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Critical behavior near the nematic—smectic-*A* transition in butyloxybenzylidene octylaniline (40.8)

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We report a high-resolution heat-capacity and x-ray study of the nematic—smectic-*A* transition in the single-layer smectic material butyloxybenzylidene octylaniline (40.8). We find that the transition is second order to within 3 mK, with critical behavior closely similar to that observed previously in bilayer smectic materials such as octyloxycyanobiphenyl (8OCB). For the critical exponents we measure $\gamma = 1.31 \pm 0.02$, $\nu_{\|} = 0.70 \pm 0.01$, $\nu_{\perp} = 0.57 \pm 0.01$, and $\alpha = \alpha' = 0.15 \pm 0.05$. These exponents are consistent with the anisotropic hyperscaling relation $\nu_{\|} + 2\nu_{\perp} = 2 - \alpha$. In addition, we find that the ratio of the amplitudes of the critical heat capacities in 40.8 and 8OCB is inversely proportional to the ratio of the correlated volumes as measured with x rays. The smectic longitudinal correlation length measured directly with x rays agrees quantitatively with that deduced by von Känel and Litster from the director fluctuations. Substantial disagreements with the superconducting analog model remain unexplained.

I. INTRODUCTION

The nematic—smectic-*A* transition, which corresponds to the establishment of a one-dimensional density wave in a three-dimensional (3D) fluid, would appear to be one of the simplest examples of solidification in nature.[1] Further, as first pointed out independently by McMillan[2] and Kobayashi,[3] this transition may be second order. A particularly elegant formulation of the nematic—smectic-*A* (*N*-*A*) problem was given by de Gennes,[4] who suggested that this transition could be described by a Landau-Ginzburg functional closely analagous to that of a superconductor. Based on this analogy, it was anticipated that the transition should belong to the same universality class ($d = 3$, $n = 2$ isotropic) as a superfluid and should exhibit 3D *XY* critical behavior.[5] It was recognized from the beginning, however, that there are some important differences between the superconductor and a smectic-*A* liquid crystal. For the smectic, these include an anisotropic guage,[6] highly anisotropic bare lengths,[2] a complex elastic free energy with a large difference in the nematic elastic constants,[1] a coupling between the density wave fluctuations of the nematic director,[2,3] and finally algebraic decay rather than true long-range order in the smectic phase.[7] It was not clear whether these differences would cause significant deviations from the anticipated *XY* critical behavior.

These theories have stimulated a number of high-precision measurements using, for example, light-scattering,[8] x-ray scattering,[9] and ac calorimetry techniques.[10,11] Indeed, one of the attractive features of *N*-*A* transition is that it may be studied with a wide range of probes. Most of these experiments have been performed on bilayer smectics, primarily because of their ready availability from commercial sources. These measurements show that although the superconducting analog model gives qualitatively correct predictions there are a number of important quantitative discrepancies.[11,12] For example, in all materials measured, the smectic layer compressibility B goes to zero like $(T_c - T)^{0.3}$ rather than the predicted $(T_c - T)^{2/3}$. In the bilayer smectics cyanobenzylidene-octyloxyaniline (CBOOA), octyloxycyanobiphenyl (8OCB), and octylcyanobiphenyl (8CB) the susceptibility (σ_0) and longitudinal correlation length ($\xi_{\|}$) in the nematic phase both exhibit critical exponents close to those in helium ($\gamma \simeq \frac{4}{3}$ and $\nu_{\|} \simeq \frac{2}{3}$, respectively). However, the transverse correlation length ($\xi_{\perp}$) appears to diverge more weakly with an exponent $\nu_{\perp} = 0.5$ to 0.6 rather than the isotropic value $\nu = \frac{2}{3}$. Further, this difference between $\nu_{\|}$ and $\nu_{\perp}$ suggests that the *N*-*A* transition is characterized by *two* divergent lengths rather than one, in violation of conventional scaling ideas. Heat-capacity measurements on the bilayer smectics[11,13,14] give exponents ranging from $\alpha=\alpha'=0$ to 0.30 but with the most probable values near ~ 0.20. This again is in disagreement with the helium value of $\alpha=-0.02$.

All of the experiments cited above are on bilayer materials, and it might be suspected that the discrepancies are in some way related to the bilayer nature of the smectic phase. In addition, both CBOOA and 8OCB under pressure exhibit re-entrant nematic behavior.[15] The only single-layer material in which the *N-A* transition has been studied in considerable detail by a variety of probes is 4-*n*-pentyl-phenylthiol-4′-octyloxybenzoate ($\bar{8}$S5).[10,16] In $\bar{8}$S5 the heat capacity[10] and transverse correlation lengths[16] appear to exhibit 3D *XY* behavior, whereas the susceptibility and the longitudinal correlation length[16] diverge more strongly than expected for an *XY* model. Again there appear to be two different divergent lengths. Thus the $d=3$, $n=2$ model also fails for $\bar{8}$S5, albeit in a different fashion than for 8OCB, 8CB, and CBOOA. This then raises the natural question of whether or not these differences originate in the single-layer versus double-layer nature of the smectic state in the different materials. Clearly, it is very important to obtain high-precision data on the *N-A* transition in other single-layer smectic-*A* materials.

Recently, a number of groups have carried out detailed studies[17–19] of the smectic-*A* –crystal-*B* transition in butyloxy-benzylidene octylaniline (40.8), which has a single-layer smectic-*A* phase. In the course of these studies it was discovered that 40.8 exhibits an *N-A* transition which is second order to within ±3 mK. Thus 40.8 is an attractive material for study. von Känel and Litster[20] have carried out a comprehensive light-scattering study of the *N-A* transition in 40.8. They find behavior for the nematic bend elastic constant K_3, the bend viscosity η_{bend}, the smectic layer compressibility *B*, and the smectic orientational parameter *D* which are essentially identical to those obtained in *bilayer* systems. The critical divergences observed for K_3 and η_{bend} agree with the *XY* model predictions whereas both *B* and *D* vanish near T_c more steeply than expected.

Stimulated by the work described above, we have carried out high-resolution diffuse x-ray scattering experiments together with precision ac calorimetry measurements of the nematic–smectic-*A* transition in 40.8. X rays couple to the mass density fluctuations and hence, one is able to directly measure the divergent smectic transverse and longitudinal correlation lengths, as well as the smectic susceptibility in the nematic phase. By use of perfect silicon resolution techniques, it is possible to monitor the correlation lengths over distances varying from several angstroms to several microns. With use of modern ac calorimetry techniques we are able to measure the divergent heat capacity in both the nematic and smectic phases with a temperature resolution of about 10^{-3} K. A rather complete set of empirical information characterizing the *N-A* transition in 40.8 can be deduced from light-scattering, x-ray scattering, and heat-capacity measurements. These results enable us to test such features as anisotropic hyperscaling,[21] two-scale-factor universality,[22] the relationship between divergent quantities such as K_3 and $\xi_{\parallel}$,[1,4] and the basic applicability of the superconducting analog model. We will also be very interested in comparisons of the *N-A* critical behavior in 40.8 with that in bilayer materials, especially 8OCB.

Before concluding this Introduction we should note that there have been a number of theoretical attempts to extend the de Gennes model. One of the most interesting analyses, due to Lubensky and co-workers,[21] allows for the possibility of a series of crossovers from mean-field to anisotropic critical to isotropic critical (*XY*) regimes, and finally, to a very weak first-order transition. The behavior in the anisotropic regime permits $\nu_{\parallel} > \nu_{\perp}$ with nonuniversal values for the exponents. Another theory, based on a dislocation unbinding mechanism, has been constructed by Nelson and Toner.[23] This model predicts that asymptotically close to the transition $\nu_{\parallel}=2\nu_{\perp}$. We shall discuss these models within the context of our experimental results.

The format of this paper is as follows. Section II describes the x-ray scattering measurements and the power-law analysis of these data. Section III gives the corresponding heat-capacity data and analysis. Section IV contains an intercomparison of the different results obtained in 40.8, as well as in the other materials mentioned above, with explicit tests of current theoretical models.

II. X-RAY MEASUREMENTS AND ANALYSIS

We have described our x-ray scattering techniques briefly in several papers.[9,12,24] Full details are given in theses by Kaplan[25] and Safinya.[16] The sample of 40.8 (from CPAC-Organix) was vacuum pumped for several hours to remove any residual solvents. The sample volume for x-ray scattering was $12\times12\times1$ mm^3, contained between flat beryllium plates (0.25 mm thick). Temperature control of ~2 mK over a period of several hours was provided by a computer-controlled two-stage oven with Kapton windows. The director was aligned in the scattering plane (that is, parallel to the beryllium plates) by a magnetic field of 4 kG. The x-ray spectrometer is shown schematically in Fig. 1. The x-ray source is a Rigaku 12-kW rotating anode generator with a copper anode. The monochromator and analyzer crystals were standard commercial Si(111) crystals whose rocking curves each have a half-width at half-maximum (HWHM) of ~4 sec; this is determined primarily by the Darwin width. The monochromator θ and 2θ angles and the slits were chosen so as to select the Cu $K\alpha_1$ ($\lambda=1.5405$ Å) and $K\alpha_2$ ($\lambda=1.5443$ Å) lines. The slits were set in a relatively wide-open configuration so as to maximize the signal. Although this gave an undesirably large uniform background of ~7 counts per second, such a background was inconsequential except for the few points taken at the highest temperatures.

With this configuration the longitudinal in-plane resolution is 1.1×10^{-4}-Å^{-1} HWHM at the Bragg scattering angle of $2\theta=3.129°$. The analysis must, of course, include both the $K\alpha_1$ and $K\alpha_2$ lines. The longitudinal resolution function is, to a good approximation, a simple Lorentzian. As discussed by Safinya[16] there are subtle corrections to this Lorentzian form which must be included for deconvolution of spectra with correlation lengths in the micron range. However, we have verified that these corrections are unimportant in all of the data presented here. The transverse in-plane resolution is $<10^{-5}$ Å^{-1}, which is much better than required. As discussed in Ref. 26, the ability to measure transverse correlation lengths is, in fact, strongly affected by mosaicity effects, that is, the extent to which the smectic planes are parallel within the illuminated volume. For reasons which are apparently serendipitous, the mosaicity at T_c in these experiments is typically $<0.05°$ HWHM so that corrections for mosaicity are negligible. Thus the transverse resolution function may be taken as a delta function. The vertical resolution is deliberately chosen to be quite coarse, ~0.047-Å^{-1} HWHM; this means that one effectively integrates over the vertical component of the fluctuation spectrum.

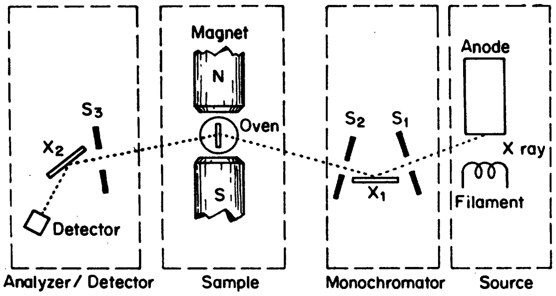

FIG. 1. Components of x-ray spectrometer, neglecting the vertical collimation. S_1, S_2, and S_3 are vertical slits. X_1 and X_2 are perfect Si (111) Bragg crystals.

We also carried out some limited measurements on a second sample with a much tighter slit configuration. In this case we placed 1-mm high horizontal slits before the sample and 0.12° Soller slits with the plates horizontal after the sample. The in-plane resolution function was identical to that discussed above. However, the vertical resolution was reduced to 0.007-Å^{-1} HWHM. This reduced the background to a negligible level. Unfortunately, the drift in T_c in this sample was too large to allow accurate measurements very close to T_c. We did, however, obtain useful data in the reduced temperature range $6\times10^{-4}<T/T_c-1<2\times10^{-3}$. The longitudinal and transverse correlation lengths obtained from these measurements agree within experimental error with the results presented below. Hence, we shall not discuss these results further here.

The critical scattering of x rays from the nematic phase is centered around the position $(0,0,q_0)$ in reciprocal space, where $q_0=0.2222\pm0.0001$ Å^{-1}; this value is only weakly temperature dependent. The in-plane liquid structure factor[19] is a ring centered at $(q_\perp^0,0,0)$ with $q_\perp^0=1.441$ Å^{-1} and HWHM of about 0.2 Å^{-1}. The ratio of the bare characteristic lengths parallel and perpendicular to the director is thus about $1.44/0.222=6.5$. In order to map out the critical scattering we carried out both longitudinal scans ($q_\perp=0$, $q_\parallel$ varied) and transverse scans ($q_\parallel=q_0$, $q_\perp$ varied) for each reduced temperature $t=T/T_c-1$. Data for several typical scans are shown in Fig. 2.

The transition temperature T_c may be taken as the temperature at which the transverse scan shows a minimum linewidth.[24,26] The physical origin of this effect is that the transverse scan continuously narrows as one approaches T_c from above (that is, as $\xi_\perp\rightarrow\infty$), while as the smectic-order parameter increases on cooling below T_c, the mosaicity also

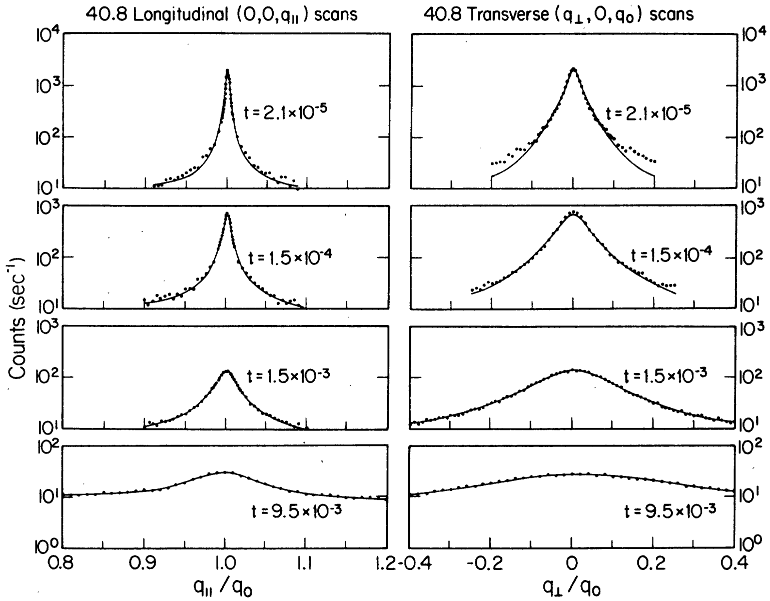

FIG. 2. Transverse and longitudinal x-ray scans in 40.8 at a series of reduced temperatures *t*. The solid lines are the results of least-squares fits with Eq. (1) convolved with the instrumental resolution function.

generally becomes worse due to increased competition between field and wall-alignment effects. In addition, the longitudinal width decreases continuously as one approaches T_c from above ($\xi_{\parallel}\rightarrow\infty$) so that the longitudinal scan becomes resolution limited at T_c. These effects were in good agreement and we could determine T_c to within ± 2 mK for any given run. Unfortunately, as found previously by von Känel and Litster[20] in their light-scattering studies, the value of T_c drifted slowly with time — at a rate of about 1.5 mK per hour. We show in Fig. 3 the variation of T_c over the period of these x-ray measurements. It should be noted that since the drift is accurately linear with time the value of T_c appropriate to a particular scan carried out between the periodic T_c determinations could be interpolated to an accuracy of ~ 3 mK. Unfortunately this drift in T_c does represent the limiting factor in the accuracy of our x-ray data in the region $T/T_c-1<10^{-4}$.

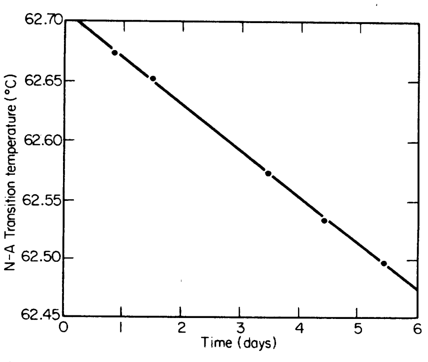

FIG. 3. Nematic—smectic-*A* transition temperature in the x-ray sample over the period of our measurements.

It has been found previously[24] that the smectic wave-vector-dependent susceptibility may be expressed analytically as

$$\sigma(\vec{q})=\sigma_0/[1+\xi_{\parallel}^2(q_{\parallel}-q_0)^2+\xi_{\perp}^2q_{\perp}^2+c\xi_{\perp}^4q_{\perp}^4]\ . \quad (1)$$

Here σ_0 is the component of the susceptibility at $\vec{q}=(0,0,q_0)$, $\xi_{\parallel}$ is the smectic longitudinal correlation length and $\xi_{\perp}$ is the transverse correlation length. In studies of the bilayer compounds[9,24,26] it was found that a small fourth-order term $c\xi_{\perp}^4q_{\perp}^4$ was necessary in order to obtain an accurate representation of the wings of the transverse scans, especially far above T_c. We note that both the x-ray polarization factor and the molecular form factor should vary negligibly over the region of $\vec{q}$ space covered in the scans shown in Fig. 2; thus, they may simply be taken as constants. Fits of our data with Eq. (1) convoluted with the instrumental resolution function are shown as the solid lines in Fig. 2. It should be kept in mind that a logarithmic intensity scale is used in these plots, so that the tail regions are enhanced visually. In general, the fits are quite satisfactory with a goodness-of-fit parameter χ_ν^2 typically between 1 and 2.

The values of the smectic susceptibility and the transverse and longitudinal correlation lengths obtained from these fits are shown in Fig. 4. We note that the longitudinal correlation length is above 1 μm for the data points nearest T_c. Thus, using these perfect Si x-ray-scattering techniques it is possible to monitor the growth of the correlations over distances ranging from angstroms to microns. We shall present detailed fits with power laws below. Here we note simply that $\xi_{\parallel}$, $\xi_{\perp}$, and σ each seem to exhibit single-power-law behavior over the investigated reduced temperature range $10^{-5} < t < 10^{-2}$. It is evident qualitatively from Fig. 4 that $\xi_{\parallel}$ and $\xi_{\perp}$ have slightly different slopes; that is, their divergences are characterized by different critical exponents. In order to exhibit this effect more explicitly we plot in Fig. 5 the length ratio $\xi_{\parallel}/\xi_{\perp}$ together with the fourth-order coefficient c. Far above T_c, the ratio of lengths is close to what might reasonably be called the "bare" value of 6.5. As discussed above this is the ratio of the q vectors from the peaks of the in-plane (1.441 Å^{-1}) and between-plane (0.222 Å^{-1}) structure factors. The length ratio increases by about a factor of 3 as the reduced temperature decreases from 10^{-2} to 10^{-5}. The fourth-order coefficient c is generally quite small, only becoming quantitatively important for $t > 10^{-3}$. We note that for data points near $t \sim 10^{-2}$, it became impossible to determine c accurately because of the high background. Accordingly, for the four highest temperature points we fixed c at 0.2. We, of course, verified that the parameters σ_0, $\xi_{\parallel}$, and $\xi_{\perp}$ did not vary drastically for a reasonable range of values for c.

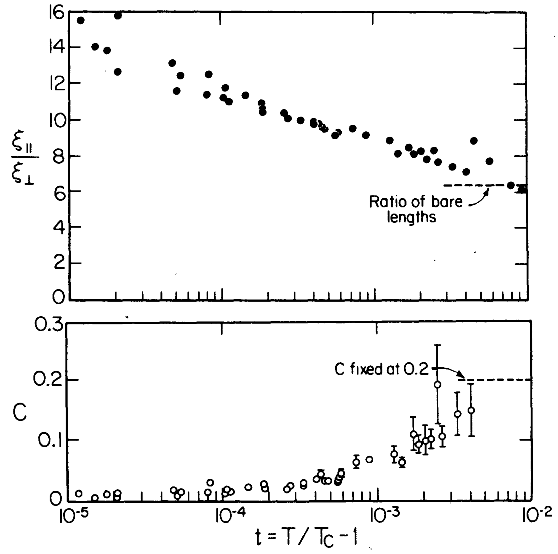

FIG. 5. Ratio of correlation lengths $\xi_{\parallel}/\xi_{\perp}$ and fourth-order coefficient c in 40.8 versus reduced temperature.

We have carried out fits of σ_0, $\xi_{\parallel}$, and $\xi_{\perp}$ to single-power-law divergences. We find that both the amplitudes and the exponents obtained in these fits are insensitive to the range of reduced temperatures included. We quote here explicitly the results of fits to all the data shown in Fig. 4 except for the four points closest to T_c. In the latter cases, the uncertainty in t due to the drift in T_c is such that they can be used only for consistency. The results of the fits are

$$\sigma_0 = (\text{const})\, t^{-1.31 \pm 0.02} , \tag{2a}$$

$$\xi_{\parallel} q_0 = (1.04 \pm 0.08) t^{-0.70 \pm 0.01} , \tag{2b}$$

$$\xi_{\perp} q_0 = (0.277 \pm 0.02) t^{-0.57 \pm 0.01} . \tag{2c}$$

The error limits are two standard deviation statistical errors. As may be seen in Fig. 4 these power laws describe the data to within the errors over the entire investigated range of reduced temperatures.

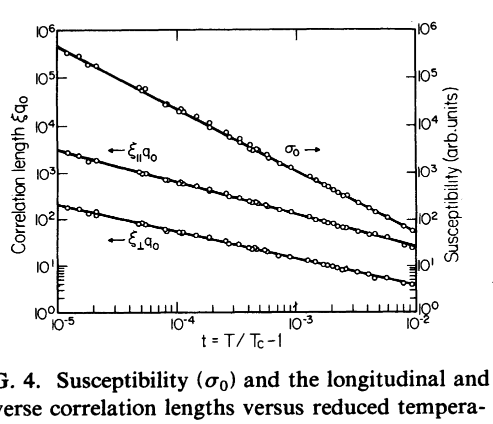

FIG. 4. Susceptibility (σ_0) and the longitudinal and transverse correlation lengths versus reduced temperature in 40.8. The value of q_0 is essentially constant (0.222 Å^{-1}), and the solid lines are the power-law fits given by Eqs. (2).

In the three bilayer materials 8OCB,[9] 8CB,[26] and CBOOA (Ref. 24) the average values of the critical exponents are $\gamma = 1.29 \pm 0.06$, $\nu_{\parallel} = 0.69 \pm 0.04$ and $\nu_{\perp} = 0.57 \pm 0.04$. It is evident that the exponents we obtain in the single-layer material 40.8 agree with these average bilayer values to well within the errors. We shall discuss this agreement in more detail in Sec. IV, where we shall make explicit comparisons with the results in 8OCB since that material has been most extensively studied. We turn now to a discussion of the heat-capacity results.

III. HEAT-CAPACITY MEASUREMENTS AND ANALYSIS

High-resolution ac calorimetric measurements on 40.8 over the range 0–95 °C have been reported previously.[17] The discussion in Ref. 17 focused principally on the behavior near the transition from rigid crystal to plastic crystal B and the crystal-B –smectic-A melting transition. An analysis of the critical heat-capacity variation near the second-order N-A transition is presented here, and a comparison is made with detailed results that are available for octyloxycyanobiphenyl (8OCB).[11]

The heat-capacity variation in the vicinity of the N-A transition is shown in Fig. 6 for both 40.8 and 8OCB. We note that the liquid-crystal sample was placed in a sealed cell for the heat-capacity measurements and the calorimetric values of T_c were stable over long periods of time (77 days for 40.8 and ~120 days for 8OCB). The cause of the slow linear drift in T_c during our x-ray measurements (see Fig. 3) has not yet been identified but might be due to air oxidation. The critical contribution per mole $\Delta\tilde{C}_p$ is the difference between the observed data and a noncritical background curve that represents the variation expected in the absence of the N-A transition

$$\Delta\tilde{C}_p=\tilde{C}_p(\text{obs})-\tilde{C}_p(\text{background}) \ . \qquad (3)$$

The choice of the 40.8 background curve shown in Fig. 6 is confirmed by a recent study of the homolog 40.7.[27] The 8OCB background is confirmed by high-pressure measurements on pure 8OCB,[11] and by a study of 8OCB-6OCB mixtures.[28]

The excess heat capacity $\Delta\tilde{C}_p(NA)$ associated with the N-A transition is shown as a function of the reduced temperature $t\equiv(T-T_c)/T_c$ in Figs. 7 and 8. It is obvious that the critical thermal behavior is very similar in 40.8 and 8OCB except for the magnitudes of $\Delta\tilde{C}_p$. This correspondence is clearly indicated by the results of least-squares fits of $\Delta\tilde{C}_p/R$ with simple power laws

$$\Delta\tilde{C}_p/R=\begin{cases}At^{-\alpha}+B, & \text{for } T>T_c\\ A'\,|\,t\,|^{-\alpha'}+B', & \text{for } T<T_c\end{cases} \qquad (4)$$

and with a scaling form ($\alpha=\alpha'$ and $B=B'$) including corrections-to-scaling terms

$$\Delta\tilde{C}_p/R=\begin{cases}At^{-\alpha}(1+Dt^{1/2})+B\\ A'\,|\,t\,|^{-\alpha}(1+D'\,|\,t\,|^{1/2})+B \ .\end{cases} \qquad (5)$$

The parameter values are listed in Table I. The 40.8 fits are based on data in the reduced temperature range $5\times10^{-5}<|\,t\,|<5\times10^{-3}$; the 8OCB parameters are taken from Ref. 11 for the comparable range $3\times10^{-5}<|\,t\,|<3\times10^{-3}$. In both materials, the parameter values are stable to range shrinking and appear to be valid out to $|\,t\,|=10^{-2}$.

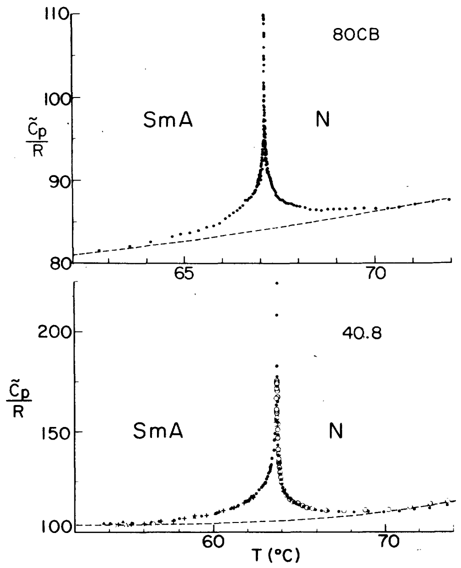

FIG. 6. Molar heat capacity of 40.8 and 8OCB in the vicinity of the N-A transition. The dashed curves representing the variation of C_p (background) are smooth extrapolations of the C_p (NI) peak for the nematic-isotropic transition (see Refs. 11 and 17). Note the substantial difference in the scales used for these two materials. The NA peak in 40.8 is considerably larger than that in 8OCB.

Separate fits for data above and below T_c with Eq. (4) show that the scaling requirements $\alpha=\alpha'$

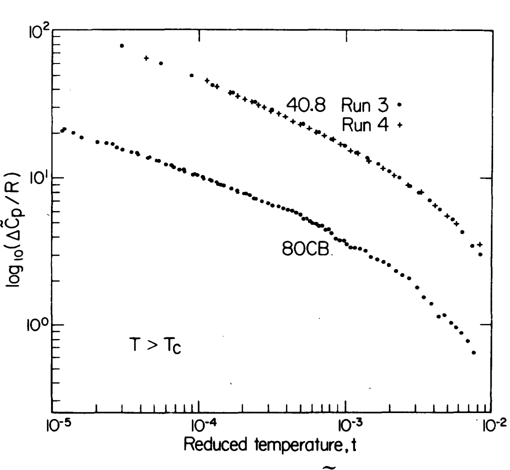

FIG. 7. Critical heat capacity $\Delta\tilde{C}_p(NA)$ in the nematic phase.

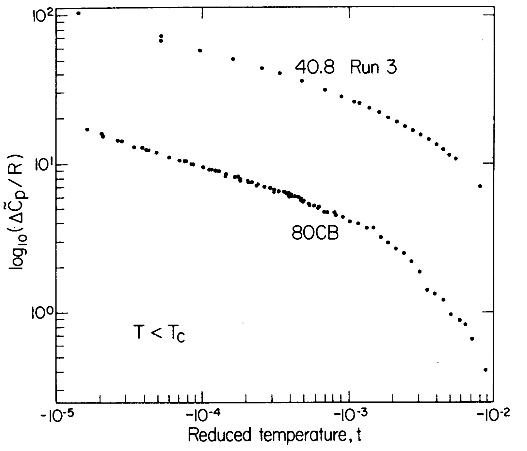

FIG. 8. Critical heat capacity $\Delta\widetilde{C}_p(NA)$ in the smectic-A phase.

and $B=B'$ are not satisfied with a simple power law. The character of the asymmetry is almost identical for 40.8 and 8OCB. If one tries to force a scaling fit with Eq. (4), the result is $\alpha=\alpha'=0.20\pm0.05$ with $\chi_\nu^2=2.09$ for 8OCB (Ref. 11) and $\alpha=\alpha'=0.23$ with $\chi_\nu^2=8.8$ for 40.8. Considerably better scaling fits can be achieved with Eq. (5), as shown in Table I. The χ_ν^2 minimum is very broad in case of 8OCB but the data are compatible with $\alpha=0.15$, the value obtained as the best fit for 40.8. A considerable variety of α values have been reported for 8OCB by other investigators: $\sim 0(\log t)$ and 0.27,[13] 0.16,[14] and 0.03, and 0.25.[29] In all these cases, the exponents were obtained from scaling fits with a simple power law although corrections-to-scaling terms are expected to be important in representing the heat capacity.[30] There is evidence that the effective α value is sensitive to sample purity,[13,29] but it seems that α lies in the range 0.15 to 0.30 for high-purity 8OCB samples. The heat-capacity exponent α can be related to the correlation length exponents $\nu_\parallel$ and $\nu_\perp$ by hyperscaling, and we shall discuss this relationship in Sec. IV.

The difference in the magnitude of the energy

TABLE I. Critical parameters for 40.8 and 8OCB obtained from separate fits of heat-capacity data above and below the N-A transition with Eq. (4) and from simultaneous fits of data in both phases with Eq. (5). The maximum in C_p was observed at 67.116 °C for 8OCB and at 63.773 °C for 40.8. In order to compare the amplitudes A from the simple power-law fits to 40.8 and 8OCB in the nematic phase, α was fixed at 0.3 for both materials.

		Single-power-law fits			
Material	A (A')	α (α')	B (B')	T_c (T_c')	χ_ν^2
	Nematic phase				
8OCB	1.17	0.27	−3.72	67.116	1.15
8OCB	0.837	(0.30)[a]	−2.83	67.115	1.20
40.8	3.74	(0.30)	−13.05	63.774	2.50
40.8	2.73	0.33	−10.12	63.773	1.67
	Smectic-A phase				
8OCB	3.14	0.18	−6.64	67.116	1.6
40.8	18.72	0.18	−3.64	63.776	1.2

			Power law with corrections-to-scaling terms					
Material	A	A'/A	α	D	D'	B	T_c	χ_ν^2
8OCB	0.656	0.925	(0.30)[a]	−17.43	−14.07	1.50	67.117	1.51
8OCB	2.671	0.979	(0.20)	0.30	1.93	−6.92	67.118	1.63
8OCB	5.805	0.993	(0.15)	2.10	2.93	−13.65	67.119	1.74
8OCB	11.61	1.000	(0.11)	2.21	2.59	−22.78	67.119	1.95
40.8	12.05	1.232	(0.20)	1.84	0.94	−34.08	63.779	5.49
40.8	26.44	1.168	(0.15)	2.83	1.63	−64.68	63.779	3.19
40.8	53.27	1.120	(0.11)	2.54	1.51	−106.70	63.779	4.48

[a] Parentheses indicate that the parameter was held fixed at the indicated value.

fluctuations above T_c in 40.8 and 8OCB can be largely understood within the context of two-scale-factor universality,[22] as discussed in the next section. The ratio $\Delta\widetilde{C}_p(40.8)/\Delta\widetilde{C}_p(\text{8OCB})$ in the nematic phase is found to be 4.5 ± 0.5 over the entire range $10^{-5}<t<10^{-2}$,[31] but one must consider the possibility of systematic errors. Although the precision of ac calorimetric data is high, the absolute accuracy is usually no better than 5–10 % and can often be worse. As a test of our heat-capacity data, we have evaluated the ratio of *specific heats* $\bar{C}_p(40.8)/\bar{C}_p(\text{8OCB})$ in the isotropic phase well above T_{NI} and in the smectic-A phase at a point unaffected by either the N-A or B-A transitions. This specific heat ratio is 1.12 in the isotropic phase at 90 °C and 1.11 in the smectic-A phase at 55 °C. Since 40.8 and 8OCB are fairly similar organic molecules, the heat capacities per gram away from any transition should be almost the same. If one introduces a correction based on this assumption, the ratio $\Delta\widetilde{C}_p(40.8)/\Delta\widetilde{C}_p(\text{8OCB})$ becomes 4.05 ± 0.6. For a discussion of two-scale-factor universality, one needs the critical heat-capacity per unit volume. The 40.8/8OCB ratio for this quantity is 3.5 ± 0.4 without correction and 3.15 ± 0.45 if the above correction is made.

As a final comment on the thermal properties, let us compare the $\Delta\widetilde{C}_p$ values in the smectic-A phase with those in the nematic phase. This comparison will indicate some differences in the behavior of 40.8 and 8OCB. Fits with Eq. (5) show that A'/A is unity or slightly less for 8OCB, while the best A'/A value for 40.8 is 1.17. Fits with Eq. (4) show that in the nematic phase the parameters A and B both increase by a factor of ~4.5 on changing from 8OCB to 40.8. In the smectic phase, however, the A ratio is 6.0 and the B ratio is 0.55. Thus the shapes of $\Delta\widetilde{C}_p$ in the smectic wing ($10^{-3}<|t|<10^{-2}$ range) are not the same for 40.8 and 8OCB. Another way to state the difference is by comparing the excess enthalpies

$$\delta H \equiv \int \Delta C_p dT$$

due to critical contributions: $\delta H=225$ J mol^{-1} for $T>T_c$ and 545 J mol^{-1} for $T<T_c$ in 40.8, whereas $\delta H=50$ J mol^{-1} above T_c and 50 J mol^{-1} below T_c in 8OCB. The large critical heat capacity and enthalpy in the smectic phase of 40.8 may be related in some way to the presence of the nearby crystal B–smectic-A transition ($T_{BA}=49.76$ °C), but the overall data given in Ref. 17 do not suggest any obvious complication in the smectic-A phase.

IV. DISCUSSION AND CONCLUSIONS

The most important empirical result of this paper is the observation that the critical behavior near the N-A transition in the single-layer material 40.8 is virtually identical to that in the bilayer materials 8OCB, 8CB, and CBOOA, which is also confirmed by the light-scattering results of von Känel and Litster.[20] We have noted in Secs. II and III that the exponents γ, $\nu_{\|}$, $\nu_{\perp}$, α, and α' agree to within the experimental errors in all four systems. We show in Fig. 9 the correlation lengths in 8OCB together with our new results in 40.8. From this figure it is evident that even the absolute lengths, measured in units of the smectic layer spacing, are quite similar. Thus the different exponents found[16] for $\overline{8}$S5 ($\gamma=1.53\pm.02$, $\nu_{\|}=0.83\pm0.01$, $\nu_{\perp}=0.68\pm0.02$, and $\alpha=\alpha'\simeq0.0$) must reflect some mechanism other than simply the single versus bilayer nature of the smectic phase. We shall return to this issue later.

We now have a rather complete empirical description of the N-A transition in 40.8. Thus it is possible to make a number of tests of aspects of the theory, other than the values predicted for the exponents themselves. First, in the de Gennes model,[4] the bend elastic constant K_3 should diverge like the longitudinal correlation length $\xi_{\|}$. In addition, by using the dynamical scaling theory of Jähnig and Brochard[32] for the q dependence of the director fluctuations, von Känel and Litster[20] have been able to deduce from their measurements of K_3 (via the crossover from the hydrodynamic to the critical regimes) a value for the bare length $\xi_{\|}^0$. They find

$$\xi_{\|}q_0=0.9(t)^{-0.69\pm0.03}\ . \tag{6}$$

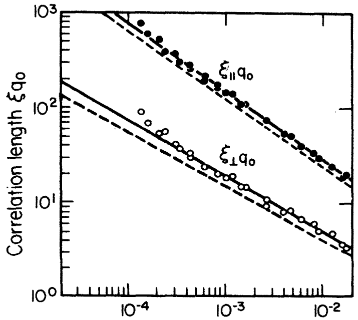

FIG. 9. Transverse and longitudinal correlation lengths in 8OCB, where $q_0=0.197$ Å^{-1}. Data are taken from Ref. 9. The dashed lines are the corresponding results in 40.8, as represented by Eqs. (2b)–(2c).

Clearly, this agrees very well with our x-ray result, given in Eq. (2b). This represents the most detailed test of this aspect of the theory to date.

Second, according to the hypothesis of two-scale-factor universality,[22] the divergent part of the free energy per correlated volume should have the same constant value independent of temperature, in all systems belonging to the same universality class. For the N-A transition this leads to

$$C_p^{\mathrm{crit}} t^2 \xi_{\|} \xi_{\perp}^2 = \mathrm{const}\ , \tag{7}$$

where C_p^{crit} is the critical contribution to the heat-capacity *per unit volume*. Equation (7) thus leads to an anisotropic hyperscaling relation for the critical exponents

$$\nu_{\|} + 2\nu_{\perp} = 2 - \alpha\ . \tag{8}$$

Using the results in Eqs. (2) one finds for 40.8

$$\begin{aligned} \alpha\ (\text{predicted}) &= 2 - \nu_{\|} - 2\nu_{\perp} \\ &= 0.16 \pm 0.03\ . \end{aligned}$$

This agrees to within the errors with the value $\alpha = 0.15$ deduced from the heat capacity using Eq. (5), which includes corrections-to-scaling terms. For fits with a single power law, Eq. (4) with $\alpha = \alpha'$, one finds $\alpha = 0.23 \pm 0.05$, again in reasonable agreement with the anisotropic hyperscaling prediction. It should be noted that scattering results[9] for 8OCB also lead to

$$\begin{aligned} \alpha\ (\text{predicted}) &= 2 - \nu_{\|} - 2\nu_{\perp} \\ &= 0.16 \pm 0.12\ , \end{aligned}$$

which is again consistent with the heat-capacity analysis. Since $\xi_{\|}$ and $\xi_{\perp}$ are known in absolute units for 40.8 and 8OCB we may also use Eq. (7) to predict the ratio of the heat capacities in these two materials. From Fig. 9 we can deduce that $\xi_{\|}\xi_{\perp}^2(\mathrm{8OCB})/\xi_{\|}\xi_{\perp}^2(40.8)$ has the constant value 2.6 ± 0.8 throughout the reduced temperature range. The error limit represents the cumulative uncertainties due to possible differences in the absolute lengths observed for different samples of the same material. This value of 2.6 ± 0.8 should be compared with the temperature-independent value of 3.15 ± 0.45 for $C_p^{\mathrm{crit}}(40.8)/C_p^{\mathrm{crit}}(\mathrm{8OCB})$. Again the agreement is quite good. It is of considerable interest that the two-scale-factor universality hypothesis works well in these anisotropic liquid-crystal systems; similar agreement has been found for the familiar 3D Ising system.[33]

Clearly, a number of important predictions of the de Gennes model work quite well in 40.8 over the reduced temperature range $10^{-5} < t < 10^{-2}$. We conclude this article with a brief discussion of the exponents themselves. Our results are given in Eqs. (2) and Table I. von Känel and Litster[20] have also measured the layer compressibility B and the molecular tilt elastic constant D in the smectic phase of 40.8. They find $D \sim t^{0.54 \pm 0.04}$ and $B \sim t^{0.32 \pm 0.03}$. According to Lubensky and Chen,[21] $D \sim 1/\xi'_{\|}$ and $B \sim \xi'_{\|}/\xi_{\perp}'^2$ where the prime denotes $T < T_c$. Thus, from the smectic elastic constants one would infer that $\nu'_{\|} = 0.54 \pm 0.04$ and $\nu'_{\perp} = 0.43 \pm 0.04$, yielding an exponent difference $\nu'_{\|} - \nu'_{\perp} = 0.11 \pm 0.02$, similar to that obtained for $T > T_c$. We emphasize, however, that the values for $\nu'_{\|}$ and $\nu'_{\perp}$ would imply

$$\alpha' = 2 - \nu'_{\|} - 2\nu'_{\perp} = 0.60 \pm 0.012$$

which differs markedly from the observed value of 0.15. Thus not only are the values for $\nu'_{\|}$ and $\nu'_{\perp}$ quite anomalous but they also do not satisfy hyperscaling. This leads one to suspect that the relationship between the smectic elastic constants and the correlation lengths given above are not correct. One possible source of this discrepancy is the fact that the smectic state is characterized by algebraic decay of the mass density correlations rather than true long-range order. In the dislocation theory of Nelson and Toner, B exhibits a jump from a finite value to zero at T_c, so that the critical exponent for B is by definition zero. We summarize all these critical exponents in Table II.

The critical exponents obtained theoretically[5] for the simple three-dimensional XY model are also listed in Table II, and it is evident that for 40.8 only γ and perhaps $\nu_{\|}$ agree reasonably with these predictions. Furthermore, one of the basic tenets of the theory of critical phenomena is that there is a single divergent length and this length diverges at the same rate above and below T_c. This expectation is clearly violated in 40.8 and in bilayer smectics, as emphasized previously.[8,12] As mentioned in Sec. I, the theory due to Lubensky and Chen[21] allows for anisotropic precritical behavior with nonuniversal exponents. This could possibly explain the results although the theory would also have to account for the single-power-law behavior observed for σ_0, $\xi_{\|}$, and $\xi_{\perp}$ over the wide reduced temperature range $10^{-5} < t < 10^{-2}$. In the absence of quantitative calculations it is difficult to know if their theory will provide a satisfactory explanation. In the dislocation unbinding model of Nelson and

TABLE II. Critical exponents characterizing the N-A transition in 40.8 deduced from x-ray, heat-capacity, and light-scattering measurements. The 3D XY exponents are listed for comparison.

	$T > T_c$	$T < T_c$	XY model
γ	1.31 ± 0.02		1.32
$\nu_{\parallel}$	0.70 ± 0.01	0.54 ± 0.04	0.67
$\nu_{\perp}$	0.57 ± 0.01	0.43 ± 0.04	0.67
$\nu_{\parallel} - \nu_{\perp}$	0.13 ± 0.02	0.11 ± 0.02	0
α	0.15	0.15	-0.02

Toner,[23] one has $\nu_{\parallel} = 2\nu_{\perp}$. If this model were correct, then a drastic crossover would be required for $t < 10^{-5}$. This seems unlikely to us although no definitive statement will be possible until an explicit crossover function is calculated.

Finally, we note that if one applies the scaling law $\gamma = \nu(2 - \eta)$, one deduces for 40.8: $\eta_{11} = 0.13 \pm 0.06$ and $\eta_{\perp} = -0.30 \pm 0.06$. A negative value for η is very unusual in the phase transition problem. These values for η would imply that $\sigma(\vec{q})$ should exhibit $(q_{\parallel} - q_0)^{-1.87}$ and $\bar{q}_{\perp}^{-2.30}$ behavior at large q. In the Caillé theory[7] in the smectic phase one predicts tails of the form $(q_{\parallel} - q_0)^{-2+x}$ and $q_{\perp}^{-4+2x}$. Thus, the anomalous value for $\eta_{\perp}$ in the nematic phase may represent a precursor for the unusual Landau-Peiers algebraic decay form[7] for $\sigma(\vec{q})$ in the smectic phase.

In summary, as noted by Nelson and Toner,[23] the nematic–smectic-A transition remains one of the major unsolved problems in the field of equilibrium critical phenomenon. On the one hand, such features as two-scale-factor universality and the predicted relationship between K_3 and $\xi_{\parallel}$ are quite well confirmed. On the other hand, the values of the critical exponents themselves, the observation of two divergent lengths, and the discrepancies between the correlation length exponents above and below T_c remain unexplained. Further, the fact that different exponents are measured in 40.8 and $\bar{8}$S5 is quite puzzling. Indeed it is important that similar experiments be carried out on additional materials in order to identify the mechanism giving rise to this nonuniversality. Clearly, a continued theoretical effort is also required.

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