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Ultrasound absorption anisotropy in the vicinity of smectic A–nematic transition

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The results of a low frequency ultrasonic study of 4-*n*-butyloxybenzylidene-4′-*n*-butylaniline (BBBA) in the vicinity of the smectic A–nematic transition are presented. The frequency and temperature dependence of the parameters describing the anisotropic ultrasound absorption are determined experimentally and compared with the predictions of fluctuation and relaxation theories of the smectic A–nematic transition. It is shown that no single theory could explain all of the experimental data.

1. Introduction

In recent years, the smectic A–nematic transition has been studied extensively both experimentally and theoretically. However, it is not clear if the proposed theories properly describe the static and dynamic behaviour of the mesogens in the vicinity of this phase transition. A great deal of theoretical work has been devoted to the study of the nature of the smectic A–nematic transition [1] and there is a wealth of experimental evidence showing it to be close to the second order phase transition. The dynamic properties of the smetic A–nematic transition have been less well investigated when compared to the static behaviour. The most recent theories often do not predict the behaviour of the dynamic parameters. Indeed even when these parameters are predicted by theory [2] there is often insufficient experimental data with which to make comparisons.

Acoustic spectroscopy is an important technique in the study of the dynamic properties of phase transitions. Frequency and wavelength changes provide fluctuation-time spectra of non-uniformities characteristic of a phase transition. However, there are difficulties in interpreting the acoustical parameter anomalies close to T_{S_AN}. This is due to the fact, that most experiments are conducted in an average frequency range (> 1 MHz), while the temperature and frequency dependencies of the acoustical parameters are obtained in the high- or low-frequency limit. Moreover, there are relaxation processes which are independent of the smectic order parameter fluctuations. In consequence, acoustic investigations of smectic A–nematic transition in a wide frequency range, that provide an experimental approach to the low and high frequency limits are most important. There are only a few such experimental studies [3–5], and as a rule, they do not deal with the ultrasonic absorption coefficient anisotropy ($\Delta\alpha$), or the parameters defining their orientation dependence, although these parameters contain the additional information on the dynamic processes near T_{S_AN}.

In this paper the experimentally determined ultrasonic absorption coefficient anisotropy in the frequency range 0·15–15 MHz is presented, it is compared with theoretical predictions of the acoustical parameters.

2. Theoretical predictions

The pecularities of ultrasound absorption coefficient anisotropy close to T_{S_AN} can be considered in the framework of two theoretical approaches. In the first [6] the observed anomalies are connected with the critical increase due to fluctuations of volume ($\nu_4\nu_5$) and shear (ν_1) viscosities included in the expressions for the dependence of the absorption coefficient anisotropy on the angle (θ) between the wavevector and the director [7]:

$$\frac{\Delta\alpha(\theta)}{f^2} = \frac{\alpha(\theta) - \alpha(90°)}{f^2},$$

$$= \frac{2\pi^2}{\varrho c_0^3}[a\cos^2\theta + b\cos^4\theta], \tag{1}$$

where

$$a = 2(-\nu_2 + 2\nu_3 + \nu_5 - \nu_4), \quad \text{and } b = 2(\nu_1 + \nu_2 - 2\nu_3), \quad \nu_2, \nu_3$$

the shear viscosity coefficients that do not diverge near T_{S_AN}, ϱ is the density and c_0 is the ultrasound velocity when $\omega = 2\pi f$ tends to zero.

From equation (1) it follows that the divergence of b is due to the divergence of the shear viscosity coefficients ν_1 alone, while a includes the critical contributions only of the difference between the volume viscosity coefficients. The behaviour of the total anisotropy of the ultrasound absorption coefficient near T_{S_AN}

$$\frac{\Delta\alpha}{f^2} = \frac{\alpha(0°) - \alpha(90°)}{f^2}$$

is defined by the combined influence of ν_1 and $\nu_5 - \nu_4$. Note, that the isotropic contribution to the critical increase of the volume viscosity coefficients, described in [1, 8], does not affect the parameters under discussion.

In the low frequency case ($\omega\tau \ll 1$), where τ is the characteristic relaxation time for the smectic order fluctuations, the critical contributions ($\tilde{\nu}_1$, $\tilde{\nu}_4$, $\tilde{\nu}_5$) to the coefficients ν_1, ν_4, ν_5 are frequency independent, and their dependence on $\Delta T_s/T = (T - T_{S_AN})/T$ are described by the power law with the index equal to $-1/3$ or $-1/2$, analogous to the λ-transition in helium [9] or in the mean field theory [10], respectively. In the high frequency case ($\omega\tau \gg 1$) $\tilde{\nu}_1$ does not depend on ΔT_s and changes with frequency, as $\tilde{\nu}_1 \sim \omega^{-1/3}$ (analogous to helium), or $\sim\omega^{-1/2}$ (mean field). The behaviour of the difference $\nu_5 - \nu_4$ in the case $\omega\tau \gg 1$ has not been considered with in the framework of fluctuation theory.

Another approach [2] constitutes associating the anomalies in the acoustic parameters near T_{S_AN} with relaxation of the smectic order (the Landau–Khalatnikoff mechanism). The difference of this mechanism from helium is that it takes place as well at the temperatures higher than the phase transition. This follows from conservation of uniaxial symmetry at the smectic A–nematic transition. In the framework of this approach an expression analogous to equation (1) for the ultrasound absorption

coefficient anisotropy can be obtained. The coefficients a and b are

$$a = \frac{1}{\eta}\frac{1}{1+\omega^2\tau^2}2\beta_\perp\Delta\beta, \tag{2}$$

and

$$b = \frac{1}{\eta}\frac{1}{1+\omega^2\tau^2}(\Delta\beta)^2, \tag{3}$$

where $\beta_\parallel$ and $\beta_\perp$ are dimensionless parameters, which characterize the dynamic connection of the smectic order with the hydrodynamic variables, $\Delta\beta = \beta_\parallel - \beta_\perp$ and η is the kinetic coefficient with the dimension of an inverse viscosity. In the low frequency case, from equation (3) it follows that the coefficients of $\cos^2\theta$ and $\cos^4\theta$, as well as the total anisotropy $\Delta\alpha/f^2$ are frequency independent. The temperature dependence of the parameters are defined by the combinations $2\beta_\perp\Delta\beta/\eta$ and $(\Delta\beta)^2/\eta$. When $\omega\tau \gg 1$, the values of a, b and $\Delta\alpha/f^2$ decrease as the square of the frequency, and their temperature dependence are defined by these combinations and the relaxation time, τ.

3. Experimental

The experimental set-up allows us to obtain the phase-time and temperature-frequency dependence of the absorption coefficient in liquid crystals under the action of a magnetic field with strength of 0·29 T whose orientation can be changed. We studied 4-*n*-butyloxybenzylidene-4′-*n*-butylaniline (T_C = 346·4 K, T_{S_AN} = 317·5 K).

The measuring cell is an acoustic resonator composed of a pair of quartz plates of a particular shape [11] (see figure 1).

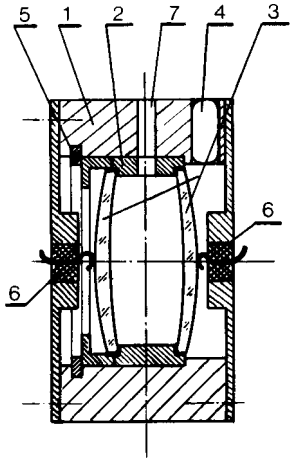

Figure 1. Measuring cell. 1, duralumin casing; 2, stainless steel ring; 3, quartz transducers; 4, quartz thermometer; 5, fixing nut; 6, contact electrodes; 7, filling hole.

The concave-convex shape of the quartz gauges, proposed by Kononenko, reduces diffractional losses in the resonator, as it concentrates the standing wave to the symmetry axis of the system. It allows the measurements at frequencies higher than 0·15 MHz, with a sample volume of 4 ml. Such a volume and the diameters of

the quartz gauges of about 30 mm lead to an initial Q-factor of the resonator (i.e. filled with a liquid with negligibly small attenuation e.g. ethanol) of about 1000 at 0·15 MHz and $10^4 - 2 \times 10^4$ in the range 0·27. . .2 MHz.

The ultrasound absorption coefficient α/f^2 was determined by measuring the Q-factor of the resonator in the frequency range 0·15–2 MHz. Then the amplitude changes of the signal passing through the resonator due to reorientation of the wavevector with respect to magnetic field direction at the frequenccy of one of the resonances were recorded. The data were recorded, with a step equal to 10° during two rotations, by means of a digital voltmeter and input directly to the internal memory of a microcomputer, where it was further processed. The dependence of the absorption coefficient, α/f^2, on the angle θ' between the wavevector and magnetic field direction was written approximately as

$$\frac{\alpha(\theta')}{f^2} = [d + a\cos^2(\theta + \varphi_0) + b\cos^4(\theta + \varphi_0)]\frac{2\pi^2}{\varrho c_0^3}, \quad \theta' = \theta + \varphi_0, \quad (4)$$

where φ_0 is the angle between the director and magnetic field direction. The unknown values of a, b, d, φ_0 were obtained by a least squares method.

The error in the measurement of α/f^2 does not exceed 5 per cent. The mean-square deviations of the approximation of equation (4) and the experimental values were 0·5–2 per cent. The errors in the calculation of parameters a, b, d, φ_0 evaluated by their variations on the deviation of the objective function (mean square deviation) from its minimum, were about 1–2 per cent, that is a part of error due to the incorrectness of the approximation. The temperature of the sample was stabilized to about $\pm 0{\cdot}01$ K.

The measurements of the ultrasound absorption coefficient anisotropy in the frequency range 3–15 MHz were produced by the modified pulse-phase method, described in [12]. The resolution of the experimental set-up was 1×10^{-14} s^{2}m^{-1}.

4. Results and discussion

We begin the discussion with the b coefficient, as there are asymptotic expressions for this both in the high and low frequency limits within the theoretical approaches. The frequency dependence of b for different ΔT_s are shown in figure 2. Far from

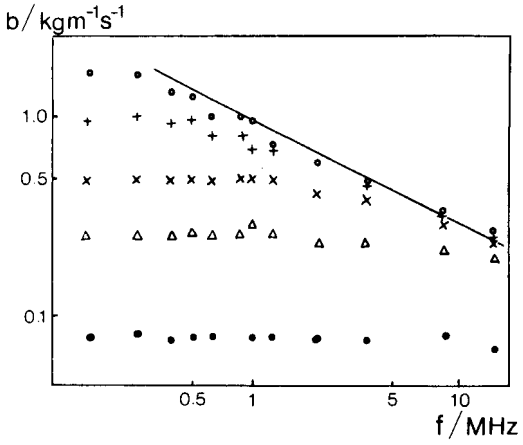

Figure 2. Frequency dependence of b at different ΔT_s: (●, 9·0 K; △, 1·8 K; ×, 0·50 K; +, 0·20 K; ○, 0·10 K).

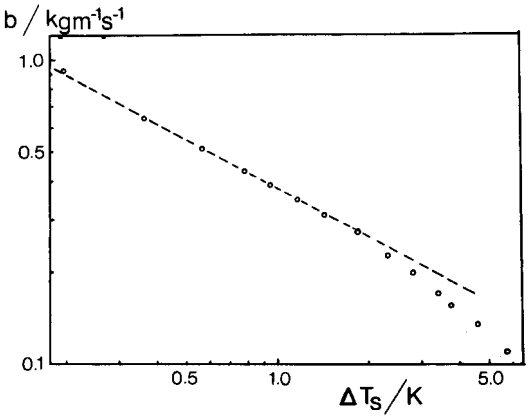

Figure 3. Temperature dependence of low frequency limit of b.

T_{S_AN} the b coefficient is frequency independent. The observed behaviour $b(f)$ in the vicinity of T_{S_AN} is in agreement with fluctuation theory predictions. (The asymptote with an index of $-1/2$ for the case $\omega\tau \gg 1$ is shown by the solid line.) Note, that in the same case the relaxation mechanism [2] predicts a much stronger dependence $b(f)$. The frequency independence of b in the low frequency region, may justify the limit $\omega\tau \ll 1$. In figure 3 the dependence in the low frequency limit on ΔT_s is shown. In the vicinity of T_{S_AN} the increase of b is in agreement with the power law $(\Delta T_s/T)^{-1/2}$, which follows from the low frequency limit of fluctuation theory. When $\Delta T_s \gtrsim 1{\cdot}5\,\mathrm{K}$ the divergence index changes; this may be due to the influence of the relaxation process [2] taking into account the possibility of a strong dependence of $(\Delta\beta)^2/\eta$ on ΔT_s [13]. It is worth noticing, that when $\Delta T_s < 1{\cdot}5\,\mathrm{K}$ the non-critical contribution to the value of b does not exceed 10 per cent and does not affect the conclusions.

The behaviour of the a coefficient is much more complicated as can be seen from its frequency dependence for different ΔT_s, shown in figure 4. The peculiarity of the

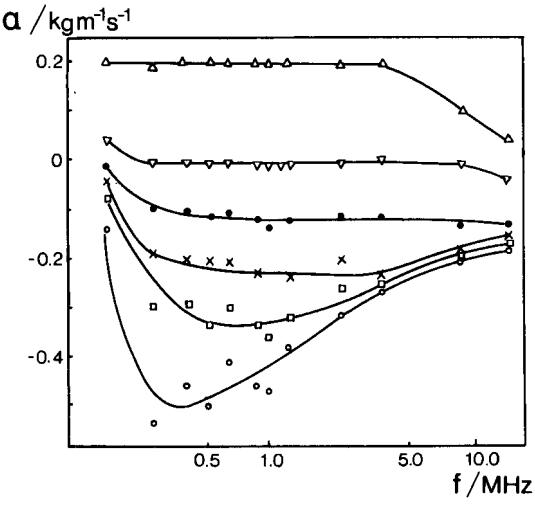

Figure 4. Frequency dependence of a at different ΔT_s: (△, 25·0 K; ▽, 3·8 K; ●, 0·96 K; x, 0·37 K; □, 0·20 K; ○, 0·10 K).

behaviour is the negative value of a close to T_{S_AN}. This observation cannot be explained in the framework of the fluctuation theory, where $\tilde{\nu}_5 - \tilde{\nu}_4 > 0$ [6].

The relaxation mechanism can lead to a negative sign for a, when $\Delta\beta < 0$. The last proposal is confirmed by the results of an ultrasound velocity anisotropy investigation in 4-nitrophenyl-4′-octyloxybenzoate [13]. However, the observed minimum of $a(f)$ dependence cannot be explained exclusively within the framework of relaxation theory (see figure 4). The a value appears to be determined by two processes with different signs. To separate the contributions in this particular work is rather difficult, as there is no explicit form for the frequency dependence of $(\tilde{\nu}_5 - \tilde{\nu}_4)$. The comparison of the frequency dependences of the coefficients a and b suggests a difference between the frequency dependences of the fluctuation contribution to the shear viscosity coefficient $\tilde{\nu}_1$ and to $(\tilde{\nu}_5 - \tilde{\nu}_4)$. Also, note, that different influences of relaxation on a an b values can be connected with different values of $\beta_\perp$ and $\Delta\beta$. The complex behaviour of a in the vicinity of T_{S_AN} is confirmed by the temperature dependence curve, shown in figure 5.

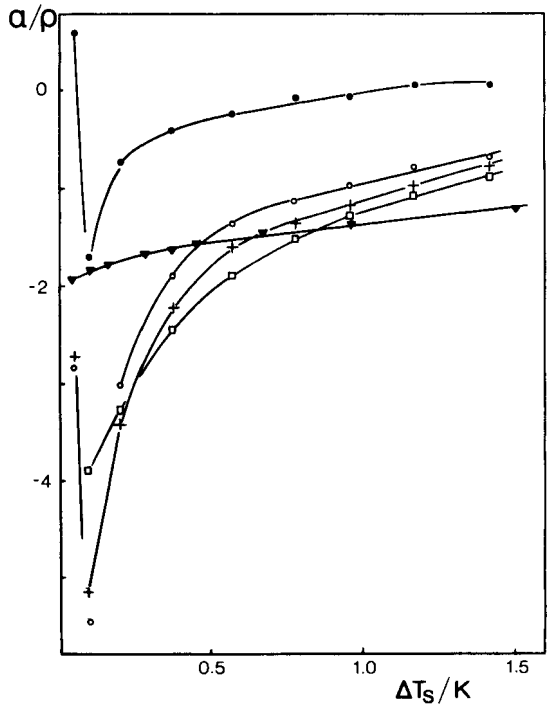

Figure 5. Temperature dependence of a at different frequencies: (●, 0·15 MHz; ○, 0·27 MHz; +, 0·51 MHz; □, 1·25 MHz; ▼, 15·0 MHz).

The analysis of the total anisotropy $\Delta\alpha/f^2$, defined by the sum of the coefficients a and b, according to equation (1) is a more complicated task. The frequency dependence of $\Delta\alpha/f^2$ (see figure 6) also justifies the low frequency process that contributes to the volume viscosities difference. We should emphasize that the values of $\Delta\alpha/f^2$ were calculated independently of the parameters a and b.

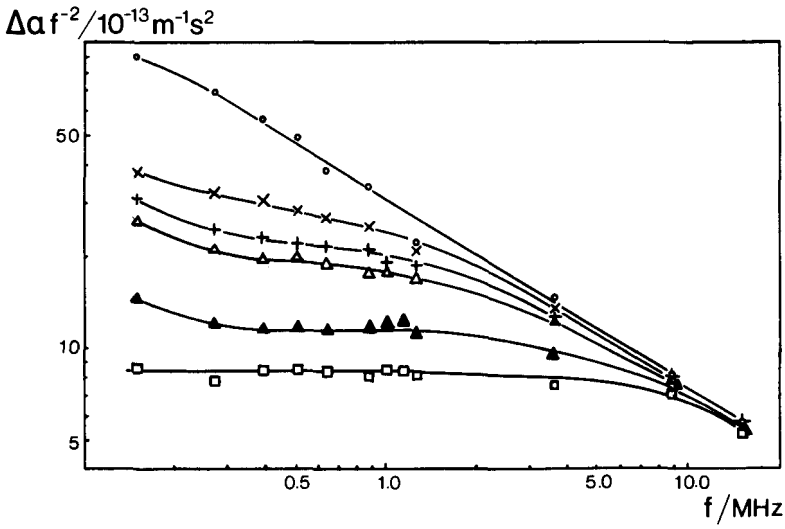

Figure 6. Frequency dependence of the total absorption anisotropy $\Delta\alpha/f^2$ at different ΔT_s: (□, 6·5 K; ▲, 2·3 K; △, 0·78 K; +, 0·57 K; x, 0·37 K; ○, 0·10 K).

5. Conclusion

In conclusion we note that our results lead to a number of theoretical and experimental questions. The first is the necessity of widening the frequency range, particularly in the low frequency interval (less than 100 kHz), that is an experimental problem. The experimental prediction of the achievement of low frequency limit ($\omega\tau \ll 1$) requires additional confirmation for every parameter under investigation. Otherwise there exists the possibility of false interpretation of the acoustical measurements. Secondly, there is the necessity of further modification to the theory to provide an explicit form for the frequency and temperature dependence of the anisotropic acoustical characteristics near the smectic A–nematic transition. Finally we note that the latest theories which we do not quote in this article, can be useful to understand the experimental data as soon as they deal with the acoustical properties of smectic A–nematic transition.

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