Smectic-A-Smectic-C Transition: Mean-Field and Critical Behaviors

L. Benguigui[(a)] and P. Martinoty
Laboratoire de Spectrométrie et d'Imagerie Ultrasonores, Université Louis Pasteur, 4, rue Blaise Pascal, 67070 Strasbourg CEDEX, France
(Received 29 March 1989)

Using the Ginzburg criterion, we demonstrate that the width of the critical region associated with the smectic-A-smectic-C transition is dependent on the observable studied. This affords an explanation of the results obtained for terephthal-*bis-p-p'*-butylaniline, which shows specific-heat behavior consistent with a Landau-type model, unlike that of the elastic constants. This analysis could apply to other phase transitions.

PACS numbers: 64.70.Md, 61.30.−v

Although the precise nature of the smectic-A-smectic-C transition has been the subject of considerable controversy, the present trend is to describe this transition using a model of the mean-field type.[1-9] This trend is based essentially on the fact that the specific-heat measurements can be analyzed within the framework of the Landau theory.[6-9] Some authors,[10,11] however, have pointed out that this model is not totally suitable for analyzing such measurements, in view of the small divergence from the mean-field behavior generally observed in the immediate vicinity of the transition temperature T_c.

Controversy as to the nature of the smectic-A-smectic-C transition has recently been brought to the fore again by ultrasound measurements taken in terephthal-*bis-p-p'*-butylaniline (TBBA).[12] These data show the existence of significant fluctuation effects (see Fig. 1) which are still visible 10 °C above T_c, and which are incompatible with the Landau model. This result is all the more surprising as the specific-heat measurements taken on the same compound do not exhibit these large fluctuation effects (see Fig. 2), and can, according to the authors of Ref. 13, be interpreted with the Landau model. The purpose of this Letter is to reconcile these apparently contradictory results by showing that the ultrasound measurements are more sensitive to fluctuation effects than the specific-heat measurements, as was suggested in Ref. 12. This explains the fact that deviation from the Landau model, which may occur in the vicinity of T_c when specific heat is concerned, becomes visible much earlier (i.e., far from T_c) in the case of velocity (or the elastic constants). In more quantitative terms, we show that the width of critical region, calculated with the Ginzburg criterion,[14] is dependent on the quantity considered (specific heat, elastic constants, etc.).

We now present our analysis of the results for TBBA, with a view to determining the critical region by means of the Ginzburg criterion. First, we calculate the coefficients of the Landau free energy using the jumps of the specific heat and of the elastic constants at the transition. Second, we consider the influence of the order-parameter fluctuations on the specific heat and the elastic constants within the Gaussian approximation. Last, we evaluate the critical regions associated with the specific heat and the elastic constants, respectively. This is done by equating the amplitude of the T_c jump of the quantity considered with that of the contribution of the

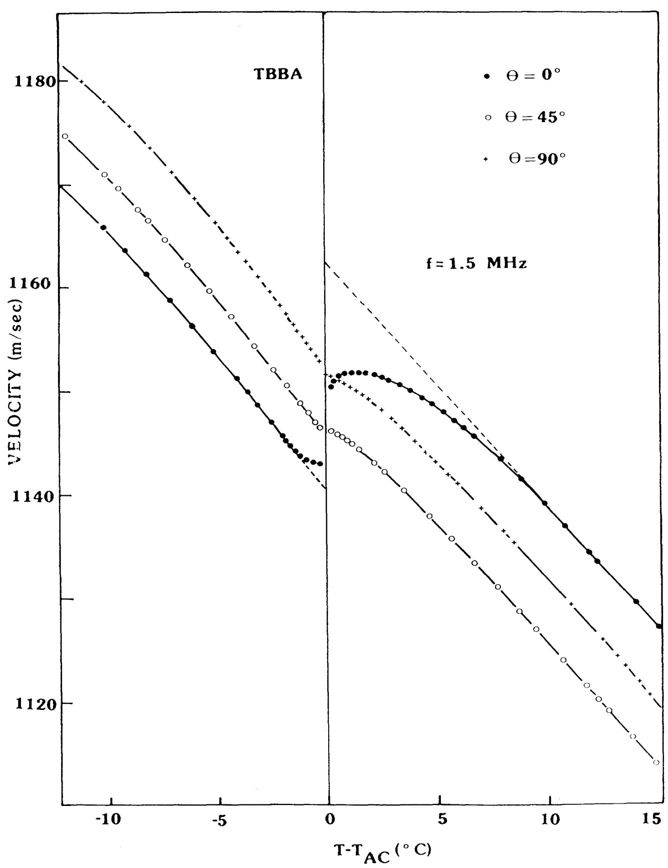

FIG. 1. Velocity curves for $\theta = 0°$, 45°, and 90° at the Sm-A-Sm-C transition. θ is the angle between the normal to the smectic layers and the sound propagation direction. The straight lines represent the behavior expected by the Landau model for $\theta = 0°$. The curves are from Ref. 12.

fluctuations to this quantity.[15]

The starting point is the free energy F used by Andereck and Swift[16] to study the behavior of sound attenuation and dispersion near the Sm-A-Sm-C transition. F is given by[17]

$$F=\int d^3r\left[\frac{1}{2}A\eta^2+\frac{1}{4}B\eta^4+\frac{1}{2m_\perp}(\nabla_\perp\eta)^2+\frac{1}{2m_2}(\nabla_2\eta)^2+\frac{1}{2}\left(\frac{\partial p}{\partial\rho}\right)_{\nabla_2 u}(\Delta\rho)^2+\frac{1}{2}\left(\frac{\partial\phi_z}{\partial\nabla_z u}\right)_p(\nabla_z u)^2\right.$$
$$\left.+\left(\frac{\partial p}{\partial\nabla_z u}\right)_p(\Delta\rho)(\nabla_z u)+\tfrac{1}{2}K_1(\nabla_x^2 u+\nabla_y^2 u)^2+\tfrac{1}{2}\gamma_\rho\Delta\rho\eta^2+\tfrac{1}{2}\gamma_u\nabla_z\eta^2\right], \qquad (1)$$

where η is the smectic-C order parameter (the tilt angle), $\Delta\rho$ the relative variation of the density, u the displacement of the smectic layers in the z direction, K_1 the Frank elastic constant, p the pressure, and ϕ_z the conjugate field associated with $\nabla_2 u$. The symbol $\perp$ refers to the plane of the layers. $m_\perp$, m_z, and B are positive constants and $A=A_0(T-T_c)$. The last two terms of (1) couple the order parameter to the density variation (coupling constant γ_ρ) and to the layer-spacing gradient (coupling constant γ_u). These two terms are very important since they show that the fluctuation effects on velocity and damping can be extremely anisotropic, the degree of anisotropy depending on the γ_u/γ_ρ ratio.[16]

It is more useful for the remainder of this Letter to rewrite the free energy as a function of the strains

$$x_1=\partial u/\partial x,\quad x_2=\partial u/\partial y,\quad x_3=\partial u/\partial z\,,$$

and of the elastic constants

$$c_{11}=(\partial p/\partial\rho)_{\nabla_z u}\,,\quad c_{13}=(\partial p/\partial\rho)_{\nabla_z u}-(\partial p/\partial\nabla_z u)_p\,,$$
$$c_{33}=(\partial p/\partial\rho)_{\nabla_z u}-2(\partial p/\partial\nabla_z u)_p+(\partial\phi_z/\partial\nabla_z u)_p\,.$$

This gives[18]

$$F=\int d^3r[\tfrac{1}{2}A\eta^2+\tfrac{1}{4}B\eta^4+\tfrac{1}{2}c_{11}(x_1+x_2)^2+\tfrac{1}{2}c_{33}x_3^2+c_{13}x_3(x_1+x_2)-\tfrac{1}{2}\gamma_\rho(x_1+x_2+x_3)\eta^2$$
$$+\tfrac{1}{2}\gamma_u x_3\eta^2+(1/2m_\perp)(\nabla_\perp\eta)^2+(1/2m_z)(\nabla_z\eta)^2]\,. \qquad (2)$$

The K_1 term has been omitted here since it is not necessary for our analysis. In the mean-field approximation, η is constant in space and the gradient terms can be suppressed.

The jumps of the elastic constants can be calculated from the formula $c_{ij}=\partial^2F/\partial x_1\partial x_j$, by using the standard procedure of minimization of the free energy ($\partial F/\partial\eta=0$). This calculation gives

$$\Delta c_{11}=-\gamma_\rho^2/2B\,,$$
$$\Delta c_{13}=-\gamma_\rho(\gamma_\rho-\gamma_u)/2B\,, \qquad (3)$$
$$\Delta c_{33}=-(\gamma_\rho-\gamma_u)^2/2B\,,$$

where $\Delta c_{ij}=c_{ij}(T_c^-)-c_{ij}(T_c^+)$.

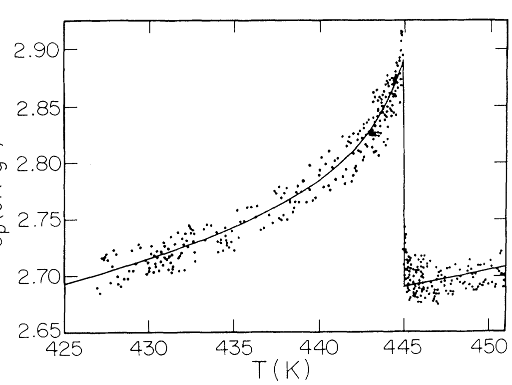

FIG. 2. Specific-heat capacity at TBBA near the Sm-A-Sm-C transition. The line represents the Landau fit to these data. From Ref. 13.

The jump of the specific heat is obtained from the Gibbs free energy $G=F-\sum_i x_iX_i$ and is given by

$$\Delta c_p=c_p(T_c^-)-c_p(T_c^+)=T_cA_0^2/2B^*\,, \qquad (4)$$

where B^* is the η^4 coefficient of the free energy G expressed as a function of η^2 and the stress X_i. B^* is related to the order parameter η by

$$\eta^2=A/B^*\,, \qquad (5)$$

with

$$B^*=B+\frac{2c_{13}\gamma_\rho(\gamma_\rho-\gamma_u)-c_{11}(\gamma_\rho-\gamma_u)^2-c_{33}\gamma_\rho^2}{2(c_{11}c_{33}-c_{13}^2)}\,. \qquad (6)$$

For comparison with the experimental results B^* can be written as a function either of the Δc_{ij} [putting in (6) γ_u and γ_ρ deduced from (3)], or of the de Gennes elastic constants $A_{el}=c_{11}$, $B_{el}=c_{11}+c_{33}-2c_{13}$ and $C_{el}=c_{11}-c_{13}$:

$$B^*=B\left[1+\frac{\Delta(c_{11}c_{33}-c_{13}^2)}{c_{11}c_{33}-c_{13}^2}\right], \qquad (7a)$$

$$B^*=B\left[1+\frac{\Delta(A_{el}B_{el}-C_{el}^2)}{A_{el}B_{el}-C_{el}^2}\right], \qquad (7b)$$

Δ indicating the jump at T_c.

Experimentally the elastic constants are deduced from the velocity measurements of Fig. 1, and their jumps determined by extrapolating, at the transition temperature, the results obtained far from the transition. The specific-heat jump is given directly by Fig. 2.

From the jump of the specific heat and the variation of η^2 with the temperature,[2] Eqs. (4) and (5) give $A_0 = 1.38\times10^6$ ergs K^{-1}cm^{-3} and $B^* = 1.77\times10^8$ ergs cm^{-3}. The jump of $A_{\rm el}B_{\rm el} - C_{\rm el}^2$ and Eq. (7b) gives $B = 10B^*$. This last result is very important since it indicates the strength of the coupling of the order parameter with the strains. It also gives an explanation of the near tricritical behavior observed in most compounds exhibiting the Sm-A-Sm-C transition. Finally, from Eq. (3), the value of B determined above, and the jumps of $B_{\rm el}$ and $C_{\rm el}$, it is found that $\gamma_u = 1.65\times10^9$ ergs cm^{-3} and $\gamma_\rho = 3.34\times10^8$ ergs cm^{-3}.

The consistency of our results can be checked by calculating the jump $\Delta\alpha$ of the thermal expansion and comparing this result with the experimental data. The theoretical result is

$$\Delta\alpha = -\frac{A_0}{2B^*}\frac{\gamma_\rho B_{\rm el} - \gamma_u C_{\rm el}}{A_{\rm el}B_{\rm el} - C_{\rm el}^2} \tag{8}$$

and the calculated value is $\Delta\alpha = 0.96\times10^{-4}$ K^{-1} in excellent agreement with the value measured, 10^{-4} K^{-1}.[19]

We shall now consider the influence of the order-parameter fluctuations on the elastic constants and the specific heat above T_c. The drops δc_{ij} in the elastic constants have been calculated by Andereck and Swift.[16] In the Gaussian approximation, they are given by

$$\delta c_{11} = -\gamma_\rho^2 I_2, \tag{9a}$$

$$\delta c_{13} = -\gamma_\rho(\gamma_\rho - \gamma_u) I_2, \tag{9b}$$

$$\delta c_{33} = -(\gamma_\rho - \gamma_u)^2 I_2, \tag{9c}$$

with

$$I_2 = \frac{kT}{8\pi\sqrt{2}} m_\perp \sqrt{m_z} (A_0)^{-1/2} (T - T_c)^{-1/2}.$$

The excess specific heat at constant pressure is obtained by differentiating the free energy G_η in relation to the temperature, $\delta c_p = -T(\partial^2 G_\eta/\partial T^2)$, and is given by[20]

$$\delta c_p = \frac{kT^2}{16\pi} m_\perp \sqrt{m_z} A_0^{3/2} (T - T_c)^{-1/2}. \tag{10}$$

G_η is equal to $-kT\ln Z_G$, where the partition function is written as a functional integral $Z_G = \int \mathcal{D}_\eta e^{-G/kT}$ calculated in the Gaussian approximation, i.e., neglecting the fourth-order term.

The jumps and the contribution of the fluctuations having been determined, the critical region can now be ascertained. Inside this region, the mean-field model breaks down and cannot be used. The width of this region is calculated by writing $\Delta c_p \simeq \delta c_p$ and $\Delta c_{ij} \simeq \delta c_{ij}$.

Thus, for the specific heat[21]

$$\Delta T_c = \left(\frac{kT_c m_\perp \sqrt{m_a}}{4\pi}\right)^2 \frac{B^{*2}}{4A_0} \tag{11}$$

and for the elastic constants

$$\Delta T_c = \left(\frac{kT_c m_\perp \sqrt{m_z}}{4\pi}\right)^2 \frac{B^2}{2A_0}. \tag{12}$$

Since we have seen above that $B = 10B^*$, the width given by (12) is about 2 orders of magnitude larger than the width given by (11). More precisely, if the critical region associated with the elastic constants (or the velocities) is $\Delta T_c \sim 10$ K (see Fig. 1), the critical region associated with the specific heat is $\Delta T_c \sim 0.1$ K. This is our main result; it explains why the specific-heat measurements are consistent with a Landau model, whereas the elastic-constant measurements are not.

Equations (9c) and (10) give

$$\delta c_p = \delta c_{33} \frac{1}{\sqrt{2}} \frac{A_0^2 T_c}{(\gamma_\rho - \gamma_u)^2}. \tag{13}$$

Since δc_{33} is known from experimental results ($c_{33} = v_z^2$, where v_z represents the velocity of sound in the direction z, parallel to the director), δc_p can be estimated from Eq. (13). At $T - T_c \simeq 0.1$ K, δc_p is found to be $\simeq 10^5$ ergs K^{-1}cm^{-3}, which is $\simeq \Delta c_p/20$ (see Fig. 2).[22] In principle, this slight increase in δc_p is measurable; it has not, however, been reported by Das, Ema, and Garland[13] owing to the scatter of the experimental data.

In conclusion, we have shown that the smectic-A-smectic-C transition in TBBA is characterized by the fact that two different observables do not share the same mean-field to critical crossover temperature, contrary to what has always been implicitly supposed for phase transitions. We think that this result may close the controversy on the nature of the Sm-A-Sm-C transition. Basically, this transition is not of the Landau mean-field type. However, several possibilities may appear, according to the compound studied. In some cases, the transition may resemble a Landau mean-field–type transition with a very small critical region for all quantities measured. In other cases the critical region could be quite broad, and observable in all experiments. Finally, some compounds, like TBBA, could exhibit a critical behavior for certain observables, and a mean-field–type behavior for others.

It must be stressed that in this Letter we are not concerned with the exact nature of the critical behavior in TBBA. A detailed analysis of the ultrasonic data (sound velocities and absorption) is required, and this will be the subject of a separate publication.[23]

One final remark: The fact that the elastic constants are more sensitive to fluctuations than the specific heat seems to be a general phenomenon, as indicated by the results obtained at the ferroelectric transition in terbium molybdate;[24] this phenomenon does not, however, seem to have been recognized as such so far.

The Laboratorie de Spectrométrie et d'Imagerie Ultrasonores is a unit (No. 851) associated with the Central National de la Recherche Scientifique. We would like to thank Dr. J. C. Toledano for calling our attention to Ref. 24 and Dr. D. Guillon for having communicated to us the results of his measurements before publication.

[(a)]Permanent address: Solid State Institute and Physics Department, Technion–Israel Institute of Technology, Haifa 32000, Israel.

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[15]This method, originally proposed by Ginzburg and subsequently developed by Kadanoff *et al.* (see Ref. 14), compares the mean-field (or Landau) theory to the Gaussian model, one of the simplest models which explicitly takes fluctuations into account. Strictly speaking, this model only allows determination of the temperature range at which Gaussian fluctuations occur. By extension, this range is considered as the critical range, even though the rigorous calculation must be made using, for example, the renormalization group.

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[17]Throughout this paper it is assumed that $\rho = 1$.

[18]$\Delta\rho = -(x_1 + x_2 + x_3)$.

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[21]Formula (11) can also be written $\Delta T_c = k^2 T_c/(16\pi)^2 \times (\Delta c_p)^2 \xi_{0\perp}^4 \xi_{0\parallel}^2$. This form is similar to the one currently used in the literature.

[22]The value of δc_p is probably slightly underestimated since the value of δc_{33}, which is measured at 1.5 MHz, does not correspond to the hydrodynamic limit near T_c.

[23]For TBBA, the high-frequency damping behavior points to non-Gaussian fluctuations (see Ref. 12).

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