Ultrasonic study of the smectic-A—isotropic phase transition in p-(n-octoxy)benzylidene-p-(n-butyl)aniline

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Ultrasonic absorption has been measured in the smectic-A—isotropic phase transition region of p-(n-octoxy)benzylidene-p-(n-butyl)aniline(OOBBA) as a function of both temperature and frequency. An anomalous increase of the ultrasonic absorption has been observed at the transition temperature T_c. The critical ultrasonic absorption in the smectic-A phase has been interpreted by assuming, as for helium, that the critical fluctuations and the relaxation of the smectic order parameter both contribute to the attenuation. The excess absorption in the smectic-A phase has also been analyzed in the light of the Mazenko-Ramaswamy-Toner theory.

I. INTRODUCTION

Measurements of ultrasonic absorption and velocity are one of the best methods available for studying the dynamics of phase transitions between the various liquid-crystalline symmetries. Thus the study of ultrasonic propagation in liquid crystals has been the subject of recent research.[1,2] Most of the studies, however, are concerned primarily with the nematic-isotropic phase transition and to date only a few ultrasonic absorption results near the smectic-A—isotropic transition have been reported.[3,4] Bhattacharya *et al.*,[4] from their ultrasonic studies, have suggested a second-order-like behavior near the smectic-A—isotropic transition even though it is known to be first order from calorimetric measurements.

Recently Mazenko, Ramaswamy, and Toner[5,6] (MRT) have predicted theoretically that the dynamic properties of the smectic-A phase of liquid crystals are profoundly affected by anharmonic effects. In particular, at low frequencies the absorption coefficient α of ultrasonic waves should be proportional to the frequency f and not to f^2 as is the case in conventional hydrodynamics. Subsequently, Bhattacharya and Ketterson[7] measured the ultrasonic absorption in terephthal-bis-p-p'-butylaniline (TBBA) and confirmed the breakdown of conventional hydrodynamics in the smectic-A phase, as predicted by MRT. More recently Gallani and Martinoty[8] also have measured the ultrasonic absorption in the smectic-A phase of TBBA in the frequency range of 1 to 4 MHz, and reported that their results are consistent with the theoretical predictions of MRT.

In this paper we report the results of ultrasonic absorption measurements near the smectic-A—isotropic phase transition in p-(n-octoxy)benzylidene-p-(n-butyl)aniline (OOBBA) as a function of frequency from 2—56 MHz at 13 temperatures from 74 °C to 90 °C. The anomalous absorption observed in the smectic-A phase has been interpreted tentatively as being due to two additive contributions: (1) critical attenuation due to order-parameter fluctuations and (2) attention due to the relaxation of the order parameter itself, i.e., Landau-Khalatnikov process. A semiquantitative analysis based on MRT theory has also been given for the excess absorption in the smectic-A phase.

II. THEORETICAL

A. Attenuation due to fluctuations and order-parameter relaxation

According to de Gennes,[9] the smectic order parameter may be defined by a density wave along the direction perpendicular to the layers. The density is represented by the equation

$$\rho=\rho_0[1+\mathrm{Re}(\psi e^{i\phi})] , \tag{1}$$

where $\psi(r)=|\psi|e^{i\phi}$ is the smectic order parameter and $|\psi|$ measures the strength of the smectic order. Here the phase $\phi=q_s z$ determines the position of layers. q_s is a constant and is related to the smectic layer spacing d by

$$q_s=2\pi/d .$$

Now the critical increase of ultrasonic absorption in the vicinity of the smectic-A transition may be explained by considering two processes: (i) thermal fluctuations of the order parameter and (ii) relaxation of the order parameter itself. We now examine the two processes individually.

(i) Attenuation due to fluctuations. This mechanism is due to the interaction of the temperature variations of the wave with the thermal fluctuations of the order parameter. And this occurs both above and below the transition.

Since the fluctuations of the order parameter have a strong spatial correlation near the transition temperature, the equilibrium correlation function cannot follow the temperature variations induced by the sound wave. This relaxation effect leads to a critical increase of ultrasonic absorption via the frequency-dependent specific heat and is written as[10]

$$(\alpha/f^2)_{\delta\psi}=\frac{2\pi^2}{V}\frac{\gamma_0^{-1}}{C_p^0}\frac{\Delta C_p}{\omega_0}xf_2(x) , \tag{2}$$

where

$$\gamma_0=C_p^0/C_V^0,\quad x=\omega_0/\omega\ ,$$
$$f_2(x)=\sqrt{2x}\,[\,|x+(1+x^2)^{1/2}|^{1/2}-\sqrt{2x}\,]\ ,$$

and where C_p^0 and C_V^0 are the heat capacity at constant pressure and at constant volume, respectively, in the absence of the fluctuations, and ΔC_p is the excess specific heat due to the fluctuations. The function $f_2(x)$ provides the theoretical curve for the frequency dispersion and has been calculated by Imura and Okano.[11] In Eq. (2) ω_0 is the relaxation frequency of the longest-wavelength mode of the correlation function.

(ii) Attenuation due to order-parameter relaxation. This mechanism assumes that the magnitude of the order parameter ψ_0 is disturbed from its equilibrium value by the sound wave and then relaxes in a finite time τ_R to a local equilibrium value determined by the temperature and the pressure. Near the transition ψ_0 cannot follow the pressure variations induced by the sound wave and this leads to an anomalous increase of absorption, as predicted for superfluid helium by Landau and Khalatnikov. In contrast to the contribution from the fluctuations, this effect occurs only in the ordered phase, where the magnitude of the order parameter is not zero.

The sound absorption due to this internal relaxation may be expressed as

$$(\alpha/f^2)_\psi=\frac{A}{[1+(f/f_r)^2]}\ , \tag{3}$$

where A is related to the relaxation strength and f_r is the relaxation frequency for the Landau-Khalatnikov process. In Eqs. (2) and (3), $(\alpha/f^2)_{\delta\psi}$ and $(\alpha/f^2)_\psi$ represent the parts associated with the fluctuations of the order parameter and the relaxation of the order parameter.

B. Attenuation due to anharmonic terms—MRT model

Recently, MRT have investigated the influence of anharmonic terms in the free energy for the smectic-A phase on the viscous properties of the smectic-A phase and have demonstrated that certain viscosities diverge as $1/\omega$ at small frequencies. This leads to an additional damping on the first sound. Hence, according to MRT, in the hydrodynamic regime, i.e., when the measurement frequency is lower than all the relaxation frequencies of the system, the total attenuation in the smectic-A phase can be written as

$$\alpha/f^2=a+b/f\ , \tag{4}$$

where a and b are anisotropic and are given by

$$a=(2\pi^2/\rho V^3)[(\eta_2+\eta_4)\sin^2\theta+\eta_1\cos^2\theta+(4\eta_3+2\eta_5-\eta_2-\eta_4-\eta_1)\cos^2\theta\sin^2\theta]\ , \tag{5}$$
$$b/f=-2\pi\{[A\delta\eta_1+2(C-A)\delta\eta_5+(B+A-2C)\delta\eta_4]\cos^2\theta\sin^2\theta$$
$$-V_1^2(\theta)(\delta\eta_4\sin^2\theta+\delta\eta_1\cos^2\theta)\}/2V_1^3(\theta)[V_1^2(\theta)-V_2^2(\theta)]\ , \tag{6}$$

in which

$$V_1^2(\theta)=(A-2C\cos^2\theta+B\cos^4\theta)/\rho\ ,$$
$$V_2^2(\theta)=(B\sin^2\theta\cos^2\theta)/\rho\ ,$$

where V_1 and V_2 are the velocities of first and second sound, respectively.

$$\delta\eta_1=(C-B)^2I(q,\omega),\quad \delta\eta_4=C^2I(q,\omega)\ ,$$
$$\delta\eta_5=C(C-B)I(q,\omega)\ ,$$

where

$$I(q,\omega)=[kT\rho_0/64(BK_1^3)^{1/2}]\omega^{-1}$$

and $\omega=2\pi f$. In Eqs. (5) and (6), η_i correspond to the different coefficients of friction and A, B, and C to the elastic constants. Therefore, from Eq. (4), α/f^2 is constant in the absence of anharmonic effects and must diverge as $1/f$ when they are present.

III. EXPERIMENTAL

The ultrasonic absorption has been measured using the conventional pulse technique in the frequency range of 2 to 56 MHz. The OOBBA sample was obtained from Dynamic Research Chemicals and has the following transition temperatures:

$$\text{smectic-}B \xleftrightarrow{65\,^\circ\text{C}} \text{smectic-}C \xleftrightarrow{69.5\,^\circ\text{C}} \text{smectic-}A \xleftrightarrow{80\,^\circ\text{C}} \text{isotropic}$$

The temperature of the sample is controlled to within $\pm 0.1\,^\circ$C using a thermostat. The accuracy of absorption measurements is better than $\pm 3\%$.

IV. RESULTS AND DISCUSSION

The temperature dependence of the ultrasonic absorption (α/f^2) of OOBBA at several frequencies is shown in Fig. 1. At lower frequencies, the absorption coefficient increases prominently as the temperature approaches T_c. However, at 56 MHz the attenuation is almost independent of temperature and does not exhibit any anomalous increase at the transition. This behavior is in accordance with that of other liquid crystals.

Further, it can be observed from Fig. 1 that in the low-frequency region the absorption coefficient of the

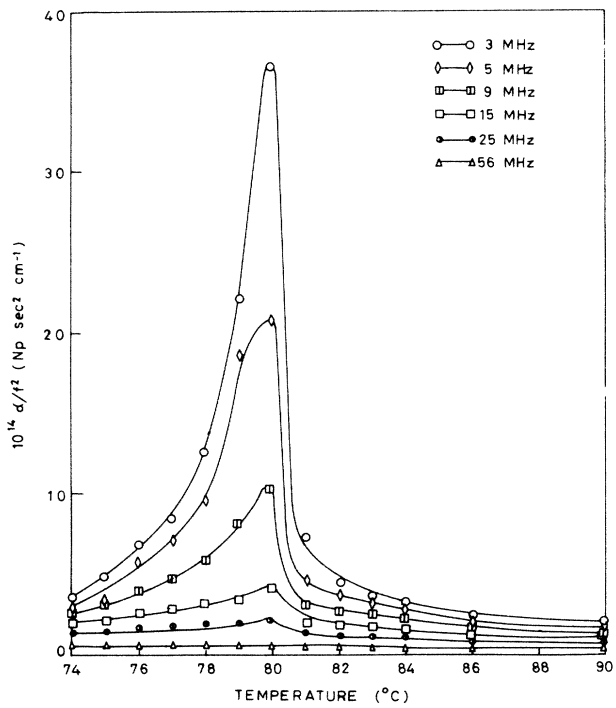

FIG. 1. Temperature variation of ultrasonic absorption α/f^2 in the smectic-A and isotropic phases of OOBBA.

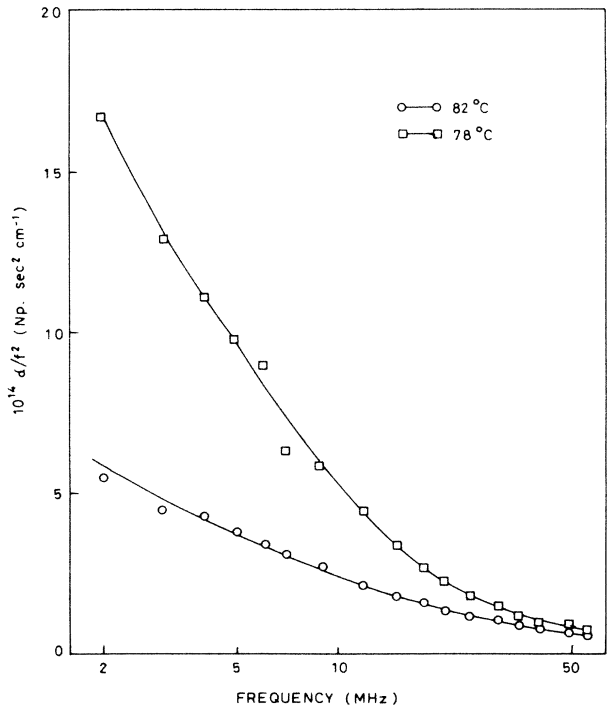

FIG. 2. Frequency dispersion of ultrasonic absorption α/f^2 in the smectic-A and isotropic phases of OOBBA.

smectic-A phase increases considerably as the frequency decreases. Similar behavior was reported earlier in the smectic phase of TBBA by Bhattacharya and Ketterson. They interpreted this increase in α/f^2, which was consistent with $(1/f)$-type behavior, based on the MRT model.

From Fig. 1 it is also apparent that the attenuation at a given frequency is asymmetric about the transition point, suggesting the existence of an additional contribution to the absorption in the smectic-A phase. Figure 2 shows the frequency dispersion of the ultrasonic absorption at $T=78\,^{\circ}\mathrm{C}$ and $82\,^{\circ}\mathrm{C}$. It is immediately apparent that the behavior of α/f^2 below T_c is different from that above the transition. This fact also reflects the existence of additional relaxation in the smectic-A phase over that in the isotropic phase.

To explain the anomalous absorption in the smectic-A phase, in the first stage, we have assumed as for helium, that there are two causes of absorption: critical fluctuations and the relaxation of the smectic order parameter itself, i.e., the Landau-Khalatnikov mechanism.

Here, we assume that the attenuation due to order-parameter fluctuations is roughly symmetrical about T_c and attenuation due to relaxation of the order parameter occurs only below T_c. According to the Landau-Khalatnikov mechanism, the relaxation frequency of the order parameter should have a linear temperature dependence.

The standard procedure for estimating the order-parameter relaxation is to subtract, from the total absorption below T_c, a part of the attenuation above T_c, which corresponds to fluctuations, and analyze the remaining absorption using Eq. (3). As for helium[12] and N-(*p*-cyano)benzylidine-*p*-(*n*-octyloxy)aniline (CBOOA) (Ref. 10), we have subtracted all the attenuation in the isotropic phase from that in the ordered phase at the same value of $\Delta T=(T-T_c)$. By fitting the resulting data to the single relaxation Eq. (3), the relaxation frequency f_r of the Landau-Khalatnikov process has been calculated. The relaxation frequency thus obtained is found to have linear temperature dependence over the range $1\,^{\circ}\mathrm{C}<\Delta T<5\,^{\circ}\mathrm{C}$. However, this subtraction procedure is suspect in that the exact quantity that should be subtracted from the absorption above T_c is not known *a priori*.

As a next step we have analyzed the data for double relaxation using the modified least-squares method developed by Ito *et al.*[13] The second relaxation frequency so obtained is found to be in close agreement with the estimate from the subtraction procedure. The temperature dependence of the two relaxation frequencies is shown in Fig. 3. From the figure it can be seen that f_r of the order-parameter relaxation varies linearly with temperature, in accordance with the Landau-Khalatnikov mechanism.

The ultrasonic absorption data in the isotropic region has been forced to fit the single relaxation equation by the modified least-squares method.[13] The relaxation frequency of the smectic-A phase and its variation with temperature is also presented in Fig. 3.

From the above studies, it may be concluded that the present two-relaxation-process model qualitatively accounts for the critical ultrasonic absorption in the smectic-A phase, at least for this substance.

We next try a semiquantitative comparison of the low-frequency part of the absorption spectra with the model proposed by MRT. To compare the experimental results

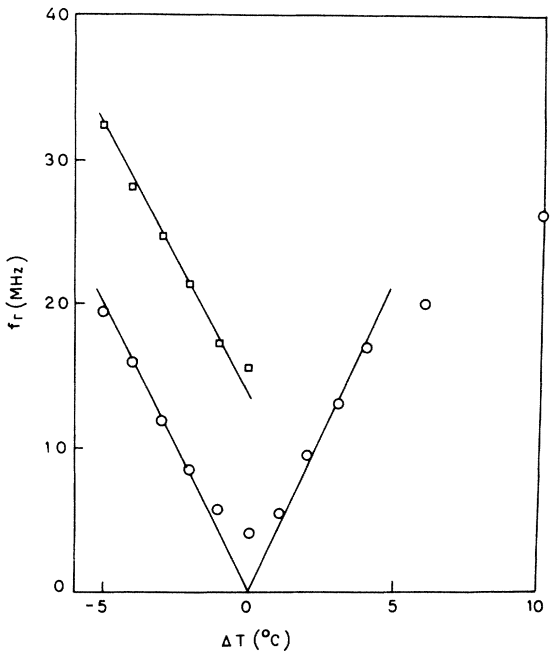

FIG. 3. Temperature dependence of f_r for the two processes.

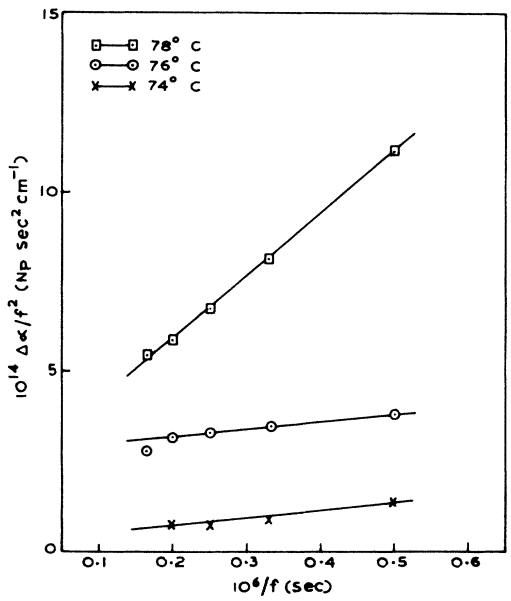

FIG. 4. Frequency dependence of the absorption $\Delta\alpha/f^2$ in the smectic-A phase.

with the predictions of MRT, we plot $\Delta\alpha/f^2$ versus $1/f$ as shown in Fig. 4. In agreement with the theory, $\Delta\alpha/f^2$ varies linearly with $1/f$. Here, $\Delta\alpha/f^2$ is the attenuation in the smectic-A phase relative to that in the isotropic phase. Thus it appears that the absorption in the low-frequency region can be interpreted based on the MRT model. In the present study the other predictions of the MRT theory, viz., the angular variation of the abnormal part of the damping and the relationship of the damping increments could not be verified as the measurements are confined to the unoriented bulk sample only.

Therefore, from the present study, one cannot conclude in favor of one specific model without performing measurements in magnetically oriented samples over a wide range of frequencies and particularly at low frequencies.

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