Anisotropy of sound anomalies near the smectic-A–hexatic-B phase transition

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Recently, anisotropic anomalies in the damping and velocity of ultrasound near the smectic-A–hexatic-B liquid-crystal phase transition have been observed. By using generalized hydrodynamics we explain this anisotropy by an anisotropic, reversible dynamical coupling between the bond-orientational order parameter and elongational flow. It turns out that only in-plane elongational flow induces (critically) bond-orientational order at the phase transition, whereas flow perpendicular to the layers is inefficient.

INTRODUCTION

Since its introduction some years ago, bond-orientational order[1] (BOO) has become an important subject of investigation. One of the few three-dimensional manifestations of this type of order is the hexatic-B liquid-crystal phase (Hex-B).[2] In Hex-B the layer structure and the orientation of the molecules are like that in the smectic-A phase (Sm-A), but in addition, the bonds (the lines between the centers of gravity of the molecules) are oriented hexagonally. In addition, there are also hexatic phases (smectic-I and -F) in which the molecules are tilted in the layers and these have been studied more recently in detail.[3,4] There is no in-plane positional order in both the smectic-A and the hexatic-B phases. Thus the Sm-A to Hex-B phase transition is a perfect candidate for studying the onset of BOO.

Very recently, Gallani *et al.*[5] reported the observation of a strong anisotropy in the ultrasound anomalies near that phase transition. Usually such anomalies occur near second-order phase transitions due to the strong order-parameter fluctuations. Since the Sm-A to Hex-B transition is only weakly first order in the compound studied, we can carry over this concept. In the following we will discuss how the order parameter couples to sound waves and which underlying physical process leads to the strong anisotropy in the anomalies.

GENERALIZED HYDRODYNAMICS

Ordinary hydrodynamics breaks down near phase transitions, since order-parameter relaxation becomes very slow due to the divergence of the susceptibility associated with the modulus of the order parameter. The common remedy in this situation is to add the order-parameter modulus (S), which describes the degree of ordering, to the list of relevant dynamical variables.[6] This kind of generalized hydrodynamics is rather successful in describing anomalies (pre- or post-critical effects) near phase transitions, which are second order or weakly first order.[7] Far away from the critical temperature (T_c) S is one of the unimportant microscopic variables not considered in ordinary hydrodynamics. The phase of the (complex) order parameter,[8] which contains the relative rotation angle describing the orientation of the bonds, is a true hydrodynamic variable below T_c.[3]

The hydrodynamic descriptions of Sm-A (Ref. 9) and Hex-B (Ref. 3) are well known and it is sufficient here to concentrate on the new effects connected with S. The dynamic equation for S reads

$$\dot{S}+\beta_1\nabla_\perp v_\perp+\beta_2\nabla_\parallel v_\parallel=-\eta\Lambda\ , \tag{1}$$

where β_1 and β_2 are two phenomenological (reactive) transport parameters characterizing the coupling of S to in-plane elongational flow and to elongational flow perpendicular to the layers, respectively, and where $\mathbf{v}$ is the velocity field. (The indices $\perp$ and $\parallel$ refer to components perpendicular and parallel to the layer normal $\hat{\mathbf{n}}^0$ respectively.) Similar reactive couplings were given before for the nematic to Sm-A phase transition[10] and the nematic-columnar transition.[11] The right-hand side of Eq. (1) describes the relaxation of S, compared to which possible additional dissipative processes have been discarded in writing down Eq. (1). Λ is the thermodynamic conjugate to S, i.e., the partial derivative of the free energy with respect to δS (δS is the deviation of S from its equilibrium value, $S_0\neq 0$ in Hex-B and $S_0=0$ in Sm-A). The damping constant η must be positive in order to guarantee positivity of entropy production. The reactive coupling terms have to be balanced by appropriate terms in the stress tensor

$$\sigma_{ij}=\cdots+[\beta_1(\delta_{ij}-n_i^0n_j^0)+\beta_2 n_i^0n_j^0]\Lambda\ , \tag{2}$$

where the dots stand for the usual hydrodynamic terms in Sm-A or Hex-B.[3,9]

To linear order in the macroscopic variables Λ is given explicitly by

$$\Lambda=\chi^{-1}(\delta S+\gamma_3\nabla_\parallel u+\gamma_4\delta\rho+\gamma_5\delta\sigma)\ . \tag{3}$$

For a second-order phase transition χ^{-1} is proportional to the prefactor of the quadratic term in the Ginzburg-

Landau free energy (but different on both sides of T_c) and vanishes at T_c. The cross susceptibilities $\gamma_{3,4,5}$ describe the static coupling to layer compression (or dilation), density, and entropy density variations. An analogous term exists for the variation of the concentration in mixtures. The special form for the cross susceptibilities has been chosen in order to ensure that S is a slow (fast) variable near (far away from) the phase transition. Its characteristic relaxation time

$$\tau \equiv \chi/\eta \tag{4}$$

is large only near T_c. The cross terms in Eq. (3) have counterparts proportional to δS in the expressions for the thermodynamic conjugate to $\nabla_{\parallel} u$, the chemical potential, and temperature variations, respectively, or explicitly

$$\begin{aligned} \Phi &= \cdots + \chi^{-1}\gamma_3 \delta S \ , \\ \delta\mu &= \cdots + \chi^{-1}\gamma_4 \delta S \ , \\ \delta T &= \cdots + \chi^{-1}\gamma_5 \delta S \ . \end{aligned} \tag{5}$$

SOUND SPECTRUM

It is now straightforward to derive the dispersion relation $\omega = \omega(k)$ for sound waves from the complete linearized hydrodynamic equations including the terms related to S discussed above. As is customary in discussing the anomalous effects near T_c we will neglect terms of order k^2 in the dispersion relation,[6] i.e., the only dissipative process kept is order-parameter relaxation in Eq. (1). A very simple expression for $\omega(k)$ is obtained by treating $\omega\tau$ as a parameter; although this gives only an implicit dispersion relation, it is rather convenient for discussing anomalous effects.[12] Our result is

$$\frac{\omega^2}{k^2} = c_A^2 + \frac{i\omega\tau}{1+i\omega\tau}\frac{1}{\rho_0\chi}\left[d_1^2 + 2d_1 d_2 - \frac{d_2^2}{i\omega\tau}\right] , \tag{6}$$

with

$$\begin{aligned} d_1 &= \beta_1 \sin^2\theta + \beta_2 \cos^2\theta \ , \\ d_2 &= \gamma_p - \gamma_3 \cos^2\theta \ . \end{aligned} \tag{7}$$

Here θ is the angle between $\hat{\mathbf{n}}^0$ and the wave vector $\mathbf{k}$, c_A is the (slightly angle-dependent) sound velocity far away from T_c [in Sm-A (Ref. 9) as well as in Hex-B (Ref. 3)] and $\gamma_p \equiv \rho_0\gamma_4 + \sigma_0\gamma_5$ is the derivative of the pressure with respect to δS. (ρ_0 and σ_0 are the equilibrium values of density and entropy density, respectively). The complex part of Eq. (6) describes the anomalies of the sound velocity, $c_1 \equiv \mathrm{Re}(\omega/k)$, and of the sound damping, $\alpha \equiv \mathrm{Im}(\omega/c_1)$, near T_c. Usually these anomalies can consist of cusplike features in the damping and (rather small) dips in the velocity—depending on the behavior of the prefactor [the large parentheses in Eq. (6)].

The very striking feature in the observation of the anomalies near the Sm-A to Hex-B phase transition by Gallani *et al.*[5] was the marked anisotropy. There was either no effect (in the velocity) or only a much weaker effect (in the damping) for $\theta = 0°$ compared to $\theta = 90°$. Obviously the susceptibility γ_p cannot explain this anisotropy, since it enters Eq. (6) isotropically. The susceptibility coupling layer compression to order parameter γ_3, contributes to the anomalies only for $\theta = 0°$, but not for $\theta = 90°$. It could, in principle, describe the observed anisotropy, if $\gamma_p = \gamma_3$. There is, however, no physical reason for such a relation and it is highly unlikely that layer compression reacts to order-parameter variations with the same strength as the pressure. Nevertheless, if accidentally such a relation holds in the specific compound used in Ref. 5, a repetition of the experiment with different compounds could clearly rule out this possibility.

Here we propose a different explanation for the anisotropy, which is quite general for that phase transition and which can be understood physically. If $\beta_1 \gg \beta_2$, the anisotropy can be explained. Although a quantitative determination of the β's from the published data is not possible, it seems that β_1 diverges at T_c, while β_2 certainly does not. The meaning of that result is clear in the present framework: An in-plane elongational flow ($\nabla_{\perp} v_{\perp}$) leads to (in-plane) BOO, and at T_c already an infinitesimal flow is enough to build up that order, while a flow perpendicular to the layers cannot lead to (in-plane) BOO. We thus propose that it is this anisotropic coupling of flow to order-parameter fluctuations that results in the anisotropy of the sound anomalies near the Sm-A to Hex-B phase transition.

Further experiments could corroborate our explanation. Since the leading term, β_1^2 comes with a $\sin^4\theta$ factor, sound under 45° should show only about one-quarter of the anisotropy shown at 90°. Another possibility for further tests are anomalies in second sound[9] near T_c. The dispersion relation for this kind of excitation near T_c is

$$\frac{\omega^2}{k^2} = \sin^2\theta\cos^2\theta\left[4c_2^2 + \frac{i\omega\tau}{1+i\omega\tau}\frac{1}{\rho_0\chi}\left[(\beta_1-\beta_2)^2 + 2\gamma_3(\beta_1-\beta_2) - \frac{\gamma_3^2}{i\omega\tau}\right]\right] , \tag{8}$$

where c_2 is the magnitude of the second sound velocity far away from T_c (Refs. 3 and 9) (at $\theta = 45°$). Here the anomalous effects should be strongest at 45°, although their ratio with the nonanomalous terms should be angle independent. If the proposed anisotropy in the β's would not be present, i.e., if $\beta_1 \approx \beta_2$, there would be no strong anomaly at all, while we predict such a strong anomaly in Eq. (8) due to the diverging $\beta_1 (\gg \beta_2)$.

CONCLUSIONS

In this communication we propose that a new mechanism, the anisotropic coupling of BOO to elongational

flow, is responsible for the anisotropy of sound anomalies near T_c. Such anisotropic anomalies can also be expected near other phase transitions, where BOO starts or increases sharply (e.g., smectic-C to smectic-I or -F phase transition). The experimental findings of such anisotropies in the latter phase transitions would give further support to our theoretical picture.

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