Simultaneous Magnetic-Deformation and Light-Scattering Study of Bend and Twist Elastic-Constant Divergence at the Nematic–Smectic-*A* Phase Transition

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Simultaneous magnetic-deformation and light-scattering studies of the nematic bend and twist constant exponents respectively suggest that the nematic–smectic-*A* critical point is weakly anisotropic, in disagreement with all theories of the nematic–smectic-*A* transition. This study also suggests that the bend exponent is universal and very close to the helium value.

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Interest in the smectic-*A* (and *C*) phases of liquid crystals transcends that of most other spatially ordered systems because of the fundamental question of the stability of layered structures first raised by Landau and Peirels[1] and studied by de Gennes[2] in connection with liquid crystals. The role of the nematic director is unique in this problem and leads to a striking but incomplete analogy with superconductors,[2] and to curious critical phenomena near the nematic–smectic-*A* phase transition.

For example, x-ray studies[3] of the smectic-*A* correlation lengths $\xi_\parallel^x$, $\xi_\perp^x$ suggest that the nematic–smectic-*A* critical point is weakly anisotropic ($\nu_\parallel^x - \nu_\perp^x \sim 0.12$). This is in disagreement with the isotropic and anisotropic de Gennes models[2,4] ($\nu_\parallel = \nu_\perp$ and $\nu_\parallel = 2\nu_\perp$), de Gennes's isotropic superfluid analogy[2] ($\nu_\parallel = \nu_\perp \sim \frac{2}{3}$), the dislocation-loop model of Helfrich[5] studied by Nelson and Toner[6] ($2\nu_\perp = \nu_\parallel$), and the inverted *X-Y* model of Dasgupta and Halperin[7] ($\nu_\parallel = \nu_\perp$), i.e., with all theories of this complex phase transition.[8] Therefore, the nematic–smectic-*A* phase transition remains one of the most interesting unsolved examples of static critical phenomena.

Lubensky and co-workers[9] have argued that $\xi_\parallel \sim \delta K_3 \sim t^{-\rho_3}$, $\xi_\perp \sim (\delta K_2 \delta K_3)^{1/2} \sim t^{-(\rho_3+\rho_2/2)}$ are the thermodynamic lengths rather than $\xi_\parallel^x, \xi_\perp^x$; δK_2 (δK_3) is the divergent part of the nematic twist (bend) elastic constant. For $2\nu_\perp \geqslant \nu_\parallel$ they find $\nu_\parallel^x = 2\nu_\perp^x$, implying that the fixed point may be isotropic ($\rho_3 = \rho_2$) even if $\nu_\parallel^x \neq \nu_\perp^x$. Therefore, a question of high current interest is whether $\rho_2 = \rho_3$.

We report the first high-resolution magnetic-deformation study of the bend elastic-constant exponent ρ_3, and compare it with ρ_2 from a simultaneous light-scattering study.[10] This is also the first high-resolution study of K_3 in the hydrodynamic regime. Previous light-scattering measurements encountered the nonhydrodynamic regime below relatively large reduced temperature ($\sim 10^{-3}$). Hence, we are also now able to compare high-resolution ρ_3's measured in the nonhydrodynamic regime against universality and the predictions of the superfluid and other models. The critical advantage of a simultaneous study of K_2 and K_3 is the technical advantage that a precise determination of T_c from light scattering allows it to be applied as a constraint in the fitting of the K_3 data.

The four materials studied were octyloxycyanobiphenyl (8OCB),[11] 4-*n*-pentylphenylthiol-4′-*n*-octyloxybenzoate ($\bar{8}$S5),[12,13] 4-*n*-nonylphenyl-4′-*n*-pentylbenzthiolate (9S5),[12] and 4-*n*-hexyloxybenzoate ($\bar{6}$O9),[11] for which there exist (except for 9S5) published x-ray measurements of $\nu_\parallel^x$ and $\nu_\perp^x$. The heat-capacity exponent α has also been measured for 8OCB[14] and ($\bar{8}$S5),[15] allowing the first tests of anisotropic hyperscaling[4,8,9] in the form $\rho_2 + 2\rho_3 = 2 - \alpha$.

It has long been known that just above T_c a severely bent nematic undergoes the so-called stripe instability. Cladis and Torza[16] studied this experimentally and theoretically. Chu and McMillan[17] suggested that it is due to a first-order transition to a highly strained state at a field below the Fréedericksz field, H_c.

We studied the stripe regime carefully as a function of the angle between the field and the undistorted director $\hat{\mathbf{n}}_0$. Remarkably, for $\mathbf{H} \perp \hat{\mathbf{n}}_0$ the stripes always set in at H_c when $T - T_c \lesssim 0.06$ K, and not at all for $T - T_c \gtrsim 0.06$ K (see Fig. 1, inset). This is true of all four samples independent of thickness. For fields at an angle θ from the perpendicular the stripe threshold is higher than H_c by an amount which decreases with $T - T_c$ until H_c and the stripe boundary are concurrent for $T - T_c < \Delta T(\theta)$. For even slight deviations from $\theta = 0$ the decrease in ΔT is quite dramatic.

The 8OCB and $\bar{6}$O9 experiments were done at $\theta \sim 0.14°$ where $\Delta T \sim 0.02$ K. The $\bar{8}$S5 experiment was done at both $\theta \sim 0°$ and $\theta = 45°$ and the 9S5 sample at 45°. In the 45° experiments the transmitted intensity vs H data were analyzed in the vicinity of the first fringe to determine H_c.[12]

Figure 1 shows that the Fréedericksz and stripe boundaries join smoothly near $T-T_c=\Delta T$. Data analyses confirmed that inclusion of data below ΔT leaves the exponent unchanged. This was further confirmed in the $\overline{8}$S5 experiments; i.e., the 45° experiment with no stripes gave the same result as the $\theta \sim 0°$ experiment with stripes. The 45° data are reported since they extend closer to T_c.

An unusual feature accompanied the $\theta \sim 0°$ experiments, where it was discovered that T_c increased slightly (and reproducibly) with field. The effect was small (~ 0.003 K maximum) and the correction for it was accurately made by use of $T_c(H)$ measured by light scattering[11,13]; however, ρ_3 was independent of the correction to within its error bars. The effect did not occur in 8OCB or in the oblique-field (45°) experiments. We have no explanation for it; however, excellent agreement with the light-scattering T_c occurred when the temperature of each data point was reduced by $T_c(H_c)-T_c(0)$.

The data were fitted by the equation

$$H_c^2 = At^{-\rho_3}(1+Ft^{1/2})+B, \qquad (1)$$

where B and F are background and correction-to-scaling[18] contributions, respectively. The results are given in Table I and in Figs. 1 and 2.

For 8OCB, $\rho_3 = 0.67 \pm 0.05$, $F=0$, gives a good fit ($\chi^2 = 1.2$) for $1.2\times10^{-5} < t < 5\times10^{-3}$ and the fitted value of T_c (66.780 ± 0.002) is in excellent agreement with the light-scattering value (66.7799 ± 0.0005). Thus, for 8OCB, $\rho_3 = 0.67 \pm 0.05$ and $\rho_2 = 0.36 \pm 0.05$,[10] for $1.2\times10^{-5} < t < 5\times10^{-3}$ and $6\times10^{-6} < t < 2\times10^{-2}$, respectively, consistent with a weakly anisotropic fixed point (Table I), i.e. $(\rho_3-\rho_2)/2 = 0.16 \pm 0.04$, with ρ_3 very close to the helium value.

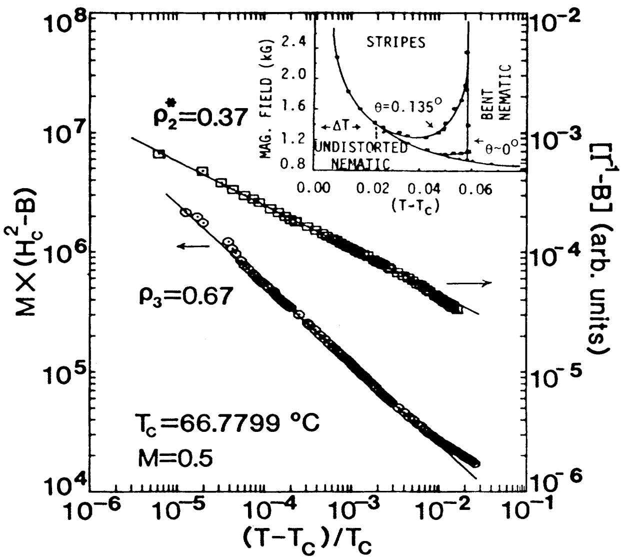

FIG. 1. Log-log graphs of the diverging part of the square of the bend Fréedericksz field (H_c) and the inverse of the light scattering intensity vs reduced temperature for 8OCB. See text about inset. M is a convenient scale factor. ρ_2^* is the slope before correction due to $K_3 q_\parallel^2$ (Ref. 10).

For $\overline{8}$S5, $\rho_3 = 0.88 \pm 0.02$ for all the data ($6\times10^{-5} < t < 3\times10^{-2}$) with $F=0$. This is close to the x-ray result (Table I), but the fit was poor ($\chi^2 = 1.5$) and the fitted value of $T_c = 63.390 \pm 0.002$ was outside the range allowed by light scattering (63.398 ± 0.002). Truncating the data set at $t_{max} = 1.3\times10^{-2}$, the x-ray data limit,[19] gave $\rho_3 = 0.83$, precisely the x-ray result. Range shrinking toward the asymptotic limit monotonically decreased ρ_3 and χ^2 but ρ_3 failed to stabilize below any value of t_{max}. Adding the correction-to-scaling term ($F = -21 \pm 2$) led to an excellent fit of all data [Fig. 2(a)], stable parame-

TABLE I. Comparison of ρ_3 with $\nu_\parallel^x$ and $(\rho_3-\rho_2)/2$ with $\nu_\parallel^x - \nu_\perp^x$. $t_u(t_l)$ = upper (lower) reduced temperature limit of fitted data.

Compound	$\log t_u / \log t_l$	ρ_3	$\nu_\parallel^x$	$\frac{\rho_3-\rho_2}{2}$	$\nu_\parallel^x - \nu_\perp^x$
8OCB	2.3 / 4.9	0.67 ±0.05	0.71[a] ±0.04	0.16 ±0.04	0.13[a] ±0.06
$\overline{8}$S5	1.5 / 4.3	0.68 ±0.03	0.83[b] ±0.01	0.15 ±0.04	0.15[b] ±0.02
$\overline{6}$O9	1.5 / 4.5	0.66 ±0.02	0.78[c] ±0.02	0.09 ±0.02	0.10[c] ±0.03
9S5	1.5 / 4.6	0.68 ±0.02	. . .	. . .	. . .

[a]Reference 3.
[b]Reference 19.
[c]Reference 20.

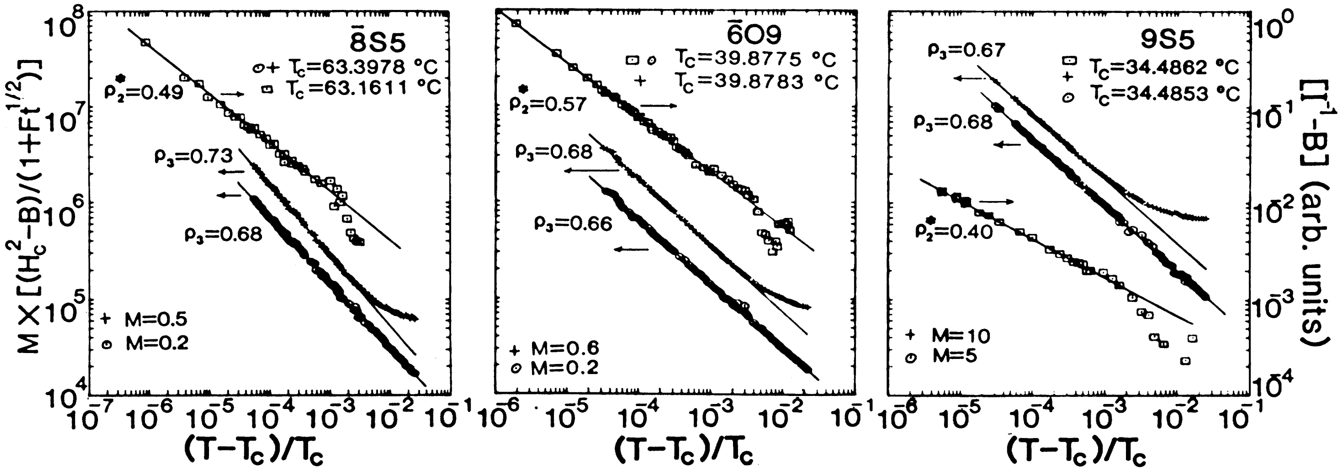

FIG. 2. Log-log graphs of the diverging part of the square of the bend Fréedericksz field (H_c) and the inverse of the light scattering intensity vs reduced temperature for $\overline{8}$S5, $\overline{6}$O9, and 9S5. Pluses (no correction to scaling; $t_{\max} \sim 1.3\times10^{-3}$); dotted circles (with correction to scaling; all data). ρ_2^* is the slope before correction due to $K_3 q_\parallel^2$ (Ref. 10). For $\overline{8}$S5 note that T_c (light scattering) $\neq T_c$ (magnetic deformation) due to the use of two different samples. (See Refs. 12 and 13.)

ters, and a much lower $\chi^2(0.8)$. The exponent, $\rho_3=0.68\pm0.03$, was comparable with the 8OCB value and the fitted value of T_c (63.398 °C ±0.002) agreed very well with light scattering. Thus, for $\overline{8}$S5, $\rho_3=0.68\pm0.03$ and $\rho_2=0.37\pm0.07$,[10] for $-4.3<\log t<-1.5$ and $-6.2<\log t<-2.7$, respectively, again suggesting a weakly anisotropic fixed point, i.e. $(\rho_3-\rho_2)/2=0.15\pm0.04$, with ρ_3 very close to the helium value.

For $\overline{6}$O9 [Fig. 2(b)] a fit of all the data $(3.4\times10^{-5}<t<3.2\times10^{-2})$ with the $F=0$ form gave $\rho_3=0.83\pm0.02$, which, as for $\overline{8}$S5, is near the x-ray value[20] (Table I), but again the fit was very poor ($\chi^2=3.0$) and the fitted value of T_c (39.871 ± 0.001) was outside the range allowed by light scattering (39.8774 ± 0.0005). For $t_{\max}=10^{-2}$, the x-ray upper limit,[10] $\rho_3=0.78$, which is again precisely the x-ray value. Range shrinking rapidly decreased χ^2 and ρ_3 and rapidly increased T_c. Unlike $\overline{8}$S5 all parameters stabilized for $5.6\times10^{-4}\lesssim t_{\max}\lesssim2\times10^{-3}$. $\rho_3=0.67\pm0.02$, $T_c=39.8783\pm0.001$, and $\chi^2=0.9\pm0.1$ characterize the stable range of $t_{\max}$. Agreement with the light scattering T_c (39.8774 ± 0.0005) is excellent but there are slightly less than two decades of data left. Adding the correction-to-scaling term led to an excellent ($\chi^2=0.75$) and stable fit of the entire data set $(3.1\times10^{-5}<t<3.2\times10^{-2})$ with $F=-20\pm1$, $\rho_3=0.66\pm0.02$, and $T_c=39.8777\pm0.001$. Agreement with the light scattering T_c (39.8774 ± 0.0005) is again excellent, as is agreement with ρ_3 (0.67 ± 0.02) from the $F=0$ fit to the restricted data set. Thus, for $\overline{6}$O9 we have $\rho_3=0.66\pm0.02$ and $\rho_2=0.48\pm0.04$[9] for $-4.5<\log t<-1.5$ and $-5.7<\log t<-2.4$, respectively, further confirming a weakly anisotropic fixed point, i.e. $(\rho_3-\rho_2)/2=0.09\pm0.02$. Again, ρ_3 is very near the helium value.

For 9S5 [Fig. 2(c)] fitting all data $(2.8\times10^{-5}<t<3.2\times10^{-2})$ with the $F=0$ form gave $\rho_3=0.82\pm0.02$ but the fit was poor ($\chi^2=1.5$) and T_c (34.483 ± 0.001) was slightly outside the range allowed by light scattering ($T_c=34.486\pm0.001$). Range shrinking caused ρ_3 and χ^2 to decrease and T_c to increase, but the parameters did not stabilize. Again adding a correction to scaling term gave an excellent fit ($\chi^2=0.80$), with $F=-20\pm2$, $\rho_3=0.68\pm0.02$, and $T_c=34.4853\pm0.0005$; the agreement with the light-scattering T_c is excellent and the parameters are stable against range shrinking. The light-scattering data for 9S5 were not included in Table I because the K_3 corrections to ρ_2 could not be made for lack of x-ray data. However, the uncorrected ρ_2 (0.45 ± 0.07) is slightly *larger* than the corrected value and is *smaller* than ρ_3, consistent with weak anisotropy.

For 8OCB and $\overline{8}$S5 anisotropic hyperscaling[4] predicts $\alpha=2-(\rho_2+2\rho_3)=0.30\pm0.11$ and 0.27 ± 0.08, respectively; the former is in reasonable agreement with calorimetry while the latter disagrees strongly.[14,15] Finally, the anisotropies $(\rho_3-\rho_2)/2$ are very close to the x-ray anisotropies $(\nu_\parallel^x-\nu_\perp^x)$ in all four materials (Table I).

The data led firmly to the conclusion that $\rho_3=\nu_\parallel\sim\frac{2}{3}$, the X-Y value, while ρ_2 is somewhat smaller. Thus, the nematic–sematic-A critical point is weakly anisotropic, at least in the ranges of T_{NA}/T_{NI} and t studied. For $\overline{8}$S5 and $\overline{6}$O9, ρ_3 is somewhat lower than $\nu_\parallel^x$ as a result of the correction-to-scaling term needed for good fits of the data. More work is needed to explain this disagreement.

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Note added.—S. Sprunt *et al.* [Phys. Rev. Lett. **53**, 1923 (1984)] have very recently published mode-two nonhydrodynamic regime light-scattering data on $\bar{8}$S5 ($2\times10^{-5} < t < 10^{-2}$), 8OCB ($10^{-5} < t < 2\times10^{-2}$), and one other material. These results are in rather strong disagreement on exponents. There exists evidence that the correction-to-scaling term (see discussion in the present work) may be responsible for the differences.

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