Critical Behavior of the de Gennes Elastic Constants near the Nematic-Smectic-*A* Transition of TBBA

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We have studied the behavior of elastic constants A, B, and C deduced from ultrasound velocity anisotropies in the vicinity of the nematic-smectic-A transition of terephthal-bis-p-p'-butylaniline. A is associated with compressibility, B with layer compression, and C with the coupling between compressibility and layer compression. We show that the exponent of A is of the preasymptotic 3D-XY type, whereas those of B and C are in between the 3D-XY values and those associated with the anisotropic fixed point. This behavior is consistent with the extended crossover regime predicted by Patton and Andereck [Phys. Rev. Lett. **69**, 1556 (1992)].

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The nematic to smectic-A (N-SmA) transition corresponds to the emergence of a one-dimensional positional order within an oriented fluid. Interest in this transition was sparked by de Gennes, who suggested that it could be continuous and exhibit 3D-XY critical behavior [1,2]. However, in spite of the large quantity of studies which have been carried out over more than 20 years, this transition is still not understood, owing to a difference between the exponents $\nu_{\parallel}$ and $\nu_{\perp}$ associated with the correlation lengths, respectively, parallel and perpendicular to the director [3]. A new impulse has been provided recently by (i) experiments showing that the anisotropy ($\nu_{\parallel} \neq \nu_{\perp}$) exists for compounds with a 3D-XY specific-heat behavior ($\alpha \sim 0$) and (ii) the Patton and Andereck theory [4] predicting the existence in the nematic phase of an extended crossover regime due to anisotropic coupling between the fluctuations of the director and the smectic order parameter.

In the smectic-A phase, few experiments have been carried out, and data are reported only for the B and D elastic constants, associated, respectively, with layer compression and deviation of the director n in relation to the normal to the layers [5]. In this Letter, we present the first ultrasound velocity measurements from which it is possible to determine the critical behavior of elastic constants A, B, and C, corresponding to the bulk compression, the layer compression, and the coupling term between bulk and layer compression, respectively. We show that A has a 3D-XY-type preasymptotic behavior which reflects that of specific heat, whereas B and C have exponents ($\varphi_B \simeq 0.31$, $\varphi_C \simeq 0.42$) which are different, and in between those associated with the 3D-XY model and those associated with the anisotropic critical point [6]. This result suggests that φ_B and φ_C are crossover exponents which may be associated with the Patton and Andereck theory.

The compound chosen for this study was terephthal-bis-p-p'-butylaniline (hereafter referred to as TBBA). It was synthesized in our laboratory and had a weakly first-order N-SmA transition around 200 °C with an enthalpy value of the order of 0.07 kcal/mol. The cell was placed between the poles of an electromagnet producing a 10 kG magnetic field, and the samples orientated by heating the compound to its N phase, then cooling it slowly within the magnetic field. Our measurements were taken as the temperature decreased, for three different orientations of the sample, defined by $\theta = 0°$, 45°, and 90°, where θ represents the angle between the director and the direction of sound propagation. A fresh sample was used for each angle θ. The experiments were carried out using the resonance technique, previously elaborated for studying anharmonic effects in TBBA [7], and which enables us to measure velocity at 1.2 MHz. The cell had an interquartz gap ranging from 3.5 to 7 mm and was thermally regulated to within ±0.01 °C. The cell was also connected to a pulse device allowing damping measurements at 3, 9, 15, 21, and 27 MHz to be taken. Velocity and damping measurements are completely uncorrelated. The analysis of the velocity measurements which is presented below was made independently of the analysis of the damping measurements reported and discussed in [8]. A detailed description of the setup, cell, and measuring protocol is to be found in Ref. [7].

In order to determine B and C accurately, the following method was used. For each angle θ, we measured the variation in velocity as a function of temperature, from $T = T_{\mathrm{AN}} + 20$ °C to the temperature at the end of the experiment. The resulting curves were then superimposed on each other in the nematic phase. This procedure is justified by the fact that the velocity measurements in the nematic phase are independent of angle θ. Uncertainty concerning the velocity measurements stems essentially from this renormalization and is of the order of ±20 cm/s for the measurements presented in this paper.

Figure 1 gives the behavior of velocity for $\theta = 0°$, 45°, and 90°. It shows that the SmA phase is characterized by marked velocity anisotropy, due to the layer structure of the phase. The measurements taken in the immediate vicinity of the transition are not reported on the figure, as they

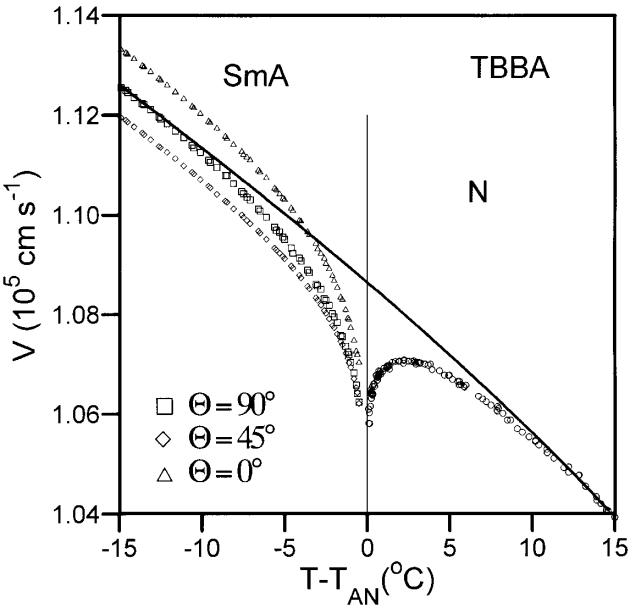

FIG. 1. Temperature dependence of sound velocity at 1.2 MHz for $\theta = 0°$, 45°, and 90°. The solid line represents the regular term for $\theta = 90°$. T_{AN} is the transition temperature determined by fitting the data for $\theta = 90°$ with Eq. (4) (see text).

involve greater uncertainty which stems from the fact that, with the resonance technique, uncertainty as to velocity measurements increases rapidly when damping becomes very considerable. Analysis of the results in Fig. 1 using the formula [9]

$$\rho V^2(\theta) = A - 2C\cos^2\theta + B\cos^4\theta \qquad (1)$$

enables us to determine the elastic constants A, B, and C [10]. The remainder of this Letter is devoted first to an analysis of the critical behavior of A, then to those of B and C.

Several mechanisms have been put forward to describe the behavior of velocity above the N-SmA transition. The first is based on a quadratic coupling between the order-parameter fluctuations and the density and leads to a critical decrease $\delta V_{\rm fluc}$ in the velocity, which is isotropic, in spite of the uniaxial symmetry of the phase [11]. This decrease is given by $V = V_{\rm reg} - \delta V_{\rm fluc}$, where $V_{\rm reg}$ is a regular term representing the variation in velocity expected in the absence of the N-SmA transition. Since $\rho V^2(\theta = 90°) = A$, the above expression can be rewritten in the form of

$$A = A_{\rm reg} - \delta A_{\rm fluc}\,, \qquad (2)$$

where $\delta A_{\rm fluc}$ behaves as $(T - T_{\rm AN})^{-\alpha}$, α being the specific heat exponent. The behavior of $\delta A_{\rm fluc}$ thus reflects that of the specific heat. This result was also obtained from a dynamic specific-heat theory [12]. Two other mechanisms have also been taken into consideration; one of them [13] couples the order-parameter fluctuations with director, and the other one [14] is associated with the order-parameter relaxation, which would occur in the nematic phase, owing to a dynamic coupling. Both of these mechanisms predict anisotropic critical effects. They will be ignored in the analysis of our results, which show the critical effects to be isotropic in the N phase.

In the SmA phase, the critical part of A is the sum of the terms which correspond to two distinct mechanisms:

$$\delta A = \delta A_{\rm fluc} - \delta A_{\rm LK}\,. \qquad (3)$$

The first term comes from the fluctuation mechanism already envisaged in the N phase, the behavior of which reflects that of the specific heat. The second represents the Landau-Khalatnikov (LK) contribution associated with relaxation of the order-parameter modulus [15]. Unlike the fluctuation mechanism, this one is very anisotropic [8,14]. It will be ignored in the analysis of our measurements which are within the $\omega\tau \ll 1$ regime. Equation (2) will therefore also be used in order to analyze the results obtained in the SmA phase.

The critical behavior of A obtained after subtracting the regular term, plotted as a solid line in Fig. 1, is shown in Fig. 2. These data have been analyzed using the following expression, which is deduced from that used for the specific-heat analyses:

$$\delta A_{\rm fluc} = E - A_0^{\pm}|t|^{-\alpha}(1 + D_1^{\pm}|t|^{\Delta_1} + D_2^{\pm}|t|^{\Delta_2}). \qquad (4)$$

In this expression, $t = |T - T_{\rm AN}|/T_{\rm AN}$ is the reduced temperature. The signs "+" and "−" refer to the N and SmA phases, respectively. A_0 is the critical amplitude and E is the so-called "cusp" constant, showing that the critical anomaly tends towards a finite value at the transition. D_1 and D_2 are the first- and second-order scaling corrections, and Δ_1 and Δ_2 the exponents associated with these two corrections. The analyses were carried out taking both phases into account at the same time in

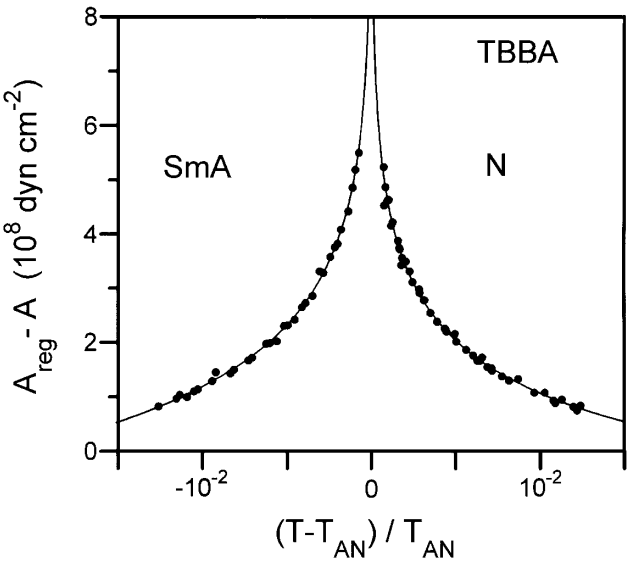

FIG. 2. Temperature dependence of the critical part of elastic constant A. The solid line is the fit made with Eq. (4). Temperatures are in K.

a temperature range which goes from 0.4 to 6 °C from the transition ($|t|_{\max} = 1.3 \times 10^{-2}$; $|t|_{\min} = 8 \times 10^{-4}$). The analyses conducted without scaling corrections show that $\alpha \sim 0$, which indicates that the data for A are compatible with 3D-XY behavior. This observation had led to our fixing exponents α, Δ_1, and Δ_2 at their 3D-XY values ($\alpha = -7 \times 10^{-3}$, $\Delta_1 = 0.5$, and $\Delta_2 = 1$), taking no account of the second-order scaling-correction term ($D_2 = 0$). Figure 2 shows that the experimental results are faithfully represented by Eq. (4). The fit is the solid line and the resulting parameters are $A_0^+ = (2.7 \pm 0.2) \times 10^{10}$ dynes/cm^2, $A_0^-/A_0^+ = 0.997 \pm 0.001$, $E = (2.6 \pm 0.2) \times 10^{10}$ dynes/cm^2, $T_{\mathrm{AN}} = (199.65 \pm 0.03)$ °C, $D_1^+ = -0.03 \pm 0.02$, $D_1^-/D_1^+ = 0.4 \pm 0.4$ with $\chi_\nu^2 = 1.19$. The amplitude of scaling correction D_1 is smaller than that associated with the specific heat of the polar compounds in Ref. [16] but comparable to that of either 40.7 [16] or the λ transition of helium [17]. The fact that a single scaling correction is sufficient for analysis of the data up to 6 °C from the transition suggests that these measurements are closer to the critical region than those of the polar compounds, which require the use of two scaling corrections. However, the critical region is not reached, since data analysis carried out over the same interval with $\alpha = -0.007$, but without the scaling correction, leads to a higher value of χ_ν^2 ($\chi_\nu^2 = 3$). It should be noted that adding the second scaling correction does not lead to any significant improvement in χ_ν^2, thus indicating that this parameter is not useful.

The 3D-XY character of A is not merely the effect of using many parameters in the fit. Figure 3 shows the critical behavior of A, in a semilogarithmic plot. The linear variation observed in both phases up to within ~6 °C of the transition indicates that the critical behavior of A is near to a logarithmic singularity ($\alpha \sim 0$). This result shows that the critical fluctuations are already developed in a temperature domain very far from the transition, in spite of it being first order. Analysis of the damping measurements led to the same conclusion [8]. The fact that the critical behavior of A remains linear in the vicinity of the transition shows on the one hand that these data belong to the hydrodynamic regime and, on the other hand, that the contribution of the order-parameter relaxation in the SmA phase is weak compared to that of the fluctuations, which confirms our original hypotheses.

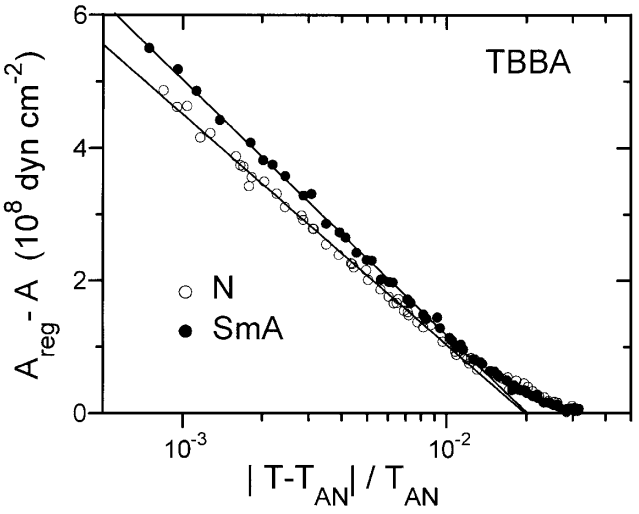

FIG. 3. Critical part of elastic constant A versus $\log|T - T_{\mathrm{AN}}|/T_{\mathrm{AN}}$. The linear behavior indicates that δA presents a logarithmic singularity ($\alpha = 0$), as for liquid helium. Temperatures are in K.

We have also carried out "first-order" analyses. In order to keep the same number of adjustable parameters, we assumed that discontinuity of E occurs for an extremely small temperature difference $T_{\mathrm{AN}}^+ - T_{\mathrm{AN}}^- \sim 0$ and imposed the A_0^-/A_0^+ ratio. The results obtained show that the direct 3D-XY fit ($A_0^-/A_0^+ = 0.9714$) and the inverse 3D-XY fit ($A_0^-/A_0^+ = 1.029$) give values of χ_ν^2 which are comparable to each other and close to those determined for $E^+ = E^-$. These analyses therefore show that it is impossible to choose conclusively between a direct or inverse 3D-XY behavior. They also show that the discontinuity of the cusp constant is weak ($\Delta E/E < 2\%$) and that its sign depends on the direct or indirect nature of the transition.

For $T = T_{\mathrm{AN}}$, Eq. (4) shows that A is written $A(T = T_{\mathrm{AN}}) = A_{\mathrm{reg}} - E$. The values of A_{reg} and E indicate that $A(T = T_{\mathrm{AN}})$ is negative, which is not physically acceptable. This result stems from the fact that it is the critical behavior of the compliance which must be taken into consideration and not that of the elastic constant. Equation (4) must be thus replaced by the following formula [18]:

$$\delta A_{\mathrm{fluc}} = \frac{E - A_0^{\pm}|t|^{-\alpha}(1 + D_1^{\pm}|t|^{\Delta_1})}{1 + A_{\mathrm{reg}}^{-1}[E - A_0^{\pm}|t|^{-\alpha}(1 + D_1^{\pm}|t|^{\Delta_1})]}. \quad (5)$$

The value of A at the transition is therefore given by $A(T = T_{\mathrm{AN}}) = A_{\mathrm{reg}}(T = T_{\mathrm{AN}})/[E + A_{\mathrm{reg}}(T = T_{\mathrm{AN}})]$, which shows that A is positive at the transition. The parameters of the fit are the following: $A_0^+ = (3.0 \pm 0.2) \times 10^{10}$ dynes/cm^2, $A_0^-/A_0^+ = 0.997 \pm 0.001$, $E = (2.9 \pm 0.2) \times 10^{10}$ dynes/cm^2, $T_{\mathrm{AN}} = (199.64 \pm 0.03)$ °C, $D_1^+ = -0.05 \pm 0.02$, $D_1^-/D_1^+ = 0.5 \pm 0.4$ with $\chi_\nu^2 = 1.16$. The value of χ_ν^2 and those of the various adjustable parameters can be seen to be quite comparable to those determined previously with the simplified Eq. (4). This comes from the fact that Eq. (4) is valid as long as $\Delta V/V_{\mathrm{reg}} \ll 1$ which is realized in the present case since the maximum value of $\Delta V/V_{\mathrm{reg}} \sim 0.01$. The two formulas are therefore equivalent within the domain of our analysis and the difference between the two of them becomes apparent only in the immediate vicinity of the transition, A becoming negative in the case of the simplified formula, whereas it has a finite value of the order of 0.35×10^{10} dynes/cm^2 in the case of Eq. (5).

We now consider the behavior of the other two elastic constants B and C. In the hydrodynamic regime, it is

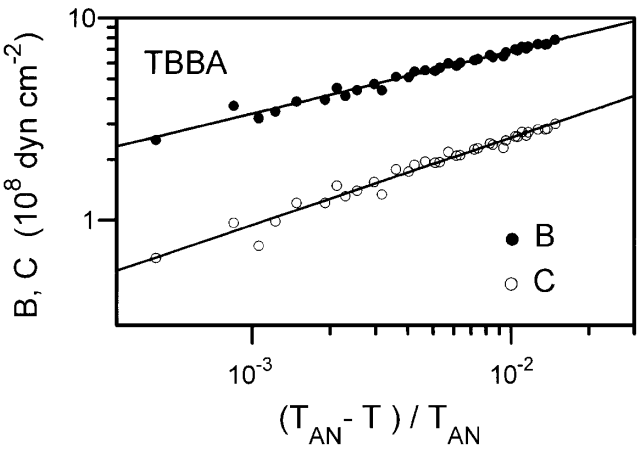

FIG. 4. Critical behavior of elastic constants B and C. The solid lines are the fits made with Eq. (6). Temperatures are in K.

predicted that B and C will have power-law behaviors.

$$B = B_0 t^{\varphi_B}, \qquad C = C_0 t^{\varphi_C}, \tag{6}$$

where φ_B and φ_C represent the critical exponents associated with these two constants. Anisotropic scaling predicts that $\varphi_B = 2\nu_\perp - \nu_\parallel$ [19] and $\varphi_C = \nu_\parallel + \eta_\perp \nu_\perp$ [20]. $\eta_\perp$ is an exponent associated with the Fisher equality $\gamma = (2 - \eta_\perp)\nu_\perp$, where γ is the susceptibility exponent. The fits were carried out over a temperature interval between 0.5 and 7 °C. They are shown by the solid-line curves in Fig. 4 and indicate that the measurements of B and C do indeed follow the power laws given by Eq. (6). The associated parameters are $\varphi_B = 0.31 \pm 0.02$, $B_0 = (28 \pm 2) \times 10^8$ dynes/cm^2, $\varphi_C = 0.42 \pm 0.03$, $C_0 = (17 \pm 3) \times 10^8$ dynes/cm^2. The important result is that the values of φ_B and φ_C differ from each other and also from the value expected for the 3D-XY model ($\varphi_B = \varphi_C = 0.66$). It should also be noted that the value of φ_B is identical, within the limits of experimental error, to that determined for other compounds from inelastic light-scattering or dynamic compression experiments [21]. The value of φ_C is obtained here for the first time.

The values of φ_B and φ_C suggest that the measurements of B and C are within a critical regime, in between the 3D-XY regime ($\varphi_B = \varphi_C = 0.66$) and the regime associated with the anisotropic critical point ($\varphi_B = 0$, $\varphi_C = \nu_\parallel$ with $\nu_\parallel$ nonspecified). Such a regime has recently been suggested by Patton and Andereck [4] to explain why the exponents $\nu_\perp$ and $\nu_\parallel$ measured in the N phase are different and nonuniversal. This regime is dependent on the anisotropic character of the coupling between the δn fluctuations of the director and the smectic order parameter ψ. Since φ_B and φ_C are functions of $\nu_\parallel$ and $\nu_\perp$, the fact that B and C have exponents which are very far from all the theoretical predictions suggests that these two elastic constants are under the influence of this coupling, unlike A, which involves the density coupling. The influence of the ψ-δn coupling on the behavior of B and C could be tested by doping the liquid crystal with molecules which are nonmesogenic, but which have a formula close to that of the liquid crystal.

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