

### 3D $XY$ Behavior of a Nematic-Smectic- $A$ Phase Transition: Confirmation of the de Gennes Model

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A high-resolution x-ray study of the nematic-to-smectic- $A_1$  phase transition of 8OPCBOB gives a critical exponent for the susceptibility  $\gamma=1.39\pm 0.08$ , and for the parallel correlation length  $\nu_{\parallel}=0.71\pm 0.04$ . These values, as well as the known exponent of the heat capacity, agree with the predictions from the 3D  $XY$  model. The different critical behavior of the perpendicular correlation length ( $\nu_{\perp}=0.56\pm 0.05$ ) is shown to be related to the quartic term in  $q_{\perp}$  present in the structure factor. Our analysis resolves a long-standing puzzle about the critical behavior of this phase transition.

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The nematic-to-smectic- $A$  ( $N$ - $S_A$ ) phase transition involves the development of a one-dimensional density modulation in an orientationally ordered fluid of elongated organic molecules [1]. In the de Gennes [2] model this phase transition is shown to be analogous to the normal-to-superconducting phase transition. Its critical behavior has stimulated much theoretical and experimental work because of two special features. These are the algebraic decay of the long-range smectic order (Landau-Peierls instability due to the fact that the smectic- $A$  phase is at its lower marginal dimensionality), and the coupling of the smectic order parameter with nematic director deformations, in particular the splay term. The latter feature has no equivalence in the superconductor case which makes the analogy somewhat imperfect. Some extensions [3] of the de Gennes model which account for the role played by topological defects predict isotropic inverted 3D  $XY$  critical behavior [4] (see Table I). Experimentally, the exponent  $\alpha$  characterizing the heat capacity [5-7] varies from values close to this theoretical value in a couple of cases where the nematic range is wide, through intermediate values, to values close to  $+0.50$  at the tricritical point where the transition becomes first order. The tricritical point occurs for a sufficiently narrow nematic range; this range is not universal but depends on the class of substances. Though the x-ray results agree with this picture for the tricritical

point [8], they show overall major disagreement with the theory [9]. This involves the following: (1) There is a failure so far to observe 3D  $XY$  exponents, both for the exponents  $\nu_{\parallel}$  and  $\nu_{\perp}$  describing the critical behavior of the correlation lengths parallel,  $\xi_{\parallel}$ , and perpendicular,  $\xi_{\perp}$ , to the director, and for the exponent  $\gamma$  connected to the smectic susceptibility  $\sigma$ . (2) The exponents for the correlation lengths invariably show some anisotropy, with  $\nu_{\parallel}/\nu_{\perp}$  varying between 1.2 and 1.6, although the anisotropic scaling relation  $2-\alpha=\nu_{\parallel}+2\nu_{\perp}$  is usually obeyed within the accumulated error limits. In this Letter we report on high-resolution x-ray measurements of the critical exponents of the substance octyloxyphenylcyanobenzoyloxybenzoate (8OPCBOB, see inset of Fig. 1). These show for the first time 3D  $XY$  values for  $\gamma$  and  $\nu_{\parallel}$  (though  $\nu_{\parallel}/\nu_{\perp} > 1$ ), in agreement with the already reported 3D  $XY$  value for  $\alpha$  [10]. The full set of results is in complete agreement with a Monte Carlo simulation of the  $N$ - $S_A$  phase transition by Dasgupta [11], and the theoretical discussion by Lubensky [3] of the difference in gauges between the superconductor and liquid-crystal cases. Essential for understanding the anisotropy of the correlation lengths is the quartic term needed to describe the

TABLE I. Theoretical values for the 3D  $XY$  critical exponents (in the superconductor gauge), the modified predictions for the liquid-crystal gauge, and the experimental values for 8OPCBOB.

Exponent	3D $XY^a$	Liquid-crystal gauge <sup>b</sup>	8OPCBOB
$\alpha$	-0.007	-0.007	-0.007 <sup>c</sup>
$\gamma$	1.32	$\leq 1.32$	$1.39 \pm 0.08$
$\nu_{\parallel}$	0.67	0.67	$0.71 \pm 0.04$
$\nu_{\perp}$	0.67	$< 0.67$	$0.56 \pm 0.05$
$\nu_s$	...	...	$0.41 \pm 0.04$

<sup>a</sup>Reference [4].

<sup>b</sup>Reference [10].

<sup>c</sup>Reference [3].

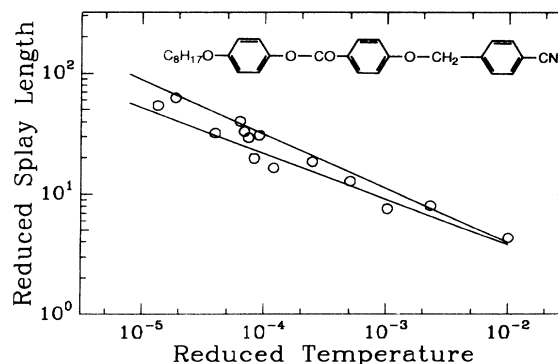


FIG. 1. The reduced splay length  $\xi_s q_0$  ( $q_0=0.2145 \text{ \AA}^{-1}$ ) plotted as a function of reduced temperature. The solid lines present the two limiting fits by a single power law that are used to obtain the error limits in the other fitting parameters describing the structure factor. Inset: Structure of 8OPCBOB.

TABLE II. Critical exponents and bare correlation lengths obtained from the line-shape analysis for two limiting fits of the critical behaviors for  $\xi_s$  (see text). Values in parentheses were held fixed at the specified value.

Fit No.	$\gamma$	$\nu_{\parallel}$	$\nu_{\perp}$	$\nu_s$	$\xi_{\parallel}^0 q_0$	$\xi_{\perp}^0 q_0$	$\xi_s^0 q_0$
1	$1.37 \pm 0.06$	$0.70 \pm 0.03$	$0.51 \pm 0.03$	(0.38)	1.55	0.48	(0.66)
2	$1.42 \pm 0.06$	$0.72 \pm 0.03$	$0.55 \pm 0.03$	(0.45)	1.42	0.43	(0.50)

structure factor for  $q_{\perp}$  [12]. The critical behavior of this term is also reported and discussed. Inclusion of this term in the analysis solves the long-standing problem of putting the  $N$ - $S_A$  phase transition in the correct theoretical framework.

The sample of 8OPCBOB was kept in a beryllium container inside a two-stage oven. The inner oven was resistively heated and stabilized to within 2 mK. The phase-transition temperature  $T_{NA} = 393.6$  K could be determined by a sharp cusp in the linewidth with a relative accuracy of 2 mK and was found to decrease by 0.6 mK/h. Temperature variations over the sample were estimated to be 3 mK by measuring scattering from different parts of the sample. This value limits our temperature resolution. A magnetic field of 0.9 T was used to align the director. The x-ray source was a 15-kW Enraf Nonius GX-21 rotating-anode generator. A standard triple-axis spectrometer was used with Si(111) crystals at the monochromator and analyzer positions to select the Cu  $K\alpha_1$  line. The longitudinal resolution (parallel to the director) could be described by a Lorentzian with a HWHM of  $1.4 \times 10^{-4} \text{ \AA}^{-1}$ , and the transversal out-of-plane resolution by a trapezium with a HWHM of  $2.6 \times 10^{-2} \text{ \AA}^{-1}$ . The transversal in-plane resolution, limited by the  $0.2^\circ$  mosaicity of the sample, was a Lorentzian with a HWHM of  $1.1 \times 10^{-3} \text{ \AA}^{-1}$ . The wave vector corresponding to the modulation period,  $q_0 = 2\pi/d$ , was found at  $0.2145 \text{ \AA}^{-1}$  and hardly shifted with temperature ( $1 \times 10^{-4} \text{ \AA}^{-1}/\text{K}$ ).

The structure factor could be described by the following expression:

$$S(\mathbf{q}) = \sigma / [1 + \xi_{\parallel}^2 (q_{\parallel} - q_0)^2 + \xi_{\perp}^2 q_{\perp}^2 + \xi_s^4 q_{\perp}^4], \quad (1)$$

which includes a quartic term for the perpendicular momentum transfer, of which the magnitude is determined by a correlation length  $\xi_s$ . For each temperature a longitudinal and transversal in-plane scan was fitted to this expression, convoluted three dimensionally with the resolution function and the mosaicity. During the fitting procedure  $\chi^2$  was found to have a broad minimum with respect to  $\xi_s$ , so that the quartic term in Eq. (1) cannot be well determined (as noted before by Chan *et al.* [13]). Evidently this affects the fitted value for  $\xi_{\perp}$  directly, while via integration in the vertical direction this couples to  $\xi_{\parallel}$  and  $\sigma$ . Leaving  $\xi_s$  free gives a large spread on the resulting values of the fitting parameters. In the literature this problem has often been circumvented by assuming for  $\xi_{\perp}$  and  $\xi_s$  the same critical behavior, by taking

$\xi_s^4 = c \xi_{\perp}^4$ , where  $c$  is a constant. However, this can lead to incorrect values of the exponents, which might explain the somewhat erratic behavior if results for  $\gamma$ ,  $\nu_{\parallel}$ , and  $\nu_{\perp}$  from various experiments are compiled. Therefore we adopted the following procedure. First we let  $\xi_s$  vary freely and determine from these fits the error limits in the critical behavior in  $\xi_s$  (see Fig. 1). These two limiting results for  $\xi_s$  are then used to refit the data to obtain the other parameters. This results in a relatively large uncertainty in the critical exponents. It should be emphasized that similar uncertainties are implicitly present in earlier high-resolution x-ray studies in which the quartic term was not well determined. The data have been fitted by a single power law over the reduced temperature range of  $1.3 \times 10^{-5} < \tau < 1.0 \times 10^{-2}$ , where  $\tau = (T - T_{NA})/T_{NA}$ . The stability of the fit parameters was checked by range shrinking. The procedure chosen results in two sets of fits listed in Table II, of which the first one is also represented in Fig. 2. For each of these sets the quoted errors are mainly due to the uncertainty in the determination of  $T_{NA}$ . Smaller contributions to the errors are due to uncertainties in the corrections for mosaicity and resolution. The bare correlation lengths are roughly the same as in previous experiments on other monomeric liquid crystals. The combined result of the two sets of fits is shown in Table I. Together with the exponent for the heat capacity  $\alpha$  from Garland *et al.* [10] the set  $\alpha$ ,  $\gamma$ , and  $\nu_{\parallel}$  for

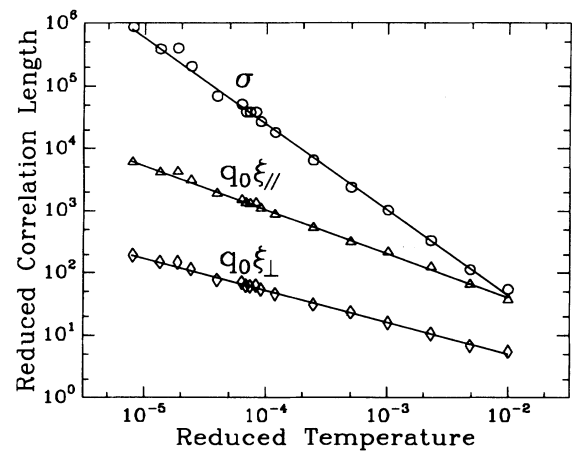


FIG. 2. The susceptibility  $\sigma$  (arbitrary units) and the reduced correlation lengths  $\xi_{\parallel} q_0$  and  $\xi_{\perp} q_0$  as obtained from fit 1, plotted as a function of reduced temperature. The solid lines present a fit by a single power law.

8OPCBOB is the first complete example in agreement with the predictions of the 3D  $XY$  model.

To understand the behavior observed for  $\xi_{\perp}$  it is necessary to discuss the critical behavior of the quartic term in some detail. This behavior results from a crossover [12] of the line shape from the usual form  $q_{\perp}^{-2}$  expected in the nematic phase to the behavior in the smectic phase described by  $q_{\perp}^{-4+2\eta}$  ( $\eta \ll 1$ ) due to the algebraic decay of the smectic order [14]. For that reason we did not write this term in the usual form  $c\xi_{\perp}^4 q_{\perp}^4$ . The latter form suggests incorrectly a connection with the critical behavior of  $\xi_{\perp}$  and introduces a coefficient  $c$  that becomes smaller on approaching  $T_{NA}$ , while in fact for a given  $q_{\perp}$  the contribution of the quartic term becomes dominant closer to

$$f(\psi, \delta \mathbf{n}) = \frac{1}{2} A |\psi|^2 + \frac{1}{4} C |\psi|^4 + \frac{1}{6} E |\psi|^6 + C_{\parallel} |\nabla_{\parallel} \psi|^2 + C_{\perp} |(\nabla_{\perp} - iq_0 \delta \mathbf{n}) \psi|^2 + \frac{1}{2} [K_1 (\nabla \cdot \delta \mathbf{n})^2 + K_2 (\mathbf{n} \cdot \nabla \times \delta \mathbf{n})^2 + K_3 (\mathbf{n} \times \nabla \times \delta \mathbf{n})^2]. \quad (3)$$

The first five terms correspond to the Ginzburg-Landau formalism, in which the phase transition is driven by a change in sign of  $A$ . In the fifth term for the perpendicular gradient, director fluctuations have been included to preserve invariance of the free energy with respect to small uniform rotations of the director and the smectic planes. The last three terms describe the Frank distortion free energy for a nematic,  $K_1$ ,  $K_2$ , and  $K_3$  being the elastic constants for splay, twist, and bend, respectively.

Below  $T_{NA}$  in the smectic phase the amplitude of the order parameter  $|\psi|$  can be taken as constant. Moreover, then the twist and bend terms can be disregarded and only undulations of the layers (with which a splay deformation is associated) are still allowed. The quartic term can now be derived from the splay term in Eq. (3) assuming that the director is perpendicular to the layers [2]. If we make the same assumptions for the nematic phase close to  $T_{NA}$ , we can derive from Eq. (3) in a standard mean-field approach

$$\xi_s = [K_1 / A q_0^2 |\psi|^2]^{1/4}. \quad (4)$$

Therefore, associating the change in sign of  $A$  at  $T_{NA}$  with the exponent  $\gamma$ , we expect the critical behavior of the splay length  $\xi_s$  to be approximately described by a critical exponent  $\nu_s \approx \gamma/4$ , as observed in our measurements where  $\gamma/4 = 0.35$  and  $\nu_s = 0.41$ . Close to  $T_{NA}$  the quartic term dominates because the term  $C_{\perp} |(\nabla_{\perp} - iq_0 \delta \mathbf{n}) \psi|^2$  in Eq. (3) disappears (just as in the smectic phase). This latter term gives rise to the  $\xi_{\perp}^2 q_{\perp}^2$  line shape in the nematic phase further away from  $T_{NA}$  where the above assumptions break down. Because of the increasing importance of the undulations associated with the quartic term, on approaching  $T_{NA}$  the correlations described by  $\xi_{\perp}$  cannot grow as fast as in the absence of the splay term, leading to  $\nu_{\perp}$  being smaller than the 3D  $XY$  value, as observed. This does not apply to  $\xi_{\parallel}$ , which explains the anisotropy  $\nu_{\parallel} > \nu_{\perp}$ . Hence essential for a full understanding of the critical behavior is the competition

$T_{NA}$ . The form  $\xi_s^4 q_{\perp}^4$  used in Eq. (1) makes the independent critical behavior of  $\xi_s$  (where  $s$  stands for splay for reasons to be explained below) explicit.

The interpretation of the quartic term given above can be further clarified using the Landau-de Gennes free energy [3]. The smectic order parameter  $\psi(\mathbf{r})$  is a field that determines the amplitude and the phase of the density modulation. If the director  $\mathbf{n}$  is parallel to the  $z$  direction, the density modulation around the average density  $\rho_0$  can be described by

$$\rho(\mathbf{r}) = \rho_0 \{1 + \text{Re}[\psi(\mathbf{r}) \exp(iq_0 z)]\}. \quad (2)$$

The free energy describing the phase transition can be written as

between the terms  $C_{\perp} |(\nabla_{\perp} - iq_0 \delta \mathbf{n}) \psi|^2$  and  $K_1 (\nabla \cdot \delta \mathbf{n})^2$  in the free energy.

The experimental results on 8OPCBOB are in excellent agreement with the Monte Carlo simulation of Dasgupta [11] of the de Gennes model. In this simulation inclusion of the splay term leads to an anisotropy in the growth of the correlation lengths as well as the occurrence of a quartic term, both of which are not present in the superconducting case. Another striking result of this simulation is *noninverted* critical behavior for the heat capacity. This is in agreement with calorimetric measurements of substances having a 3D  $XY$  exponent for  $\alpha$ .

It should be emphasized that the observed anisotropy does not mean that the  $N$ - $S_A$  phase transition cannot be described by the isotropic 3D  $XY$  model. As discussed by Lubensky [3], with x rays the correlation function is measured in the liquid-crystal gauge. The exponents are, however, calculated for the superconducting gauge. The critical behavior of thermodynamic quantities such as the specific heat and the internal energy is independent of the gauge used, in contrast to that of the correlation function. The predictions from these gauge transformations are also given in Table I, and agree with the experimental values for the exponents. This also means that the anisotropic scaling relation  $\alpha + \nu_{\parallel} + 2\nu_{\perp} = 2$  is not valid in the liquid-crystal gauge, in agreement with our experiment where  $\alpha + \nu_{\parallel} + 2\nu_{\perp} = 1.82 \pm 0.13$ .

In conclusion, we found complete agreement between the experimental results for the critical behavior of the  $N$ - $S_A$  phase transition in 8OPCBOB and the Monte Carlo simulations of the de Gennes model, which provides the first unambiguous proof of the correctness of the latter description of this transition. Both the Monte Carlo simulations and the structure factor show a quartic term illustrating the importance of the splay term, thus making the superconductor analogy somewhat imperfect. The competition between the splay term and the perpendicu-

lar gradient term in the free energy explains the connection between the anisotropy of the correlation lengths and the quartic term in the structure factor. This is also in agreement with the work by Chan *et al.* [13] who found  $v_{\parallel} = v_{\perp}$  for a smectic- $A_1$ -to-smectic- $A_2$  transition. In that case the  $A_2$  fluctuations in both the longitudinal and transversal directions could be described by a pure Lorentzian without a quartic term.

Some differences between the experiments and the Monte Carlo simulations, on the one hand, and the formal theory, on the other hand (inverted or noninverted 3D  $XY$  behavior), still need to be clarified. X-ray experiments to measure the critical behavior of the experimentally more accessible 7CB-8CB mixture (for which a 3D  $XY$  value for  $\alpha$  has been reported by Thoen, Marynissen, and Van Dael [5]) are in progress.

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