Dynamic Scaling of Ultrasonic Damping near the Nematic-Smectic-*A* Transition of TBBA

P. Sonntag, D. Collin, and P. Martinoty
Laboratoire de Dynamique des Fluides Complexes, Unité Mixte de Recherche C.N.R.S.-U.L.P. No. 7506, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France
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We report a detailed study of the ultrasonic damping near the nematic-smectic-*A* phase transition of terephtal-bis-p-p'-butylaniline (TBBA). Two mechanisms contribute to the damping. One is isotropic; it is associated with the critical fluctuations, and leads to a scaling behavior of the 3D-*XY* type which is observed up to 15 °C from the transition, even though the transition is first order. The other is anisotropic; it appears only in the smectic-*A* phase, and is associated with the relaxation of the order-parameter modulus.

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The nematic-smectic-*A* transition represents one of the most difficult questions posed in statistical physics. Most theoretical studies predict that this transition should be of the 3D-*XY* type [1]. Experimental results, however, show that the critical exponents belonging to the same compound do not all agree with these predictions. In addition, this transition is always first order, as was predicted by Halperin and Lubensky [2], and was first demonstrated experimentally by Cladis *et al.* [3]. The dynamic properties of the transition have also been the subject of numerous theoretical studies, and three different mechanisms have been put forward to explain the sound anomaly in the vicinity of the transition. The first of these involves a coupling between the order-parameter fluctuations and the director, and leads to anisotropic critical effects [4,5]. The second is based on a quadratic coupling between the order-parameter fluctuations and the variation in density ($\delta\rho$-ψ^2 coupling), and gives isotropic critical effects, even though the phase symmetry is uniaxial [6,7]. The last is associated with the order-parameter relaxation modulus. It was first introduced by Landau and Khalatnikov (LK) [8] for the λ transition of helium, and is characterized by the fact that the damping α goes through a maximum for $\omega\tau^{\mathrm{LK}} = 1$, in such a way that the position of the damping peak shifts towards lower temperatures as frequency increases (τ^{LK} is the associated critical relaxation time, and $\omega = 2\pi f$ where f is the frequency). Liu [9] has shown that this mechanism leads to anisotropic effects for the N-Sm*A* transition, and that it could also exist in the nematic phase, because of the existence of dynamic couplings. However, very few experiments have been carried out to test these predictions quantitatively [6,10]. In this Letter, we present a detailed study of the behavior of ultrasound damping in the vicinity of the N-Sm*A* transition in terephtal-bis-p-p'-butylaniline (TBBA), the purpose of which is precisely to identify the mechanisms governing the dynamics of this transition.

TBBA was synthesized in our laboratory, and had an N-Sm*A* transition around 200 °C with a transition enthalpy of ~0.07 kcal/mol. The samples were oriented by a 10 kG magnetic field, and the measurements taken as temperature decreased for three different orientations, defined by $\theta = 0°$, 45°, and 90°, where θ is the angle between the magnetic field and the direction of sound propagation. A fresh sample was used for each angle θ. The measurements were taken by the pulse technique at 3, 9, 15, 21, and 27 MHz. The cells had interquartz distances ranging from 3.5 to 7 mm, and were thermally regulated to within ±0.01 °C. In order to prevent sample deterioration during the experiments, the sample was degassed inside the cells, and the measurements taken under an inert atmosphere. A detailed description of the setup, cells, and measuring protocol is to be found in Ref. [11].

Figure 1 gives the behavior of α/f^2 for $\theta = 0°$ in a temperature domain going from +15 to −15 °C from the N-Sm*A* transition. In the Sm*A* phase, the anharmonic effects [11] have been subtracted. α/f^2 can be seen to present near the transition a peak which increases as

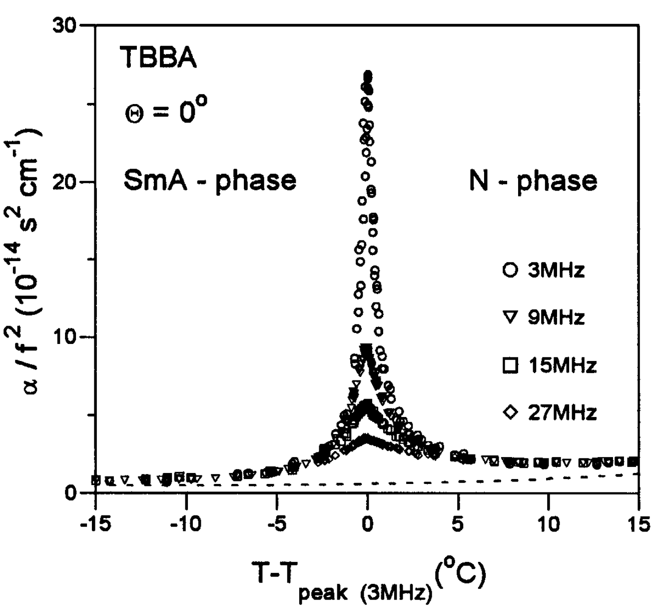

FIG. 1. Temperature dependence of α/f^2 for $\theta = 0°$ at 3, 9, 15, and 27 MHz. In the Sm*A* phase, the anharmonic effects have been subtracted. The dashed line represents the background term (see text).

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frequency decreases. Far from the transition, all of the experimental points, whatever their frequency, fit onto a single curve which characterizes the hydrodynamic regime ($\omega\tau \ll 1$). As the transition is approached, the curves associated with the various frequencies diverge. This separation marks the end of the $\omega\tau \ll 1$ regime, and a shift towards the $\omega\tau \gg 1$ regime, which is reached at the transition itself. The behavior of the other two orientations, $\theta = 45°$ and $\theta = 90°$, is similar to that presented in Fig. 1.

The results obtained for $\theta = 90°$ show that the damping peak shifts towards lower temperatures as frequency increases. This shift corresponds to the behavior predicted by the LK mechanism [8]. It is marked more for $\theta = 90°$ than for $\theta = 45°$, and, within the limits of our experimental resolution, could not be observed for $\theta = 0°$ [12]. These differences in behavior show that the Landau-Khalatnikov mechanism is very anisotropic, which agrees with Liu's predictions [9]. On the other hand, the measurements taken in the N phase show that the differences $\alpha(0°) - \alpha(90°)$, $\alpha(0°) - \alpha(45°)$, and $\alpha(45°) - \alpha(90°)$ have no critical increase when $T \rightarrow T_{\mathrm{AN}}$. This result, obtained by revolving the electromagnetic field around the cell, indicates that the critical effects are isotropic [13]. As a result, the anisotropic contributions predicted above T_{AN} for the fluctuations [4,5] and the relaxation of the order parameter [9] are negligible for this compound [14].

We shall now analyze the measurements at $T \sim T_{\mathrm{AN}}$ which correspond to the critical regime ($\omega\tau \gg 1$). In this regime, the Landau-Khalatnikov effect rapidly tends towards zero, and only the fluctuation mechanisms contribute to the damping. Since the fluctuation effects are isotropic, we shall consider only the mechanism associated with the $\delta\rho$-ψ^2 coupling. This coupling leads to a damping which, in the critical regime, is given by [7]

$$\frac{\alpha}{f^2} = (2\pi)^{1+y} A t^{-2\overline{\alpha}} f^{-1+y} + B\,, \qquad (1)$$

where the term involving A is the abnormal part of the damping, and term B represents the background term containing all the effects other than the critical effects associated with the N-SmA transition. y is an exponent equal to $\overline{\alpha}/z\nu_\perp$ where $\overline{\alpha}$ is the specific exponent and $z\nu_\perp$ the exponent of the critical relaxation time τ which is defined by $\tau \sim \xi_\perp^z$ where $\xi_\perp$ is the correlation length perpendicular to the director and $\nu_\perp$ the associated exponent. Thus, analysis of the $\omega\tau \gg 1$ regime allows the scaling law given by Eq. (1) to be tested, and gives the value of the background damping in the vicinity of the transition temperature, which will be decisive in the remainder of the analysis.

We shall begin by considering the results obtained for $\theta = 0°$, which is the simplest geometry, as the damping peaks all occur at the same temperature, which can therefore be considered to be the transition temperature. The results obtained at this temperature are given in Fig. 2, which shows that α/f^2 varies as $1/f$. Hence this result characterizes the behavior of α/f^2 at the transition, and, according to Eq. (1), indicates that exponent y, and consequently $\overline{\alpha}$, is close to 0.

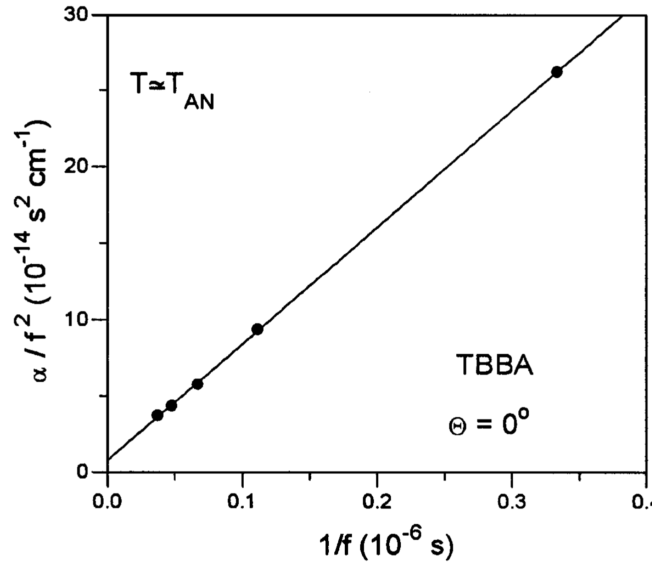

FIG. 2. Variation of α/f^2 as a function of $1/f$ in the critical regime. The straight line is a fit by Eq. (1).

We shall now consider the results obtained for $\theta = 90°$ and $\theta = 45°$. Since the ultrasound peaks shift towards lower temperatures as the frequency increases, the transition temperature T_{AN} is higher than the temperature associated with the 3 MHz peak. As we have just shown that the critical regime is characterized by a $1/f$-type linear behavior of α/f^2, we have looked for any measurements above $T_{\mathrm{peak}}(3\ \mathrm{MHz})$ for which this behavior might be observed. The results obtained show that the behavior of α/f^2 as $1/f$ is verified for measurements taken at $T = T_{\mathrm{peak}}(3\ \mathrm{MHz}) + 0.12\,°\mathrm{C}$ for $\theta = 90°$ and $T = T_{\mathrm{peak}}(3\ \mathrm{MHz}) + 0.06\,°\mathrm{C}$ for $\theta = 45°$. These two temperatures must be very close to the transition temperature T_{AN} and will be subsequently associated with T_{AN}. This association will be confirmed later, by analysis of the thermal behavior of the critical damping.

The values of A and B determined from Eq. (1) for all three angles are the following: $2\pi A = (7.63 \pm 0.05) \times 10^{-7}\ \mathrm{s\,cm^{-1}}$, $(7.63 \pm 0.07) \times 10^{-7}\ \mathrm{s\,cm^{-1}}$, $(7.62 \pm 0.06) \times 10^{-7}\ \mathrm{s\,cm^{-1}}$ and $B = (800 \pm 70) \times 10^{-17}\ \mathrm{s^2\,cm^{-1}}$, $(590 \pm 100) \times 10^{-17}\ \mathrm{s^2\,cm^{-1}}$, $(350 \pm 80) \times 10^{-17}\ \mathrm{s^2\,cm^{-1}}$ for $\theta = 0°$, $45°$, and $90°$, respectively. As can be seen, the amplitude A of the critical effects is the same whatever the angle θ considered, which confirms that the critical effects are isotropic. On the other hand, the background term B is anisotropic, as expected, reflecting as it does the uniaxial symmetry properties of the system.

In order to pursue the analysis of our data further, it is necessary to know the thermal variation of the background damping, which must take into account the influence of the nematic-isotropic and SmA-SmC transitions. The way it had been determined is described in Ref. [15]. Here we simply wish to emphasize that this term was obtained for each angle θ: (1) by requiring it to pass through the value determined at $T = T_{\mathrm{AN}}$ (term B), and (2) by taking into consideration only the data which are the farthest from the N-SmA transition, i.e., those for $|T - T_{\mathrm{AN}}| > 25\ ^\circ\mathrm{C}$. The background term so determined for $\theta = 0^\circ$ is represented by the dashed line in Fig. 1.

Figure 3 shows the variation of the $\delta\alpha/\delta\alpha_c$ ratio as a function of the reduced variable $\omega\tau^+$ in the N phase. $\delta\alpha$ is the critical part of the damping, $\delta\alpha_c$ its value at $T = T_{\mathrm{AN}}$, and $\tau^+ = \tau_0^+ t^{-z\nu_\perp}$ the critical relaxation time. The $+$ sign is used here to indicate the N phase; the $-$ sign will be used later for the SmA phase. The results in this figure have been obtained using the values of $\delta\alpha_c$ ($\delta\alpha_c = 2\pi A f$) and T_{AN} determined above for each angle θ, and the value of $z\nu_\perp$ expected for the 3D-XY model ($z\nu_\perp = 1$). The fact that all the experimental points fit onto a single curve, whatever their temperature and frequency, indicates that the $\delta\alpha/\delta\alpha_c$ ratio is a scaling function of the reduced variable $\omega\tau^+$. It should be stressed that this conclusion is deduced without recourse to any explicit formulation of the $\delta\alpha/\delta\alpha_c$ ratio. In addition, this ratio is independent of angle θ, which once more indicates that the critical effects are isotropic. On the other hand, the form of the scaling function is independent of the value of the critical relaxation time, since all value proportional to τ_0^+ simply shift the whole set of data along the temperature axis (in a semilogarithmic plot). The solid-line curve corresponds to the scaling function $F(\omega\tau^+) = (\omega\tau^+)/(1 + \omega\tau^+)$. This is an empirical function, which presents the same asymptotic high- and low-frequency behaviors as those predicted by the Swift and Mulvaney theory [7]. The value of τ_0^+ ($\tau_0^+ = 5 \times 10^{-11}$ s) used in Fig. 3 is the mean value determined by analyzing the variation of α/ω as a function of temperature for each angle θ with the formula $\delta\alpha/\omega = AF(\omega\tau^+)$. These same analyses, carried out with T_{AN} as a free parameter, also show that the values of T_{AN} are identical, to within standard deviations ($\pm 0.02\ ^\circ\mathrm{C}$), to those determined during analysis of the critical regime, thus validating the latter. The fact that the $\delta\alpha/\delta\alpha_c$ ratio follows a scaling law for the N-SmA transition in TBBA, but does not do so for the λ transition in helium, even though these two transitions both belong to the same universality class, has been explained in Ref. [16].

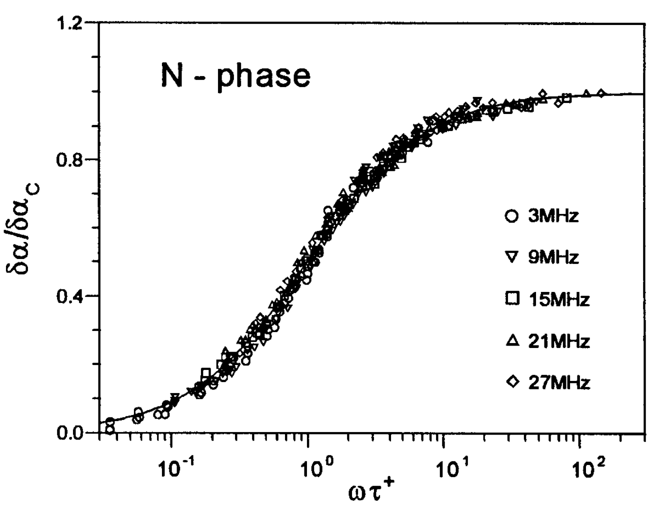

FIG. 3. Scaling plot of the normalized damping in the N phase for various frequencies as a function of $\omega\tau^+$. The data for $\theta = 0^\circ$, 45°, and 90° have been incorporated into the plot. The solid line corresponds to the scaling law $F(\omega\tau^+) = (\omega\tau^+)/(1 + \omega\tau^+)$.

In the SmA phase, the $\delta\alpha/\delta\alpha_c$ ratio also shows a scaling behavior, except in the $\omega\tau^- \sim 1$ regime for $\theta = 90^\circ$, as is shown in Fig. 4. The overall behavior is different from that of the N phase, as a result of the relaxation of the order-parameter modulus being added to the contribution of the fluctuations. This relaxation effect, which takes the form of a hump, is anisotropic: it is very marked for $\theta = 90^\circ$, and hardly visible for $\theta = 0^\circ$. The slight departure from the scaling observed in the $\omega\tau^- \sim 1$ regime for $\theta = 90^\circ$ might be explained by envisaging the existence of a mixing of the fluctuation and relaxation contributions, as has already been the case for the λ transition of helium [17]. This mixing could be more significant for $\theta = 90^\circ$ than for $\theta = 0^\circ$, owing to the anisotropy of the relaxation contribution. The results for $\theta = 0^\circ$ have been analyzed using the formula

$$\frac{\delta\alpha}{\omega} = AF(\omega\tau^-) + A_{\mathrm{LK}} G(\omega\tau^{\mathrm{LK}}), \tag{2}$$

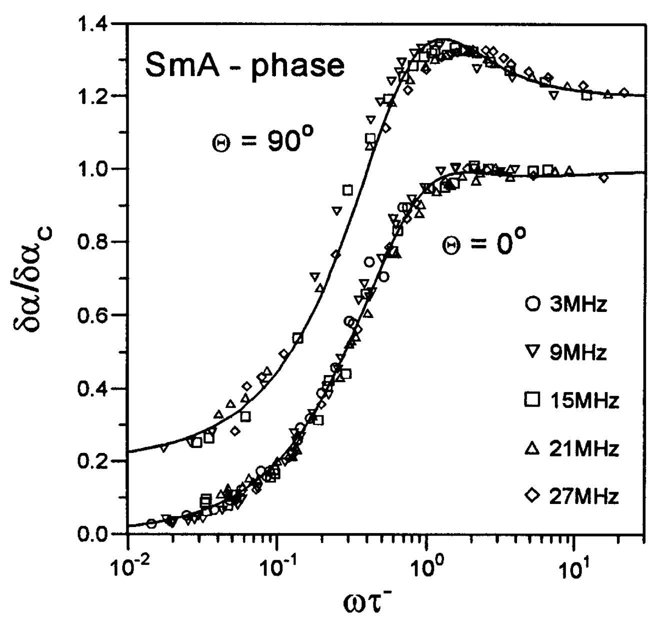

FIG. 4. Scaling plot of the normalized damping in the SmA phase for $\theta = 0^\circ$ and 90°. The solid lines represent fits made with Eq. (3). For reasons of clarity, the 90° data have been moved 0.2 along the vertical axis.

where $F(\omega\tau^{-})$ and $G(\omega\tau^{\mathrm{LK}})$ are the scaling functions, respectively, associated with the fluctuations and the relaxation of the order parameter. Owing to the symmetry of the fluctuation effects, $F(\omega\tau^{-})$ have a form which is analogous to that of $F(\omega\tau^{+})$. $G(\omega\tau^{\mathrm{LK}})$ is given by

$$G(\omega\tau^{\mathrm{LK}}) = \frac{\omega\tau^{\mathrm{LK}}}{1 + (\omega\tau^{\mathrm{LK}})^2}, \tag{3}$$

where $\tau^{\mathrm{LK}} = \tau_0^{\mathrm{LK}} t^{-z\nu_\perp}$. As in the N phase, the analyses were carried out as a function of temperature to allow the critical relaxation times τ_{LK} and τ^{-} to be determined. In order to reduce the number of adjustable parameters, we used the similarity hypotheses, which postulate that the dynamic exponent $z\nu_\perp$ and the specific heat exponent $\overline{\alpha}$ should be the same on each side of the transition; $z\nu_\perp$ and $\overline{\alpha}$ have therefore been fixed at the values that were determined for them in the nematic phase ($z\nu_\perp = 1$ and $\overline{\alpha} = 0$). We have also imposed the values of parameters A and T_{AN} deduced from the analysis of the critical regime. The fit, shown as a solid line in Fig. 4, gives a satisfactory account of the experimental data, and shows that the discontinuities associated with the first-order nature of the transition are weak. The resulting parameters are $2\pi A_{\mathrm{LK}} = (6.9 \pm 1) \times 10^{-7}\ \mathrm{s\,cm^{-1}}$, $\tau_0^{\mathrm{LK}} = (1.39 \pm 0.05) \times 10^{-11}$ s and $\tau_0^{-} = (1.2 \pm 0.3) \times 10^{-11}$ s. The value of τ_0^{LK} is, as expected, comparable to that of τ_0^{-}.

Although the scaling is not totally respected for $\theta = 90°$, the results obtained for this geometry have also been analyzed with Eq. (2). In this analysis, we have imposed the values of A and T_{AN} determined during analysis of the critical regime, and also the values of τ_0^{-} and τ_0^{LK} deduced from the analysis of the $\delta\alpha/\delta\alpha_c$ ratio for $\theta = 0°$. A_{LK} is thus the only adjustable parameter. Figure 4 shows that the fit accounts of the overall behavior of the $\delta\alpha/\delta\alpha_c$ ratio. The value of A_{LK} $[2\pi A_{\mathrm{LK}} = (9.9 \pm 0.3) \times 10^{-7}\ \mathrm{s\,cm^{-1}}]$ is higher than that determined for $\theta = 0°$, as expected, since the hump associated with the behavior of $\delta\alpha/\delta\alpha_c$ is more marked for $\theta = 90°$ than for $\theta = 0°$.

To conclude, we have shown that only two mechanisms contribute to the damping. One is isotropic and is associated with the quadratic coupling between the order-parameter fluctuations and the variation in density. It leads to a scaling behavior of the 3D-XY-type which is observed very far from the transition, even though the transition is first order. The other is anisotropic; it appears only in the SmA phase, and is associated with the relaxation of the order-parameter modulus. The observation of a 3D-XY-type behavior for the damping does not guarantee that the other observables also have the same behavior. Analysis of the velocity measurements taken on the same compound should make it possible to determine the behavior of the three de Gennes elastic constants, and to have a complete view of the dynamics of the transition.

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