Critical Behavior of Sound Damping in the Vicinity of the Smectic-*A*–Smectic-*C* Transition in $\bar{8}$S5

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We present ultrasound damping measurements taken in the vicinity of the smectic-*A*–smectic-*C* transition of 4-*n*-pentylphenylthiol-4-*n'*-octyloxybenzoate ($\bar{8}$S5). The results obtained, unlike previous measurements taken on the same compound, reveal marked pretransitional effects above the transition. These effects show that the transition is not of the Landau mean-field type, even though specific-heat, x-ray, and dilatometric measurements suggest this to be the case.

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The smectic-*A*–smectic-*C* transition (Sm*A*-Sm*C*) has, in recent years, been the object of numerous experiments, motivated by the de Gennes [1] model, which puts this transition in the 3D *XY* universality class ($d = 3, n = 2$). While some experiments [2,3] are in favor of this model, the present trend [4], based essentially on specific-heat measurements [5], is to describe this transition with a Landau mean-field type model.

This description of the transition has recently been questioned by the ultrasound velocity and damping measurements we have taken in TBBA [6], which show significant fluctuation effects above T_{AC} in contrast with the specific-heat measurements [7] taken on the same compound. This difference in behavior, which has been explained [8] by showing that the Ginzburg criterion depends on the observable under study, shows that ultrasounds are more sensitive to fluctuation effects than the specific heat. The ultrasound technique is therefore the key for determining whether the transition is of the Landau mean-field or critical type.

4-*n*-pentylphenylthiol-4-*n'*-octyloxybenzoate ($\bar{8}$S5) is the second example of a compound for which ultrasound [9] and specific-heat [10] measurements are available. While the specific heat does indeed show the Landau-type behavior usually observed, the ultrasound data obtained by Bhattacharya *et al.* [9] do not show any fluctuation effect above T_{AC}. This absence of pretransitional effects above T_{AC} would appear to indicate that, for this compound, the Sm*A*-Sm*C* transition could be of the Landau mean-field type, since unlike TBBA, the two observables seem to present the same critical region. Such behavior, while possible, surprised us in view of the specific-heat data [10] which reveal a slight deviation from the Landau-type behavior in the vicinity of the Sm*A*-Sm*C* transition. This observation led us to undertake an ultrasound study of the compound. Our damping measurements show that $\bar{8}$S5 does indeed have marked pretransitional effects above the transition, which indicates that the latter is not of the mean-field type, as suggested by specific-heat data [10] and the other experiments carried out (x ray [11] and dilatometry [12]).

$\bar{8}$S5 was recrystallized three times in ethanol. The N-I, N-Sm*A*, and Sm*A*-Sm*C* transition temperatures were determined by optical microscopy, and their values found to be 86 °C, 62.9 °C, and 55.5 °C respectively. These values are comparable to those reported in the literature on the subject, which indicates that our compound has an identical degree of purity.

The ultrasound measurements were taken with a setup capable of operating in either resonance or pulse mode. The two methods are complementary, since the resonance technique enables velocity and damping to be determined at a value of the order of 1 MHz, whereas the pulse technique enables damping to be determined at higher frequencies, i.e., 3, 9, and 15 MHz. A simple switch enables both types of measurements to be taken on the same cell, and thus on the same sample. A detailed description of the setup can be found in Ref. [13], and we shall only mention essential technical details here. The cell, cylindrical in shape, was fitted with matched 3 MHz gold-plated quartzes, optically polished. In order to avoid the parasitic effects associated with the side walls, the diameter of the sample ($\phi = 38$ mm) was greater than that of the ultrasound beam ($\phi = 25$ mm). The cell had a gap of ≈ 6.6 mm, and thermal regulation to within ± 0.02 °C. It was placed in a Plexiglas box, between the poles of an electromagnet producing a magnetic field of 10 kG. The cell was filled under vacuum, in order to extract from the compound the dissolved oxygen. Once the cell had been filled, nitrogen was injected into the box in order to restore the atmospheric pressure within the cell, and to allow measurements to be taken in an inert atmosphere. These precautions avoid the sample deterioration during the experiments.

The Sm*A* and Sm*C* samples were obtained by orienting the compound in the nematic phase with the 10 kG magnetic field, then letting it cool slowly. The field was cut off a few degrees below the N-Sm*A* transition [14].

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The ultrasound measurements were taken for the three orientations defined by $\Theta = 0°, 45°$, and $90°$, where Θ represents the angle between the normal to the smectic layers and the direction of sound propagation. They were taken for each angle Θ, while the temperature was lowered from the nematic phase to the smectic C phase, and in the order $\Theta = 0°$, $90°$, and $45°$. After taking these measurements, we once more studied the $\Theta = 0°$ geometry, in order to verify that the initial conditions were still obtained, and to determine any possible fall in the temperatures associated with the N-Sm*A* and Sm*A*-Sm*C* damping peaks. The obtained values were found to be identical, to within our experimental resolution limits, to those determined in the initial cycle, which shows that the compound had not suffered any notable deterioration during the ultrasound experiments. This absence of deterioration was confirmed by observing the transition temperatures of the sample taken from the cell with a polarizing microscope. The same probes were used for both the ultrasound experiments and the optical observations. Any uncertainty in determining the transition temperatures and the position of the damping peaks can be estimated at ±0.1 °C.

Figures 1, 2, and 3 show the behavior of the ultrasound damping for $\Theta = 0°$, $45°$, and $90°$. The resonance technique was used to take the 1.5 MHz measurements, and the pulse technique for those at 3, 9, and 15 MHz. In the case of the latter, the damping value was obtained in relation to an absolute value determined at a temperature at which damping is weak (several echoes). These three figures call for the following observations.

(1) The results obtained at 1.5 MHz for $\Theta = 0°$ reveal the existence of substantial pretransitional effects appearing about 5 °C above the Sm*A*-Sm*C* transition. This is our essential result, and indicates that, contrary to the conclusions of Ref. [9], the Sm*A*-Sm*C* transition is not of the Landau type in this compound.

(2) The critical effects are more marked for $\Theta = 0°$ (Fig. 1) than for $\Theta = 45°$ (Fig. 2) and $\Theta = 90°$ (Fig. 3). This anisotropy of the critical effects is comparable to that observed for the Sm*A*-Sm*C* transition in TBBA [6]. It may be accounted for by the Andereck and Swift theory [15], which includes in the free energy terms which couple the order-parameter fluctuations with density variation and the layer-spacing gradient.

(3) The Andereck and Swift theory [15] predicts that $\alpha/f^2 = a + bf^{(-1+\bar{\alpha}/z\nu)}$ at $T = T_{AC}$, i.e., when the data correspond to the $\omega\tau \gg 1$ regime, where τ is the critical relaxation time. Experimental results show that $\alpha/f^2 \sim a + b/f$, which suggests that $\overline{\alpha} \sim 0$, and the fluctuations are of the 3D *XY* type. Too much credit should not, however, be given to this conclusion, since α/f^2 can also be seen to present a $1/f$-type behavior in the middle of the Sm*A* phase ($T = 60$ °C), where the critical fluctuations associated with the Sm*A*-Sm*C* transition are not in the $\omega\tau \gg 1$ regime. This result suggests that the

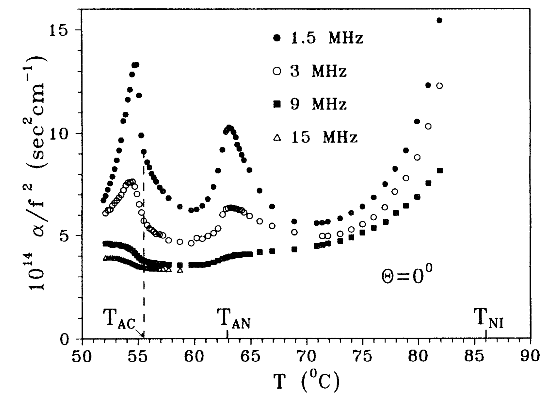

FIG. 1. Temperature dependence of the ultrasonic attenuation for $\Theta = 0°$ at different frequencies.

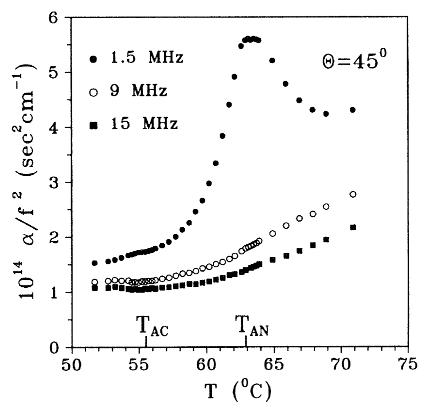

FIG. 2. Same as Fig. 1 but $\Theta = 45°$.

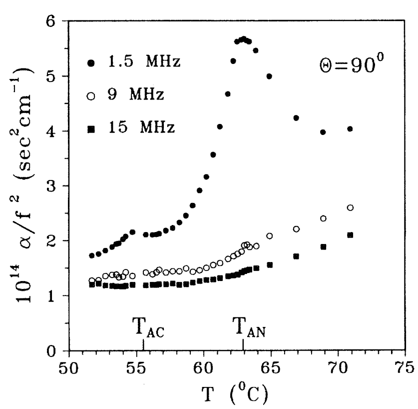

FIG. 3. Same as Fig. 1 but $\Theta = 90°$.

$1/f$-type behavior of α/f^2 is essentially governed by the anharmonic effects which are characteristic of smectic phases [16], and by chain relaxation effects [17]. It should be noted, in this respect, that a $1/f$-type variation of α/f^2 can be observed at $T = T_{AC}$ for the other two orientations ($\Theta = 45°$ and $\Theta = 90°$), even though the latter are not characterized by any marked critical behavior.

(4) The data in Fig. 1 concerning the $\Theta = 0°$ orientation show the damping peak to shift towards low temperatures as frequency increases. This shift, of the order of 0.6 °C at 1.5 MHz and 1 °C at 3 MHz, is indeed a real physical effect, since it is greater than the aggregate of the errors made in determining T_{AC} (± 0.1 °C) and the position of the damping peak (± 0.1 °C). It corresponds to the behavior predicted by the Landau-Khalatnikov mechanism associated with relaxation of the order-parameter modulus [18]. The same behavior was observed at the Sm*A*-Sm*C* transition in TBBA for $\Theta = 0°$ [6]. It should also be noted that, within the limits of experimental error, there is no peak shift at the N-Sm*A* transition. This observation, already made for TBBA at $\Theta = 0°$ [19], suggests that the Landau-Khalatnikov effect is much smaller at the Sm*A*-N than at the *A*-*C* transition.

(5) Figure 1 shows that the Sm*A*-Sm*C* fluctuation effect has completely disappeared at 9 and 15 MHz, while it is still visible at these frequencies in TBBA [6]. This would indicate that the critical relaxation time τ is greater for $\overline{8}$S5 than for TBBA. The same conclusion can be obtained from the velocity measurements taken at 1.5 MHz for $\Theta = 0°$, which show no marked pretransitional effects above T_{AC}. In principle, this time can be determined by analysis of the Landau-Khalatnikov effect, but that would require us to subtract from the data the term associated with the order-parameter fluctuations, and the residual damping term which, in this particular case, includes the critical effects associated with the N-Sm*A* transition, the chain-relaxation effects, the Martin-Parodi-Pershan viscosity term [20], and the anharmonic effects. Since all of these contributions are unknown, τ cannot be determined from the Landau-Khalatnikov effect. Similarly, analysis of data from the Sm*A* phase, which should also have enabled τ to be determined, is not possible either.

To return to our main observation, i.e., the existence of marked pretransitional effects above T_{AC}, it is our opinion that, in view of the multiple experimental precautions taken, the existence of these effects constitutes an essential and well-established feature of Sm*A*-Sm*C* transition in $\overline{8}$S5. This contradicts the result reported by Bhattacharya *et al.* [9], which indicated that this transition is characterized by the absence of any pretransitional effects above T_{AC}. Without wishing to speculate on the origin of the behavior found by Bhattacharya *et al.*, it should be noted that the latter may well be due to their having simply attributed to temperatures T_{AN} and T_{AC} the values reported in the literature, without having obtained prior proof of these. This poor choice would explain not only the incorrect conclusions concerning the Sm*A*-Sm*C* transition, but also why all the critical damping associated with the N-Sm*A* transition is situated below T_{AN}, which would appear to indicate that this latter transition is also of the mean-field type, whereas it is, in fact, of the critical type. A simple shift of ≈ 2 K in the values of T_{AN} and T_{AC} would lead to a behavior agreeing qualitatively with our experiments.

To conclude, we have shown that the Sm*A*-Sm*C* transition in $\overline{8}$S5 is not of the Landau mean-field type as is suggested by all previous experiments on this compound. In our opinion, this conclusion, which goes along with that obtained for TBBA, is probably valid for most Sm*A*-Sm*C* transitions. The only exception would appear to concern 40.7 [4], for which a Landau mean-field type behavior has been observed in the reduced-temperature range, down to with 10^{-5} of the transition. It would be interesting to confirm this behavior with ultrasound measurements.

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suggests the existence of chain relaxation, the characteristic frequency of which is within the domain covered by our measurements.

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