Critical behavior at the nematic–smectic-A transition in butyloxybenzylidene heptylaniline (4O.7)

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High-resolution ac calorimetric, x-ray, and light-scattering measurements have been made on N-[4-(*n*-butyloxy)benzylidene]-4′-(*n*-heptyl)aniline (4O.7) near the nematic–smectic-A phase transition. This transition is second order, with a variation in C_p which is well described by a critical exponent $\alpha=\alpha'=-0.026$ corresponding to the three-dimensional XY model. The longitudinal and transverse correlation lengths exhibit single-power-law divergences over the reduced-temperature range 10^{-2} to 3×10^{-5} with exponents $\nu_{\|}=0.78\pm0.02$ and $\nu_{\perp}=0.65\pm0.02$, respectively. The anisotropic hyperscaling relation $\nu_{\|}+2\nu_{\perp}+\alpha=2$ is satisfied to within the errors. A dynamical-scaling analysis of light-scattering measurements of the bend-mode director fluctuations with elastic constant K_3 yields values for $\xi_{\|}$ which agree absolutely with the x-ray measurements. Thus the data are all internally consistent, and they appear to exclude all current theories of the nematic–smectic-A transition. It is observed that the overall critical behavior in smectic liquid crystals is sensitive to the width of the nematic range; this may offer an explanation for the apparent nonuniversality of the exponents.

I. INTRODUCTION

There is not yet a theoretical or experimental consensus about the universality class for the critical behavior at the nematic (N) to smectic-A (Sm-A) phase transition in liquid crystals. Lubensky[1] has recently provided a theoretical overview of this transition that is based on an extensive analysis of the de Gennes model.[2] For a three-dimensional (3D) system with finite splay elasticity, Lubensky argues that this model allows two asymptotic possibilities: an isotropic critical point in the same universality class as type-II superconductors, or an anisotropic critical point whose universal behavior is not yet well defined. The isotropic critical point should be described by the inverted XY model[3–5] for which the critical exponents for heat capacity, correlation lengths, and susceptibility are $\alpha=-0.026$, $\nu_{\|}=\nu_{\perp}=0.67$, and $\gamma=1.32$, respectively. There are no theoretical predictions of the critical exponents for the anisotropic universality class, but it is known that $\nu_{\|}=2\nu_{\perp}$ in this class.[6] Certain theories[4,5] have as an essential feature the theoretical XY exponents describing the properties of an unphysical transformed order parameter. It is predicted that thermodynamic quantities such as heat capacity and nematic elastic constants should exhibit transformation-independent divergences whereas x-rays, which couple to the physical mass density fluctuations, should present different behavior. For example, for the isotropic fixed point Lubensky *et al.*[4] predict simple XY behavior for longitudinal correlations but crossover behavior for transverse correlations $\nu_{\|}(\text{x ray})=\nu_{XY}$, $\nu_{\perp}(\text{x ray})=\nu_{XY}$ crossing over to $\nu_{\perp}(\text{x ray})=\frac{1}{2}\nu_{XY}$ as $T\to T_c$. Toner,[5] on the other hand, suggests $\nu_{\|}(\text{x ray})=\frac{6}{5}\nu_{XY}$ and $\nu_{\perp}(\text{x ray})=\frac{4}{5}\nu_{XY}$.

None of the above models is in complete agreement with the available experimental data, and there is some evidence that the effective critical behavior observed experimentally is sensitive to the width of the nematic range. Various measurements of the heat-capacity variation[7–10] near the N–Sm-A transition have yielded rather large positive values for the critical exponent α (in the range 0.15–0.30) with the exception of 4-(*n*-pentyl)phenylthio-4′-(*n*-octyloxy)benzoate (8S5), for which $\alpha=0$ has been reported.[9] Concomitantly, the correlation-length exponents change so that the anisotropic hyperscaling relation $\nu_{\|}+2\nu_{\perp}+\alpha=2$ is satisfied to within the errors.[7] The largest α values seem to occur in liquid crystals with narrow nematic ranges in contrast to

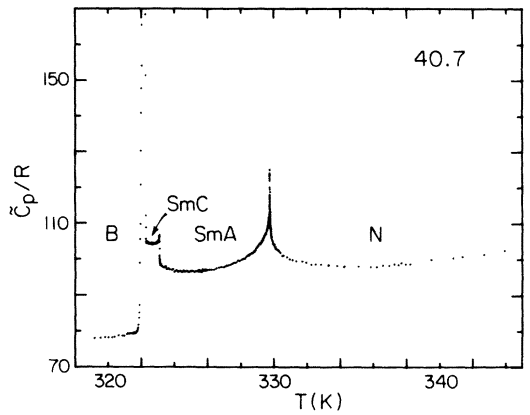

FIG. 1. Heat capacity of 4O.7 obtained with a high-resolution ac calorimeter.

8S5 where the nematic phase exists over a range of 23 K. Thus it is of interest to carry out high-resolution heat capacity and scattering investigations of another liquid crystal with an extensive nematic phase. N-[4-(*n*-butyloxy)benzylidene]-4′-(*n*-heptyl)aniline (4O.7) is an attractive system since the nematic phase is stable over a range of 26 K (Ref. 11); further, accurate data are available for the homolog 4O.8 which has a narrower nematic range so that direct comparison is possible.[7,12]

We report the results of these studies in this paper. In Sec. II the heat-capacity measurements and analysis are presented. Section III contains the x-ray and light-scattering results and analysis. Discussion and conclusions are given in Sec. IV.

II. HEAT CAPACITY

The 4O.7 sample, obtained from Goodby of Bell Laboratories, was of high purity as indicated by the sharp transitions and high-transition temperatures. The heat capacity C_p was measured over the 319–345-K range with a computer-controlled ac calorimeter described elsewhere,[8,13] and the overall variation is shown in Fig. 1. These results are of much higher resolution than earlier measurements on a sample of lower purity.[11] Second-order N–Sm-A and Sm-A–Sm-C transitions occur at 329.751 K and 323.106 K, respectively, and a first-order transition between the smectic-C and plastic crystalline B phase occurs at 321.90–322.25 K (two-phase coexistence range). The weakly first-order nematic-isotropic (I) transition at 356.0 K was not reinvestigated.

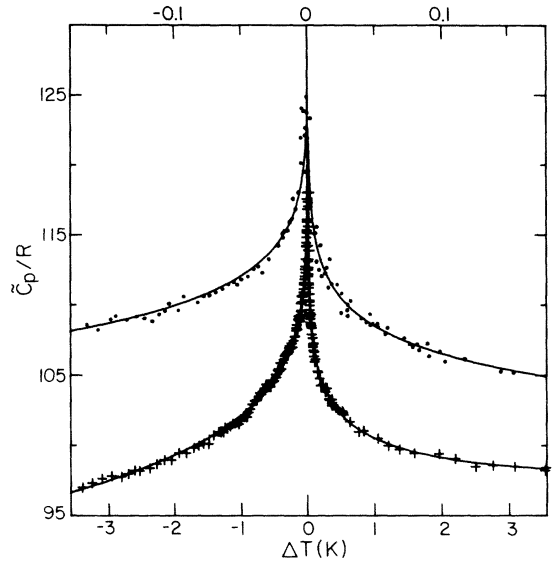

FIG. 2. Detail of C_p variation near the N–Sm-A transition in 4O.7. $\Delta T = T - T_c$ scale on the bottom corresponds to the data points (+) in range 1, for which $|t| \leq 10^{-2}$. Greatly expanded ΔT scale at the top corresponds to the data points (●) in range 2, for which $|t| \leq 5\times10^{-4}$. Lines represent the best fit with the XY model, i.e., Eq. (1) using the parameters of fit 2.

Figure 2 shows in detail the C_p data near the N–Sm-A transition and the best fit with a power-law singularity. The general form for the heat capacity near a second-order transition, including corrections-to-scaling terms, is

$$\tilde{C}_p/R = \begin{cases} At^{-\alpha}(1+Dt^{\Delta_1})+B+E(T-T_c), & T>T_c \\ A'|t|^{-\alpha'}(1+D'|t|^{\Delta_1'})+B'+E'(T-T_c), & T<T_c \end{cases} \quad (1)$$

where $\tilde{C}_p$ is the molar heat capacity, R is the gas constant, and the reduced temperature $t \equiv (T-T_c)/T_c$. The terms $E\Delta T$ and $E'\Delta T$ represent the noncritical variation due to the regular contribution to the free energy, and both regular and critical terms contribute to the quantities B and B'. From scaling arguments, one expects that $\alpha=\alpha'$ for the critical exponents, $\Delta_1=\Delta_1'$ for the correction-to-scaling exponents, $B=B'$, and $E=E'$. We have fixed Δ_1 at the value 0.5 predicted for the 3D XY

TABLE I. Least-square parameters for a simultaneous fit to heat-capacity data above and below T_c with Eq. (1) and the scaling constraints $\alpha=\alpha'$, $\Delta_1=\Delta_1'$, $B=B'$, and $E=E'$. The exponent Δ_1 was set equal to 0.5, and the slope E was held fixed at 0.25 K^{-1}. Parentheses indicate that a parameter was held constant at the indicated value. The reduced temperature ranges used in the fits were (1) $1.5\times10^{-5}<|t|<10^{-2}$ for which $\tilde{\nu}=191$ and (2) $1.5\times10^{-5}<|t|<5\times10^{-4}$ for which $\tilde{\nu}=83$.

Fit	B	A	A'	α	T_c	D	D'	Range	χ_ν^2
1	140.85	−79.04	−69.45	(−0.10)	329.7515	−1.398	−0.187	1	1.36
2	223.72	−145.26	−140.10	(−0.026)	329.7515	−0.213	0.128	1	1.17
3	28.22	59.49	62.53	(0.034)	329.7515	−0.069	−0.048	1	1.19
4	96.51	3.58	4.62	(0.15)	329.7519	−9.556	−8.420	1	1.43
5	225.29	−146.93	−142.42	(−0.026)	329.7515	(0)	(0)	2	1.75
6	24.57	62.14	64.77	0.034	329.7515	(0)	(0)	2	1.68

model. We have also estimated from Fig. 1 that $E=E'=0.25$ K^{-1} represents a physically reasonable choice for the regular background slope. The least-squares values of the remaining parameters in Eq. (1) are given in Table I, along with the reduced chi-squared value

$$\chi_\nu^2=\frac{1}{\tilde{\nu}}\sum_{i=1}^{n}\sigma_i^{-2}[y_i(\text{obs})-y_i(\text{calc})]^2\,, \tag{2}$$

where y denotes $\tilde{C}_p/R$ and $\tilde{\nu}=n-p$ is the number of degrees of freedom, n being the number of data points and p the number of adjustable parameters.

Data points within ±5 mK of T_c were omitted from the fits since the ac temperature oscillations were approximately ±5 mK and such data are systematically distorted by instrumental effects. Thus $|t|_{\min}\cong1.5\times10^{-5}$, and $|t|_{\max}$ was chosen to be 10^{-2} for the largest fitting range. The results in Table I show that there is a broad minimum in χ_ν^2 for α values close to zero.[14] This conclusion is unaffected by small shifts in T_c, range shrinking, or variations in the slope E. When T_c was fixed at 329.750 K, which represents the center of the cluster of peak C_p values omitted from the fit, the χ_ν^2 values increased by ~0.1 but there was no significant effect on the fitting parameters or on the location of the χ_ν^2 minimum. Fits 5 and 6 show that shrinking the range drastically has almost no effect. Although the narrow range 2 close to T_c gives a small positive α as the best least-squares value, the difference between the quality of fits 5 and 6 is not statistically significant. Finally, it is possible to improve the χ_ν^2 values somewhat if $E=E'$ is allowed to be a freely adjustable parameter. The main effect of this is to broaden the χ_ν^2 minimum so that fits with $\alpha=-0.026$, 0.034, and 0.15 are of equal quality. However, this apparent improvement in the $\alpha=0.15$ fit is artifical since it requires an unreasonably large slope ($E=1.02$) and large asymmetric D values ($D=-10.51$ and $D'=-5.16$).[15] It should also be noted that although the parameters E, D, and D' are strongly coupled, a variation of E has very little effect on any of the other parameter values.

In summary, the best empirical value for the critical exponent α must lie close to zero in 4O.7 and the data are clearly consistent with the XY value $\alpha=-0.026$. The amplitude ratio A/A' associated with this α value is 1.035, and this value is not sensitive to variations in E or to the presence of the rather small corrections-to-scaling terms. The experimental ratio differs somewhat from the value of 0.90 for the inverted XY model and, in fact, is closer to the normal XY value of 1.1.

III. SCATTERING MEASUREMENTS

A. X-ray scattering

The smectic mass density fluctuations in the nematic phase may be probed directly using x-ray scattering techniques.[7,16–18] The experiments were carried out using Cu $K\alpha$ x rays from a Rigaku 12-kW rotating-anode source operating at 8 kW. A longitudinal in-plane resolution of 1.1×10^{-4} Å^{-1} half-width at half maximum was achieved by using perfect Si(111) crystals as monochromators and analyzers. A relatively tight slit configuration was used so that the background was only 0.2 counts per second compared with $\sim10^4$ counts per second in the smectic peak at the N—Sm-A transition. The 4O.7 samples were placed in beryllium cells in a two-stage computer controlled oven; the temperature was stable to ±0.002 K over the period of a scan.

Two separate samples were studied: Sample 1, which was obtained from CPAC Organix, had an N—Sm-A transition at 328.08 K. Sample 2, which was synthesized by Goodby and which was of rather higher purity, exhibited an N—Sm-A transition at 329.48 K. This is close to, but slightly lower than,

the heat-capacity value for a sample from the same batch. The samples were aligned with a magnetic field of 4 kG. A full discussion of x-ray measurements of all of the phases and phase transitions in 4O.7 (N, Sm A, Sm C, B, and restacked B) will be given in a separate publication.[19] In this paper we limit ourselves to a presentation of the N–Sm-A critical behavior results.

In the nematic phase the critical scattering is centered about the points $(0, 0, \pm q_{||}^0)$. As demonstrated previously,[17,18] the scattering is well represented by the form

$$\sigma(\vec{q})=\frac{\sigma_0}{1+\xi_{||}^2(q_{||}-q_{||}^0)^2+\xi_\perp^2 q_\perp^2(1+c\xi_\perp^2 q_\perp^2)} . \quad (3a)$$

Thus from scans through $(0, 0, q_{||}^0)$ along q_z and q_x it is possible to measure σ_0, $\xi_{||}$, and $\xi_\perp$. The results so obtained are shown as functions of reduced temperature in Fig. 3. It should be noted that for both samples T_c could be determined to within 2 mK from the width of the transverse scans. For these data the fourth-order coefficient c is negligible for $t<10^{-3}$ and rises to about 0.25 for $t=10^{-2}$.

There are a number of qualitative features of interest. The ratio $\xi_{||}/\xi_\perp$ evolves from 11 at $t=10^{-2}$ to 22 at $t=2\times10^{-5}$. These may be compared with the molecular length-to-width ratio of about 7.

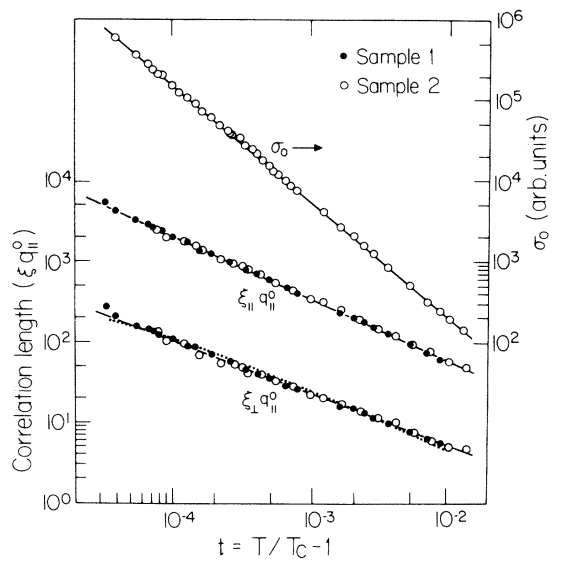

FIG. 3. Smectic susceptibility and longitudinal and transverse correlation lengths in the nematic phase of 4O.7. For samples 1 and 2, $T_c=328.08$ K and 329.48 K, respectively. Susceptibility data are only shown for sample 2; those for sample 1 are identical to within the errors. Solid lines are the power laws, Eqs. (3b)–(3d), as discussed in the text. Dotted line is the result of a fit to Lubensky's crossover function with $\nu_{||}=0.78$.

Thus the two lengths diverge at different rates as observed previously for all well-documented N–Sm-A transitions.[7,18,20,21] It is also quite gratifying that the absolute lengths in samples 1 and 2 agree very well over the complete range 10^{-2} to 3×10^{-5} in spite of the fact that $T_{c2}/T_{c1}-1=4\times10^{-3}$. We conclude, therefore, that the impurities causing the depression of T_c in sample 1 have no measurable effect on the critical behavior. Least-squares fits of the data in Fig. 3 to single power laws over the range $10^{-2}\le t\le3\times10^{-5}$ yield the following results:

$$\sigma_0\sim t^{-1.46\pm0.03} , \quad (3b)$$

$$\xi_{||}q_{||}^0=1.55t^{-0.78\pm0.02} , \quad (3c)$$

$$\xi_\perp q_{||}^0=0.25t^{-0.65\pm0.02} , \quad (3d)$$

where $q_{||}^0=0.2337$ Å^{-1}. It is evident from Fig. 3 that these single power laws fit the data quite well. We have also fitted the $\xi_\perp q_{||}^0$ data to the crossover form suggested by Lubensky and co-workers[1,4]; this form involves a crossover from $\nu_\perp=\nu_{||}$ to $\nu_\perp=0.5\nu_{||}$ at $t\cong3\times10^{-4}$. The result,[19] shown as the dotted line in Fig. 3, clearly provides an adequate description of the data although there are systematic discrepancies from the experimental results.

B. Light scattering

Using light-scattering techniques one may probe the effects of smectic order on the director fluctuations; in the nematic phase, these include the critical behavior of the nematic elastic constants and the twist viscosity. In this paper we focus our attention on the critical behavior of the bend elastic constant K_3. The samples, which utilized the 4O.7 synthesized by CPAC Organix and purified by us, were prepared in planar or homogeneous alignment. Alignment was achieved using surface relief gratings as discussed previously.[22]

By choosing the scattering geometry such that the momentum transfer is along the nematic axis the relevant correlation function is given by

$$\langle\delta\epsilon_{zx(y)}(\vec{q},0)\delta\epsilon_{zx(y)}(\vec{q},\tau)\rangle=\frac{\epsilon_a^2 kT}{K_3 q_z}e^{-\Gamma_b\tau} , \quad (4)$$

where $\Gamma_b=K_3q_z^2/\eta_{\text{bend}}$. The intensity is given by Eq. (4) with $\tau=0$; that is,

$$I\cong\frac{\epsilon_a^2}{K_3} . \quad (5)$$

However, because the measurements are carried out at finite wave vector, there is a crossover from the hydrodynamic to the critical region as $T\to T_c$. As discussed by Jähnig and Brochard,[23] this crossover

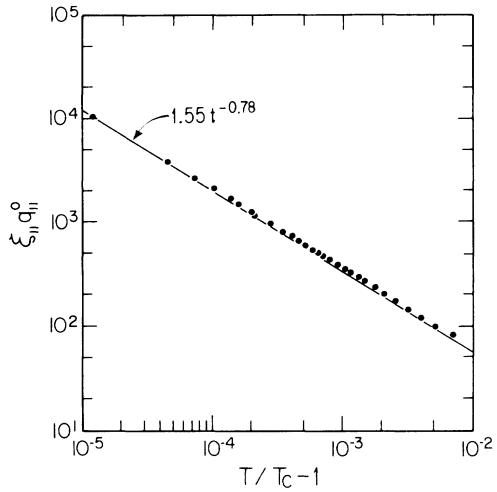

FIG. 4. Temperature dependence of the longitudinal correlation length deduced from the $q_\perp=0$ light-scattering intensity as discussed in the text.

effect may be incorporated into Eq. (5) by writing

$$K_3=K_3^0+\frac{kT(q_{\parallel}^0)^2}{8q_z}\left|\left[1+\frac{1}{X^2}\right]\tan^{-1}X-\frac{1}{X}\right|, \tag{6}$$

where $X=\frac{1}{2}q_z\xi_{\parallel}=\frac{1}{2}q_z\xi_{\parallel}^0 t^{-\nu_{\parallel}}$. Analysis of the data with Eqs. (5) and (6) thus allows one to extract absolute smectic correlation lengths from the light-scattering data.

For the 4O.7 sample studied, T_c was 329.51 K in good agreement with the x-ray and heat-capacity values. The results for $\xi_{\parallel}$ obtained from the K_3 light-scattering data using Eqs. (5) and (6) are shown in Fig. 4. The solid line is Eq. (3c), the best power-law fit to the x-ray longitudinal correlation length results. In extracting $\xi_{\parallel}$ from the light-scattering data, only K_3^0 is adjusted to yield the best fit; there are no other adjustable parameters in the comparison of the x-ray and K_3 measurements. We note also that $\xi_{\parallel}$ deduced from Eqs. (5) and (6) is insensitive to K_3^0 for $t<10^{-3}$. Clearly, these results place severe restrictions on theories which predict that the nematic elastic constants and the mass density fluctuations may exhibit different divergences.

IV. DISCUSSION AND CONCLUSIONS

The results of this investigation as well as high-precision results for other materials are summarized in Table II. It is evident that the two materials with the widest nematic ranges $\bar{8}$S5 and 4O.7 have closely similar critical exponents γ, $\nu_{\parallel}$, $\nu_\perp$, and α. It is also apparent that α increases continuously as the nematic range decreases (see also Refs. 9, 10, and 25). A similar trend, albeit in the opposite direction, holds for the correlation-length exponents. One of the striking features of Table II is that the anisotropic hyperscaling relation

$$\alpha+\nu_{\parallel}+2\nu_\perp=2 \tag{7}$$

seems to be quite well obeyed. The experimental precision in determining $\alpha+\nu_{\parallel}+2\nu_\perp$ is not sufficient to rule out a value as high as 2.1, but there does not appear to be any systematic trend in this quantity with changes in nematic range. The one case where the deviation from hyperscaling appears to exceed the combined experimental errors is $\bar{8}$S5. However, there is a recent report[25] that $\alpha=-0.17\pm0.03$ for $\bar{8}$S5, which would yield $\alpha+\nu_{\parallel}+2\nu_\perp=2.02$. Unfortunately this $\alpha=-0.17$ value is based on data rather far from T_C ($|t|_{\min}\cong10^{-4}$), but it does suggest that the best α value for $\bar{8}$S5 may be negative. A second interesting feature of Table II is the fact that within the experimental errors $(\nu_{\parallel}-\nu_\perp)$ is almost constant, independent of nematic range with a median value

$$\nu_{\parallel}-\nu_\perp=0.13\ . \tag{8}$$

Finally, for each of the compounds in Table II the

TABLE II. Effective critical exponents obtained from heat-capacity and x-ray scattering experiments near the N–Sm-A transition in several liquid crystals. Note the trends with T_{NA}/T_{NI}, which is a measure of the width of the nematic range. 8OCB represents 4-cyano-4′-(*n*-octyloxy)biphenyl; CBOOA represents N(4-cyanobenzylidene)-4′-(*n*octyloxy)aniline.

Material	References	T_{NA}/T_{NI}	$\alpha=\alpha'$	$\nu_\perp$	$\nu_{\parallel}$	γ	$\alpha+\nu_{\parallel}+2\nu_\perp$
XY model	24		−0.026	0.67	0.67	1.32	2
8CB	10 and 20	0.977	0.31	0.51	0.67	1.26	2.00±0.13
8OCB	8 and 17	0.963	0.2	0.58	0.71	1.32	2.07±0.17
4O.8	7	0.958	0.15	0.57	0.70	1.31	1.99±0.08
CBOOA	17 and 18	0.94	0.15	0.62	0.70	1.30	2.09±0.14
$\bar{8}$S5	9 and 21	0.936	0.0	0.68	0.83	1.53	2.19±0.16
4O.7		0.926	−0.03	0.65	0.78	1.46	2.05±0.10

critical behavior of K_3 is identical to that of $\xi_{||}$. Indeed in 4O.7 and N-[4-(*n*-butyloxy)benzylidene]-4′-(*n*-octyl) aniline (4O.8) it has been shown that the absolute lengths deduced from the K_3 measurements agree with the x-ray measurements to within the errors. It should also be noted that for all of the materials, single-power-law fits to all quantities typically work well over the reduced temperature range 10^{-2} to 2×10^{-5}. There appears to be no indication of crossover effects in the data. This is particularly well documented in 4O.7, 4O.8, and 4-cyano-4′-(*n*-octyl)biphenyl (8CB).

No current theory seems to be capable of accounting for all of these results. It is possible that the trend with T_{NA}/T_{NI} is caused by incipient *tricritical* behavior which would occur for $T_{NA}/T_{NI}\cong0.98$. Johnson and co-workers[9] have explained the trend of the heat-capacity data in the 4-(*n*-pentyl)phenylthio-4′-(*n*-alkoxy)benzoate ($\bar{n}$S5) series on this basis. This idea clearly deserves more careful examination both experimentally and theoretically. However, this will require reconciling the high-quality single-power-law fits in 4O.8 and 8CB with an appropriate tricritical crossover model. The exponents themselves, of course, still remain a puzzle. It should also be mentioned that both $\bar{8}$S5 and 4O.7 have nearby Sm-C phases. We do not believe that this is an important differentiating feature; nevertheless it would be valuable to obtain data in a system with a long nematic range and with no Sm-C phase.

Finally, we compare the predictions of various theories with our 4O.7 results. First, the original de Gennes model[2] which predicts simple XY behavior accounts adequately for α, $\nu_\perp$, and the relationship between K_3 and $\xi_{||}$. However, it gives incorrect results for γ and $\nu_{||}$ and, of course, cannot account for the anisotropic growth of the correlation lengths. It has been felt for some time that the length anisotropy originates in the divergent phase fluctuations characterizing the smectic phase and recent theories have attempted to incorporate those features. Both Lubensky *et al.*[1,4] and Toner,[5] building on the dislocation loop model of Nelson and Toner,[6] predict that the thermodynamic quantities should exhibit inverted XY critical behavior.[3] This again appears adequate for the heat capacity but it clearly fails for K_3. In these models, the x-ray measurements should measure transformed lengths with critical behavior $\nu_{||}=\nu_\perp=\nu_{XY}$ crossing over to $\nu_{||}=\nu_{XY}$, $\nu_\perp=\frac{1}{2}\nu_{XY}$ for the isotropic fixed point according to Lubensky *et al.*,[4] and $\nu_{||}=\frac{6}{5}\nu_{XY}$, $\nu_\perp=\frac{4}{5}\nu_{XY}$ according to Toner.[5] As discussed in Sec. III A the Lubensky *et al.* crossover form for $\xi_\perp$ gives a reasonable description of the data (although not as good as a single power law) provided that $\nu_{||}$ is fixed at 0.78 rather than ν_{XY}. Toner's value for $\nu_{||}$ is in reasonable agreement with the measured value. However, his model explicitly predicts that K_3 should exhibit pure XY behavior in disagreement with our measurements and further he predicts $\nu_\perp=0.54$ which differs considerably from the measured value in 4O.7.

It is clear that continued experimental and theoretical work is required before we are likely to obtain a satisfactory explanation of what was, at one time, viewed as the simplest possible freezing transition. Nevertheless, existing data establish a clear trend in the behavior with T_{NA}/T_{NI}. Further, all experimental data measured in the laboratory "gauge" are internally consistent. These features must be contained in the correct model of the nematic–smectic-A transition.

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[14]It should be noted that a good fit ($\chi^2_\nu = 1.18$) to the $\tilde{C}_p/R$ data in range 1 can also be obtained with the form $84.73 - 2.909 \ln|t| + AD|t|^{0.5} + 0.25(T - T_c)$, where $(AD) = 14.13$ and $(AD)' = -22.88$. This form, which represents the $\alpha \to 0$ limit of Eq. (1), is not the same as the logarithmic form used to fit $\overline{8}S5$ in Ref. 9.

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