Strong Critical Fluctuations near a Strongly First-Order Smectic-*C*–Hexatic-*F* Phase Transition

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We present the first experimental evidence of strong anomalies in both the attenuation and velocity of longitudinal ultrasound near a smectic-*C*–hexatic-*F* phase transition. These effects, which have been observed on terephthal-bis-hexylaniline, show that the hexatic order parameter is strongly coupled to density. They occur although the transition is strongly first order, with a wide two-phase region of ~3 °C. Analysis of the data enables the specific-heat exponent to be determined. The results also show that the transition occurs in a highly fluctuating layer system. [S0031-9007(97)05164-8]

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Some smectic phases, known as hexatic, possess a long-range orientational order of the bonds (the lines connecting neighboring molecules), but only short-range positional order. The molecules can be either perpendicular to the layers (hexatic *B*), or inclined with respect to the normal to the layers (hexatic *F* and *I)* [1]. The vector characterizing the direction in which the molecules are inclined points between the two closest molecules in the hexatic-*F* phase, and towards the closest molecule in the hexatic-*I* phase.

For the inclined hexatic phases, theory [2] predicts that the smectic-*C*–hexatic-*F* (Sm*C*-Hex*F*) or smectic-*C*–hexatic-*I* (Sm*C*-Hex*I*) transition is qualitatively similar to that of a liquid-gas transition, with a first-order line ending in an isolated critical point. Beyond this point, there is no longer a phase transition, but a supercritical evolution of the orientational order of the bonds and of the tilt angle within a single phase, generally known as the Sm*C* phase at high temperature and the Hex*F* (or Hex*I*) phase at low temperature. The theory also predicts that the Sm*C*-Hex*F* (or Hex*I*) critical point belongs to a new universality class which includes the Sm*A*-Sm*A* and electric-field-induced chiral Sm*C*-chiral Sm*C* critical points. The existence of the critical Sm*C*-Hex*I* point has recently been established by high-resolution calorimetry experiments, carried out in a racemic mixture of methylbutyl phenyl octylbiphenyl-carboxylate (8SI) and the octyloxybiphenyl analog (80SI) [3].

The dynamic properties of the Sm*C*-Hex*F* or Sm*C*-Hex*I* transitions, unlike their static properties, have been the object of very few experiments. In this Letter, we are presenting the first observations which show that ultrasound velocity and damping exhibit marked pretransitional effects in the vicinity of the Sm*C*-Hex*F* transition.

The compound chosen for this study was terephthal-bis-hexylaniline (hereafter referred to as TB6A), which has the following phase sequence [4]:

$$\mathrm{Cr}G \rightarrow^{143\,^\circ\mathrm{C}} \leftarrow \mathrm{Hex}F \rightarrow^{153\,^\circ\mathrm{C}} \leftarrow \mathrm{Sm}C \rightarrow^{187\,^\circ\mathrm{C}} \leftarrow \mathrm{Sm}A \rightarrow^{208\,^\circ\mathrm{C}} \leftarrow N \rightarrow^{215\,^\circ\mathrm{C}} \leftarrow \mathrm{Isotrope}.$$

It was synthesized in our laboratory and, in order to prevent sample deterioration, subjected to the same measuring protocol as that used for studying terephthal-bis-butylaniline (TBBA) [5], i.e., degassing in the measuring cell and taking measurements under an inert atmosphere.

The cell was placed between the poles of an electromagnet producing a 10 kG magnetic field, and the samples oriented by heating the compound to its nematic phase, then cooling it slowly within the magnetic field, which was switched off a few degrees before the Sm*A*-Sm*C* transition. In these conditions, the Sm*C* and Hex*F* phases had a layered structure, but orientation of the molecules, and therefore of the bonds, was not fixed (polydomain samples). 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 normal to the smectic layers and the direction of sound propagation. A fresh sample was used for each angle θ. The experiments were carried out with the use of the resonance and pulse devices previously elaborated for studying TBBA [5]. These two devices are connected to the measuring cell via a switch. The resonance device enabled us to measure velocity at 1.5 MHz, and the pulse device was used for measuring damping at 3, 9, 15, 21, and 27 MHz. The cell had an interquartz gap of 7 mm and was thermally regulated to within ±0.01 °C. The above mentioned switch allows virtually simultaneous measurements of velocity and damping. A detailed description of the setup, the cell, and the measuring protocol is found in Ref. [5].

The resonance device enabled us to show a two-phase region between the Sm*C* and Hex*F* phases. In this region the two phases separate under the effect of gravity, and become gradually superimposed one on the other within the cell, leading to a doubling of the resonance peaks [6]. This effect indicates that the Sm*C*-Hex*F* transition is of the first order. Since it is impossible to define a transition temperature for this transition, the data are shown as a function of their distance from transition temperature T_{AC}, defined as the temperature for which 3 MHz damping reaches a maximum [7].

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We shall begin by examining the behavior of ultrasound velocity. Figure 1 shows the results obtained in the SmC and Hex$F$ phases for the two orientations defined by $\theta = 0°$ and $\theta = 90°$. To enhance clarity, the data for $\theta = 45°$ are not shown, but they do present a similar behavior. Examining Fig. 1 shows velocity anisotropy to be marked in the SmC phase and slightly less so in the Hex$F$ phase [8]. The SmC anisotropy, which is characterized by $V(0°) < V(90°)$, is analogous to that already observed in TBBA [9]. Velocity anisotropy is reversed in the Hex$F$ phase, probably as a result of the proximity of the CrG phase. Velocity can also be seen to present a pronounced decrease in the vicinity of the SmC-Hex$F$ transition, which reflects the fluctuations of the hexatic order parameter. This decrease, also observed at the SmA-SmC [9], N-SmA [10], and N-I [11] transitions, is the result of quadratic coupling between fluctuations of density and fluctuations of the order parameter [12] ($\delta\rho$-Ψ^2 coupling). The two-phase region associated with the SmC-Hex$F$ transition is shown by the two vertical dashed lines. The range of this region, nearly 3 °C, shows that this is a strongly first-order transition, which agrees with the specific-heat measurements taken by Stine and Garland [13] on the same compound.

The square of the velocity $V^2(\theta)$ can be written as

$$V^2(\theta) = V^2_{\rm reg}(\theta) - \Delta V^2(\theta), \qquad (1)$$

where $V^2_{\rm reg}(\theta)$ represents the regular part of velocity and $\Delta V^2(\theta)$ the critical part. The regular part has been taken to have the following linear variation with temperature:

$$V^2_{\rm reg}(\theta) = p(\theta)(T - T_{AC}) + q_{\rm reg}(\theta), \qquad (2)$$

where $p(\theta)$ and $q_{\rm reg}(\theta)$ are constants. Since, in the case of the $\delta\rho$-Ψ^2 coupling, the critical behavior of $\Delta V^2(\theta)$ reflects that of the specific heat, we have used the expression of specific heat given by the renormalization group [14]. The behavior of $V^2(\theta)$ will thus be analyzed with the following equation:

$$V^2(\theta) = a(\theta)(T - T^*_{CF})^{-\bar{\alpha}} + p(\theta)(T - T_{AC}) + q(\theta). \qquad (3)$$

The first term represents the critical part, exponent $\bar{\alpha}$ being that of the specific heat. Constant $q(\theta)$ contains the regular part $q_{\rm reg}(\theta)$ and, as is the case for specific heat, a critical part $q_{\rm crit}(\theta)$, with $q(\theta) = q_{\rm reg}(\theta) + q_{\rm crit}(\theta)$. T^*_{CF} represents the virtual transition temperature at which the SmC-Hex$F$ transition would occur if it were of the second order. The difference between T and T^*_{CF} is related to that between T and T_{AC} by the equation

$$T - T^*_{CF} = (T - T_{AC}) + (T_{AC} - T^*_{CF}). \qquad (4)$$

Equation (3) supposes that the measurements correspond to the hydrodynamic regime, and are therefore independent of the measuring frequency. This supposition will be justified below, during analysis of the damping measurements.

The results for each angle θ have been analyzed using Eq. (3). These analyses show that the critical parameters $\bar{\alpha}$, $a(\theta)$, and $\delta T = T_{AC} - T^*_{CF}$ obtained for $\theta = 0°$, 45°, and 90° are identical, within the limits of standard deviations. This observation led us to make a simultaneous analysis of the results relating to the three angles, assuming the critical effects to be isotropic. Under these conditions, parameters $\bar{\alpha}$, a, and δT are independent of angle θ, whereas p and q are depending on this angle. The values of the parameters and standard deviations are the following: $\bar{\alpha} = 0.64 \pm 0.05$, $a = (-0.33 \pm 0.02) \times 10^{10}\ {\rm cm^2\,s^{-2}\,K^{-1}}$, $\delta T = (34.7 \pm 0.2)$ °C; $p(90°) = (-6.889 \pm 0.069) \times 10^{-3}$, $q(90°) = 1.2345 \pm 0.0049$, $p(45°) = (-7.045 \pm 0.069) \times 10^{-3}$, $q(45°) = 1.2204 \pm 0.0049$, and $p(0°) = (-7.244 \pm 0.069) \times 10^{-3}$, $q(0°) = 1.2090 \pm 0.0049$. Units for $p(\theta)$ and $q(\theta)$ are $10^{10}\ {\rm cm^2\,s^{-2}\,K^{-1}}$ and $10^{10}\ {\rm cm^2\,s^{-2}}$, respectively. The relatively high δT uncertainty stems from the fact that the temperature region near the transition must be excluded from the fit, because of the two-phase region. The slope $p(\theta)$ of the regular terms can be seen to vary slightly from one orientation to another. These differences reflect the structural anisotropy of the smectic phase. The plot made with these parameters is shown by the solid line in Fig. 2, and the quality of the fit confirms that the critical effects are isotropic. This result is quite different from those obtained for the SmA-Hex$B$ [15] or SmA-SmC [9] transitions, which are characterized by very anisotropic critical effects. For both of these transitions, the anisotropy of the critical effects stems from the fact that the free energy contains terms which couple the order-parameter fluctuations with density variation (coupling constant γ_ρ) and with the layer-spacing gradient (coupling constant γ_u) [12]. The absence of anisotropy at the SmC-Hex$F$ transition suggests that γ_u is null or

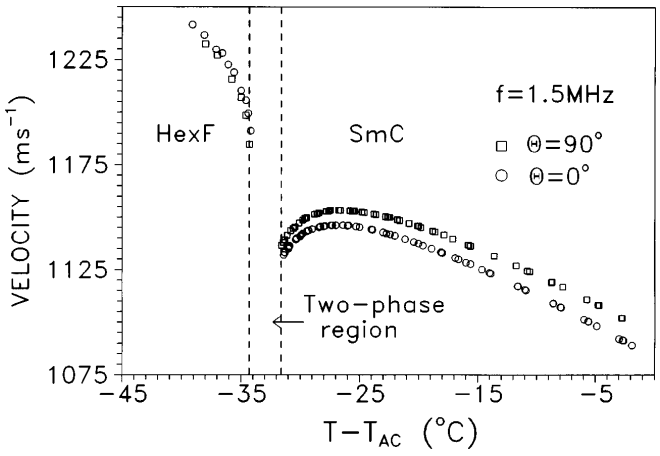

FIG. 1. Variation of velocity as a function of temperature for $\theta = 0°$ and 90° in the SmC and Hex$F$ phases. The data show that the velocity presents marked pretransitional effects near the SmC-Hex$F$ transition, which occur even though the transition is strongly first order with a two-phase coexistence region of the order of 3 °C.

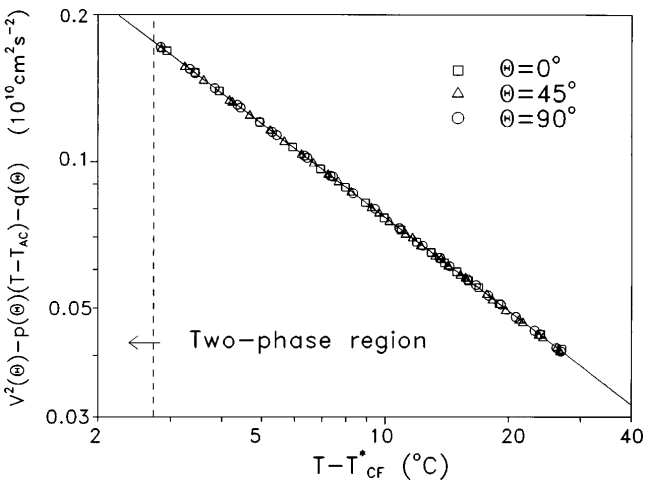

FIG. 2. Simultaneous analysis of the square of the velocity for $\theta = 0°$, 45°, and 90°, showing that the critical effects are isotropic. The solid line represents the fit to Eq. (3). T^*_{CF} is the virtual transition temperature at which the SmC-Hex$F$ transition would occur if it were of the second order.

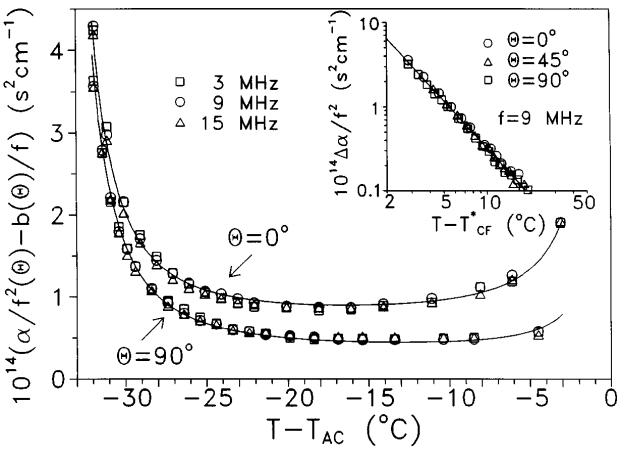

FIG. 3. Thermal variation of the damping obtained for $\theta = 0°$ and $\theta = 90°$, after subtracting the anharmonic effects. The fact that α/f^2 is frequency independent for each angle θ shows that the data correspond to the hydrodynamic regime. The solid lines represent the simultaneous fit of the data to Eq. (6). The critical part of the damping associated with the SmC-Hex$F$ transition is shown in the inset.

very small compared to γ_ρ. Exponent $\bar{\alpha}$ has a high value ($\bar{\alpha} = 0.64$), which is close to those deduced from the specific-heat measurements ($0.48 < \bar{\alpha} < 0.67$) [1] for the Sm$A$-Hex$B$ transition. Comparison with the results obtained for the SmC-Hex$F$ or SmC-Hex$I$ transitions is not possible, as the specific-heat exponent determined for these two transitions is not $\bar{\alpha}$ but γ [3].

We shall now discuss ultrasound damping behavior. The data taken at a given temperature show that α/f^2 is not constant, as in conventional hydrodynamics, but has abnormal $1/f$-type behavior, which is a function of the angle θ between the direction of sound propagation and the normal to the smectic layers. This behavior can be analyzed with the anharmonic theory [16], which predicts that α/f^2 is written as

$$\alpha/f^2(\theta) = a(\theta) + b(\theta)/f\,, \qquad (5)$$

where $a(\theta)$ is the classical damping term and $b(\theta)/f$ the anharmonic term associated with the fluctuations of the smectic layers. This analysis shows that $a(\theta)$ and $b(\theta)$ are roughly temperature independent and present the following values: $a(\theta) = 0.86$, 0.62, 0.49 (in 10^{-14} s^2 cm^{-1} units) and $b(\theta) = 0.70$, 1.64, and 2.72 (in 10^{-8} s cm^{-1} units) for $\theta = 0°$, 45°, and 90°, respectively. These values are comparable to those obtained in the SmC phase of TBBA [17].

Figure 3 shows the behavior of the damping obtained for $\theta = 0°$ and $\theta = 90°$ after subtracting the anharmonic effects (i.e., the $b(\theta)/f$ term). To enhance clarity, the data for $\theta = 45°$ are not shown, but they do present a similar behavior. It can be observed that α/f^2 shows marked pretransitional effects in the vicinity of the SmC-Hex$F$ transition, as in the case of velocity. The fact that α/f^2 is independent of frequency, whatever the angle considered, indicates that the data correspond to the hydrodynamic regime.

These data were analyzed with the following equation:

$$\Delta\alpha/f^2 = A_1 \Delta T_1^{-\beta_1} + A_2 \Delta T_2^{-\beta_2} + A_3\,, \qquad (6)$$

where $\Delta T_1 = -\Delta T_2 + T_{AC} - T^*_{CF}$ and $\Delta T_2 = T_{AC} - T$. The first term accounts for the critical damping associated with the SmC-Hex$F$ transition, and the second one does the same for the SmA-SmC transition. These two terms are independent of frequency, since the measurements, as we have just seen, correspond to the hydrodynamic regime throughout the whole range of temperatures studied. The A_3 term is a constant which takes account of the noncritical effects. In order to limit the number of adjustable parameters in Eq. (6), we have imposed the $\delta T = T_{AC} - T^*_{CF}$ difference, determined when analyzing the velocity measurements ($\delta T = 34.7$ °C), as well as the expected value of exponent β_2 for the SmA-SmC transition ($\beta_2 = 1.32$). We have also assumed the critical effects associated with SmC-Hex$F$ transition to be isotropic, as has been shown by analysis of the velocity measurements. The parameters of the adjustment made in these conditions are $A_1 = (23\,578 \pm 552) \times 10^{-17}$, $\beta_1 = 1.86 \pm 0.02$, $A_2(0°) = (5299 \pm 134) \times 10^{-17}$, $A_3(0°) = (663 \pm 12) \times 10^{-17}$, $A_2(45°) = (1828 \pm 161) \times 10^{-17}$, $A_3(45°) = (490 \pm 12) \times 10^{-17}$, $A_2(90°) = (1917 \pm 230) \times 10^{-17}$, $A_3(90°) = (306 \pm 13) \times 10^{-17}$. Units for A_1 and A_2 are (s^2 cm^{-1} K^{-1}) and (s^2 cm^{-1}) for A_3. This fit was made taking account of all the data in the SmC phase ($T - T_{AC} < -2$ °C), and is shown by the solid curves in Fig. 3. The quality of this fit confirms that the critical effects associated with the SmC-Hex$F$ transition are isotropic (the critical damping alone is shown in the inset of the figure). The critical parameters (A_1, β_1) are not affected by the critical effects associated with the SmA-SmC transition, as is shown by a fit, which was made over a

smaller temperature interval ($T - T_{AC} < -20\,^{\circ}\mathrm{C}$), using Eq. (6), in which parameter $A_2 = 0$ [18]. In the case of quadratic coupling and isotropic fluctuations, exponent β_1 and the exponent associated with the order parameter relaxation time [$\tau = \tau_0(T - T^*_{CF})^{-z\nu}$] are linked by the equation $\beta_1 = \bar{\alpha} + z\nu$. If this equation is assumed to remain valid for the SmC-Hex$F$ [19], then, since β_1 and $\bar{\alpha}$ are known, the value of $z\nu$ can be deduced, and is of the order of 1.2. The value of the critical relaxation time τ_0 can be estimated from the critical parameters determined from the analysis of the damping and velocity measurements and assuming a single-time relaxation mechanism [20]. The value obtained is $\tau_0 \simeq 5\ 10^{-12}$ s.

The presence of marked anharmonic effects shows that the SmC-Hex$F$ transition occurs in a highly fluctuating layer system, whereas the description of the hexatic phases supposes that the transition occurs in a nonfluctuating layer system. In the case of the SmA-Hex$B$ transition, Selinger [21] has shown that these fluctuations could lead to a frustration which is geometrical in origin and which introduces a coupling between the hexatic order parameter and the layer fluctuations. This coupling, which should also exist for the SmC-Hex$F$ transition, could explain the unusually high specific-heat exponent $\bar{\alpha}$, and the fact that the transition is of the first order.

The existence of important hexatic order fluctuations suggests that the SmC-Hex$F$ transition of TB6A is not very far from a critical point. Given that TB7A and TB8A exhibit a first-order transition, the critical point associated with the TBnA series should be realized for $n > 8$. An essential question is: Why does the first-order SmC-Hex$F$ transition of TB6A exhibit a fluctuation-type behavior, whereas that of the critical point associated with the 8SI-8OSI mixture is of mean-field type [3]? Ultrasound measurements on the critical 8SI-8OSI mixture would enable us to determine whether this difference in behavior is linked to anharmonic effects or not. Another important question, which may be linked to the previous one, is that of why the coupling between the hexatic order parameter and the molecular tilt field is weak for TB6A [22] and strong for supercritical 8SI-8OSI mixtures [3].

In conclusion, the purpose of this Letter is to underline the following: (1) The velocity and damping of ultrasound show high-amplitude critical effects in the vicinity of the SmC-Hex$F$ transition in T86A, even though it is a strongly first-order transition, with a two-phase region of the order of 3 °C and (2) the transition occurs in a highly fluctuating layer system. The former observation shows that the hexatic order parameter is strongly coupled to density, while the latter may give rise to a geometrical frustration, which enables the hexatic order parameter to be coupled to layer fluctuations. The importance of the critical effects observed, allied to the fact that the transition occurs in a highly fluctuating layer system, may suggest that sufficient attention may not have been paid to the lamellar structure of hexatic systems and to the coupling of the hexatic order parameter with the density.

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[7] Studying the SmA-SmC transition in TBBA shows that the 3 MHz damping peak appears at the transition for $\theta = 45°$ and $\theta = 90°$, and deviates a few hundredths of a degree towards lower temperatures for $\theta = 0°$; see Ref. [9].
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