the treatment of coupling between director fluctuations and the smectic order parameter that results in (10) are valid. However, the anisotropy of the correlation lengths poses a problem. Most theoretical treatments (Lubensky 1982) predict isotropic critical behaviour ($\nu_\parallel = \nu_\perp$) and some indicate that the N–SmA transition must always be first-order to a degree that is contradicted by experiment. Theories based on a dislocation mechanism for the N–SmA transition (Huberman *et al.* 1975; Helfrich 1978; Nelson & Toner 1981) suggest $\xi_\parallel = \xi_\perp^2$, thus $\nu_\parallel = 2\nu_\perp$. Experimental values (from Birgeneau *et al.* (1981) and references therein) are shown for several materials in table 1. As can be seen from the table, one does not have $\nu_\parallel = 2\nu_\perp$, either. There is an anisotropic version of the scaling hypothesis (Chen & Lubensky 1978) that predicts $\nu_\parallel + 2\nu_\perp = 2 - \alpha$, where the specific heat diverges as $|t|^{-\alpha}$. The 3D x–y model predicts $\nu_\parallel = \nu_\perp = 0.67$ and $\alpha = -0.02$. An interesting observation is that the anisotropic scaling law holds within experimental error for all materials that have been studied.

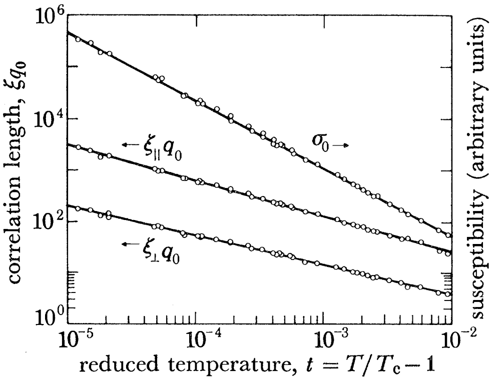

FIGURE 1. Susceptibility, σ_0, and the longitudinal and transverse correlation lengths above the SmA phase of 40.8. Data are from X-ray scattering (Birgeneau *et al.* 1981). The value of q_0 is 0.222 Å^{-1}.

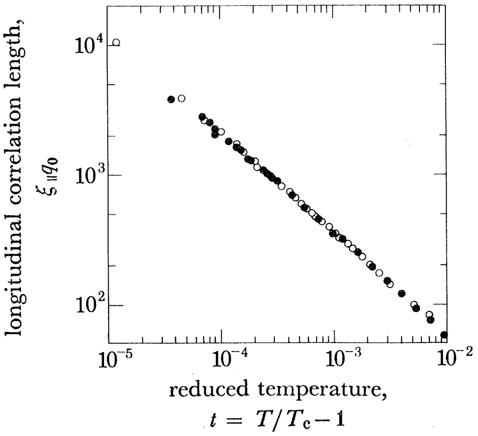

FIGURE 2. Longitudinal correlation length plotted against reduced temperature above the SmA phase of 40.7. Open circles are from light scattering, solid circles from X-ray scattering.

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Table 1. Correlation length exponents measured by X-ray scattering near the N–SmA transition

material†	$\nu_\perp$	$\nu_\parallel$	T_{NA}/T_{NI}
8CB	0.51	0.67	0.977
8OCB	0.58	0.71	0.963
40.8	0.58	0.70	0.958
CBOOA	0.61	0.72	0.940
$\overline{8}$S5	0.68	0.83	0.935
40.7	0.66	0.79	0.926

† Materials not previously defined are: 8CB, octyl cyanobiphenyl; 8OCB, octyloxy cyano biphenyl; CBOOA, cyanobenzylidene octyloxyaniline; $\overline{8}$S5, octyloxypentylphenyl thiolbenzoate.

How should we view this situation? It is widely felt that the problem is complicated by the Landau–Peierls instability or lack of true long-range order (Als-Nielsen *et al.* 1980) in the SmA phase. Some theorists also feel (Lubensky 1982) that the liquid crystal 'gauge' causes problems, because not all physical properties of the liquid crystal are gauge-invariant. (In superconductors one has $\nabla \cdot \hat{A} = 0$, while the splay elastic constant K_1 means $\nabla \cdot \hat{n} \neq 0$ in the liquid crystal gauge.) The dislocation models not only predict $\nu_\parallel = 2\nu_\perp$, but also that the elastic constants B and K_2 are constant at the N–SmA transition. Most experiments (Von Känel & Litster 1981; Litster *et al.* 1979 and references therein) show that B vanishes approximately as $t^{0.3}$; however, recent work (Fisch *et al.* 1982) on mixtures is consistent with a finite value of B at T_{NA}. It is hard to measure K_2 because of background masking the divergence, but early work (Delaye *et al.* 1973; Chu & McMillan 1975) suggests either critical or mean-field-like divergence. In my view the situation remains somewhat clouded experimentally. We need better measurements of K_2 and the elastic constants B and D. The behaviour of $\xi_\parallel$ and $\xi_\perp$ (table 1) seems well established; however, I should like to caution in its interpretation. Studies of re-entrant behaviour (Kortan *et al.* 1981) of the N–SmA transition in mixtures show that coupling of the smectic order parameter to other quantities (e.g. a temperature-dependent smectic interaction through thermal density changes) can change the divergences observed. Thus the exponents of table 1 may not be intrinsic to the N–SmA transition. There is a trend apparent in table 1 with the ratio of the N–SmA transition temperature to the nematic–isotropic transition temperature (T_{NI}). It is well known empirically that the N–SmA transition temperature becomes first-order when T_{NA}/T_{NI} is large enough. It is therefore possible that the smallest exponents of table 1 are influenced by the presence of a tricritical point (Brisbin *et al.* 1979). Experiments to clarify the situation are in progress in several laboratories around the world, and the experimental situation may be clarified within the year. Theoretically, in my view, the problem is still not solved.

(*b*) *The smectic A to smectic C transition*

When many liquid crystals in a SmA phase are cooled they have a second-order transition to a SmC phase. In the model of de Gennes (1974) the order parameter has two degrees of freedom: these are the tilt angle between the director and the smectic density wave, and the azimuthal angle of the director in the plane normal to the density wave vector. This transition should be in the same universality class as the superfluid transition in helium. The SmA–SmC transition may be studied by the usual methods: high-resolution X-ray scattering, light scattering, optical measurements, and precision calorimetry.

It has been studied by these methods by a number of laboratories and until recently the

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situation had been somewhat confused. The SmC order parameter is the tilt Φ of the director with respect to the SmC density wave. It may be directly measured by holding the director fixed in a magnetic field and measuring the angle between the field and the directions for X-ray scattering from the density wave. Experiments by Safinya *et al.* (1980) showed that in the SmC phase Φ vanished as $|t|^{0.47\pm0.04}$, as would be expected from mean-field behaviour. This was contrary to the $|t|^{0.35}$ prediction of the 3D x–y model and the helium analogue; Safinya *et al.* argued that the bare length characterizing the SmA–SmC transition was large and that the Ginzburg (1960) criterion made the critical region too small to observe in the material, octyloxypentylphenylthiolbenzoate ($\bar{8}$S5), that they had studied. Subsequently Galerne (1981) reported that by optical measurements $\Phi \approx |t|^{0.36}$ in the SmC phase of azoxy-4,4′-di-undecyl-α-methylcinnamate (AMC-11) and argued that the bare length was anomalously small. Although the Ginzburg criterion need not require crossover from mean-field to critical behaviour at identical reduced temperatures in all materials, the situation seemed unsatisfactory. Huang & Viner (1982) made the important observation that the specific heat anomaly at the SmA–SmC transition in 4-(2′-methylbutyl)phenyl 4′-*n*-nonyloxybiphenyl-4-carboxylate (2M4P9OBC) could be explained by a mean-field model with an unusually large sixth-order term in the Landau expansion of the free energy. To clarify the situation we carried out a series of experiments at M.I.T. on 40.7. These showed (Birgeneau *et al.* 1983) that the order parameter could be described by a $|t|^{0.37}$ power law in the SmC phase, consistent with Galerne's observations. They also showed that one must question the uniqueness of power-law fits to data, for light scattering from fluctuations in short-range SmC order in the SmA phase showed quite clearly a susceptibility diverging as t^{-1}, unambiguously confirming mean-field behaviour. To understand the order parameter behaviour let us consider the mean-field model used by Huang & Viner. Near the SmA–SmC transition, the free energy is written

$$F = at\Phi^2 + b\Phi^4 + c\Phi^6 + \ldots + (1/2M_{\parallel})\,|\nabla_{\parallel}\Phi|^2 + (1/2M_{\perp})\,|\nabla_{\perp}\Phi|^2 + \ldots. \tag{11}$$

If one puts $t_0 = b^2/ac$, standard thermodynamic calculations yield

$$\Phi = (b/3c)^{\frac{1}{2}}\{(1-3t/t_0)-1\}^{\frac{1}{2}} \quad (t<0) \tag{12}$$

and a heat capacity

$$\begin{aligned} c &= 0, \quad t>0 \\ &= (a^2T/2bT_{\mathrm{c}}^2)\,(1-3t/t_0)^{-\frac{1}{2}} \quad (t<0). \end{aligned} \tag{13}$$

Now, (12) predicts $|t|^{0.25}$ behaviour for $|t| \gg t_0$ and crosses over to $|t|^{0.50}$ for $|t| \ll t_0$. We found it fitted the data very well with a crossover temperature $t_0 = 1.3\times10^{-3}$ and could not be distinguished from power-law behaviour over the measured range of $-2.5\times10^{-3} < t < -1.0\times10^{-4}$. The data and fit to (12) are shown in figure 3. In figure 3 the light scattering data in the SmA phase, $T > T_{\mathrm{c}}$, are shown. From (11) one predicts $\xi_{\parallel} = (2M_{\parallel}at)^{-\frac{1}{2}} = \xi_{\parallel}^0 t^{-\frac{1}{2}}$, $\xi_{\perp} = (2M_{\perp}at)^{-\frac{1}{2}} = \xi_{\perp}^0 t^{-\frac{1}{2}}$, and $\chi = \frac{1}{2}a_0 t = \chi_0 t^{-1}$; by using these the reciprocal of the intensity of scattered light, I^{-1}, may be expressed as

$$\epsilon_a^2 kT\chi_0 I^{-1} = t + (\xi_{\parallel}^0 q_z)^2 + (\xi_{\perp}^0 q_{\perp})^2, \tag{14}$$

where ϵ_a is the anisotropy in the dielectric constant of the SmA phase. The linear asymptotic behaviour of I^{-1} in figure 3 clearly confirms the mean-field behaviour, and the slope and value at T_{c} determine $\xi_{\parallel}^0 = 20.4 \pm 0.7$ Å†; the bare length $\xi_{\perp}^0$ was similar in magnitude but less accurately determined. Birgeneau *et al.* (1983) also report specific heat data for the SmA–SmC transition

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† 1 Å = 10^{-10} m = 10^{-1} nm.

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in 40.7; these are shown in figure 4. The SmA–SmC transition lies close to a SmB phase that contributes a background. This was determined by measurements of 40.8, which lacks the SmA–SmC transition. The fit to the background term plus equation (13) is shown in figure 4; it is excellent and yields the crossover temperature $t_0 = 1.3 \times 10^{-3}$ and heat capacity jump $\Delta C = 1.8 \times 10^5\,\mathrm{J\,m^{-3}\,K^{-1}}$ at T_c. Combining all the data we calculate the Ginzburg reduced temperature for crossover to critical behaviour,

$$t_c = k_B^2\,[32\pi^2(\xi_{\parallel}^0)^2\,(\xi_{\perp}^0)^4\,(\Delta C)^2]^{-1}, \tag{15}$$

to be $t_c = 3 \times 10^{-7}$, which explains why only mean-field behaviour is observed. Birgeneau *et al.* also made specific heat measurements on AMC-11 that show the same behaviour to obtain in that material. It seems likely that all SmA–SmC transitions are mean-field because of the long correlation lengths, quite analogous to the situation in superconductors. There is a lesson to be learned: that power law fits are not always unique and that several properties must be measured together to have a correct picture of behaviour at a phase transition. There is one material, *p*-nonyloxybenzoate-*p*-butyloxyphenol, for which light-scattering measurements (Delaye 1979) self-consistently show critical behaviour; it would be valuable to have high-resolution heat-capacity and X-ray measurements for this material.

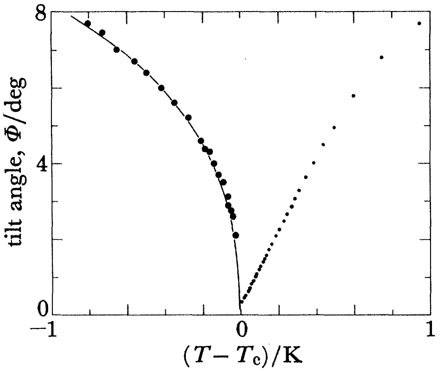

Figure 3. Large circles are the tilt order parameter, Φ, in the SmC phase of 40.7. The solid line is a fit to equation (12). Small circles are the reciprocal of the intensity (arbitrary units) scattered by tilt fluctuations in the SmA phase of 40.7. (From Birgeneau *et al.* (1983).)

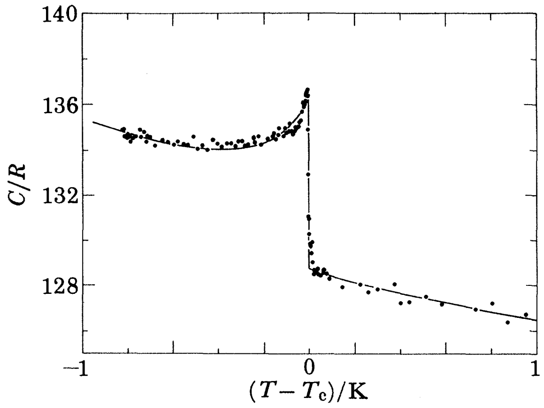

Figure 4. The specific heat in units of R near the SmA–SmC transition in 40.7. The solid line is a fit to equation (13) plus background, as discussed in the text. (From Birgeneau *et al.* (1983).)

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(*c*) *Lyotropic liquid crystal phases*

As I discussed earlier, we believe that the fundamental symmetries of an ordered phase determine its phase transition behaviour; the microscopic details of the interactions are frequently unimportant. There are lyotropic materials that are quite different microscopically from the thermotropic nematics and smectics, yet have the same gross symmetry. Thus it is interesting to explore in detail the phase transition behaviour of these lyotropic phases. At M.I.T. we have recently begun experiments (Kumar *et al.* 1982) on a system that we were introduced to by A. Saupe (Haven *et al.* 1981). This is the soap decylammonium chloride (DACl) in aqueous solution with NH_4Cl. The DACl forms micelles that, with the appropriate NH_4Cl concentration, are disc-shaped. When the micelles occupy about 50 % of the total volume, interaction between them leads to collective behaviour. An isotropic solution of micelles has a first-order phase change to a nematic in which the micellar symmetry axes tend to orient parallel to the director. Further cooling of the solution leads to a second-order transition to a neat soap phase; this transition ought to be in the same universality class as thermotropic SmA–nematic transitions. We have found the nematic–isotropic transition to behave quite analogously to that of thermotropic materials (Stinson *et al.* 1972). The nematic elastic constants, as measured by light scattering from director modes show a pretransitional divergence for K_2 and K_3 as $|t|^{-0.68\pm0.05}$. This is consistent with the 3D x–y model, and preliminary results show no sign of the anisotropy in critical exponents commonly observed in thermotropic SmA phases. It will be interesting to learn more about these interesting lyotropic phases as experimental studies proceed.

3. CONCLUSIONS

We see that the nematic–SmA transition remains a problem, as it has for several years now. It seems likely that sufficient data will be accumulated within a year or so to provide a phenomenological description of this interesting transition. It is less certain when the theoretical difficulties will be overcome. The SmA–SmC situation has recently been clarified. A mean-field description with important sixth-order terms suffices for most materials because of the long bare lengths characteristic of the problem; a microscopic understanding of this remains to be found. It appears that a number of lyotropic phases may fruitfully be examined by the approaches used for thermotropic phases, and interesting results should appear in the future.

The M.I.T. work that I have described is the result of a stimulating collaboration with my colleagues Bob Birgeneau and Carl Garland as well as several postdoctoral associates and graduate students. It is a pleasure to express my appreciation to them. My participation in that work was supported by the National Science Foundation either under grant no. DMR 78-23555 or grant no. DMR 81-19295.

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