Anisotropic nature of the velocity of ultrasound in the vicinity of the nematic-smectic-*A* phase transition

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The experimental results of anisotropic propagation of ultrasound in the vicinity of the nematic-smectic-*A* phase transition are analyzed within the framework of the Landau-Khalatnikov theory and the fluctuation theory. It is shown that the experimentally observed features of the temperature and angular dependences of the ultrasound velocity anisotropy are in qualitative agreement with the predictions of the theory.

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INTRODUCTION

Increased attention has recently been given to experimental and theoretical investigations of the nematic-smectic-*A* phase transition ($N-S_A$). The closeness of this phase transition to second-order phase transitions allows us to exploit for their description previously developed concepts concerning the λ transition in helium. In addition, there is a basis for assuming that the uniaxial symmetry inherent in the nematic and smectic-*A* phases brings on the appearance of specific features of the dynamics of the $N-S_A$ phase transition that exert, in particular, an effect on the process of the propagation of ultrasound of finite frequency. Results are given below of a comparison of existing theoretical ideas on the features of the propagation of acoustic waves in the vicinity of the $N-S_A$ phase transition with the first obtained experimental data on the anisotropic character of the ultrasound velocity in the indicated region.

The anisotropic propagation of ultrasound in the vicinity of the temperature of the $N-S_A$ phase transition (T_{NA}) has been considered in theoretical papers[1-3] from the viewpoint of two different mechanisms. The first, which is connected with the correlated fluctuations of the smectic order parameter (ψ) and is analogous to the corresponding mechanism in the vicinity of the λ transition in He^4, leads in the temperature region $T>T_{NA}$ to the following expression for the ultrasound velocity:[2]

$$c^2=c_0^2-\delta c_i^2(\omega)+\rho^{-1}\omega\,\mathrm{Im}\,\Phi(\omega)\cos^4\theta, \tag{1}$$

where $c_0=(\partial p/\partial\rho)^{1/2}$ is the value of the ultrasound velocity in the hydrodynamic region without account of fluctuations, p is the pressure, ρ is the density, δc_i^2 is the isotropic fluctuation contribution, which depends on the ultrasound frequency ω, $\Phi(\omega)$ is a function which takes into account the connection of the fluctuations of the order parameter with the density, and θ is the angle between the wave vector and the director.

For the low frequency limit ($\omega\tau\ll 1$, where τ is the characteristic relaxation time of fluctuations of the order parameter ψ), the expression (1) with account of the explicit form of the function $\Phi(\omega)$ allows us to obtain the following dependence of the relative change in the ultrasound velocity $\Delta c(\theta)/c_\perp$ on the angle of orientation:

$$\left[\frac{\Delta c(\theta)}{c_\perp}\right]_F=\left[\frac{c(\theta)-c_\perp}{c_\perp}\right]_F=\frac{1}{2\rho c_\perp^2}A\omega^2\left(\frac{\Delta T_{NA}}{T_{NA}}\right)^\beta\cos^4\theta, \tag{2}$$

where $c_\perp$ is the ultrasound velocity at $\theta=90°$, A is a coefficient that depends weakly on the temperature and frequency, $\Delta T_{NA}=T-T_{NA}$, and β is an exponent that is equal to $-4/3$ and $-3/2$ in the similarity theory and in the mean-field theory, respectively. The relation (2) and the expressions that follow below were obtained under the assumption $\Delta c(\theta)\ll c_\perp$. The index F denotes the fluctuation contribution.

For the high frequency limit $\omega\tau\gg 1$, the quantity $\Delta c(\theta)/c_\perp$ has the form

$$\left[\frac{\Delta c(\theta)}{c_\perp}\right]_F=\frac{1}{(2\rho c_\perp^2)}B\omega^{7/3}\cos^4\theta, \tag{3}$$

where B is a coefficient that depends weakly on the temperature and the frequency.

The second mechanism (the Landau-Khalatnikov mechanism)[3] is connected with the relaxation of the smectic order parameter. In contrast to the λ transition in helium, this mechanism shows an effect on the propagation of ultrasound waves of finite frequency and at a temperature that is greater than T_{NA}, which is a consequence of the conservation of uniaxial symmetry in the $N-S_A$ phase transition. It follows from the considered mechanism, in particular, that there exist two acoustic modes ("first" and "second" sound), the propagation velocities of which c and c^* are described at $T>T_{NA}$ by the expressions

$$c^2=c_0^2+\frac{\omega^2\tau}{\eta\rho(1+\omega^2\tau^2)}[\beta_\parallel\cos^2\theta+\beta_\perp\sin^2\theta]^2, \tag{4}$$

$$c_*^2=\frac{\omega^2\tau}{\eta\rho(1+\omega^2\tau^2)}(\beta_\parallel-\beta_\perp)^2\cos^2\theta\sin^2\theta, \tag{5}$$

where η is a kinetic coefficient which has a dimensionality reciprocal to those of viscosity, $\beta_\parallel$ and $\beta_\perp$ are dimensionless material coefficients characterizing the dynamical connection of the order parameter with the hydrodynamic variables. We note that numerical values of the coefficients $\beta_\parallel$ and $\beta_\perp$ and also their temperature dependences have not been established at the present time. The expression (4) allows us to obtain the relative change in the ultrasound velocity $[\Delta c(\theta)/c_\perp]_R$ which is connected with the relaxation of ψ:

$$\left[\frac{\Delta c(\theta)}{c_\perp}\right]_R=\frac{1}{2c^2\eta\rho}\frac{\omega^2\tau}{1+\omega^2\tau^2}[2\beta_\perp\Delta\beta\cos^2\theta+(\Delta\beta)^2\cos^4\theta]. \tag{6}$$

Here $\Delta\beta=\beta_{\parallel}-\beta_{\perp}$. The temperature changes of the quantity $[\Delta c(\theta)/c_{\perp}]_R$ are defined in implicit fashion, with accuracy to within the dependence $\beta_{\parallel,\perp}(T)$, in terms of the time τ, which diverges according to a power law upon approach to T_{NA}:

$$\tau=\tau_0(\Delta T_{NA}/T_{NA})^{-1}. \tag{7}$$

In this case, it follows from the relation (6) that at $\omega\tau \ll 1$,

$$\left[\frac{\Delta c(\theta)}{c_{\perp}}\right]_R\sim\omega^2\left(\frac{\Delta T_{NA}}{T_{NA}}\right)^{-1}, \tag{8}$$

and at $\omega\tau\gg 1$,

$$\left[\frac{\Delta c(\theta)}{c_{\perp}}\right]_R\sim\left(\frac{\Delta T_{NA}}{T_{NA}}\right). \tag{9}$$

We note that the applicability of the theory considered above is limited by the temperature range in which the Landau expansion in powers of ψ is valid.[4]

EXPERIMENT

In the present work, results are given of the measurement of the anisotropy of the ultrasonic velocity in the vicinity of the phase transition $N-S_A$ in butoxybenzylidene-butylaniline (BBBA). There is reason to assume that the phase transition in this material is close to a second order phase transition. In correspondence with the existing theoretical representations,[5] a decrease in the length of the terminal molecular chains in compounds forming liquid-crystal phases leads to a change in the form of the phase transition $N-S_A$ from first to second order, and also to a decrease in the ratio $r=T_{NA}/T_{NI}$ (T_{NI} is the temperature of the phase transition from a nematic to an isotropic liquid).

These regularities are confirmed by investigations of the mesophases in homologous series.[6] In BBBA the parameter r amounts to 0.920, which is less than the value $r=0.932$ in cyanobenzylidene-octyloxyaniline (CBOOA), in which the $N-S_A$ phase transition is assumed to be of second order for a number of reasons.[7] In connection with what was said above, effects connected with the deviation of the real phase transition from the classical second-order phase transition are not taken into account[8] (in particular, the possible difference between T_{NA} and the temperature corresponding to the divergence of a number of physical parameters).

TABLE I.

	15 MHz			3 MHz
T, °C	64.9	48.7	43.6	43.8
$a\cdot10^4$	8.6	0.9	−14.7	−8.2
$b\cdot10^4$	−0.1	7.1	30.0	14.9

The investigations were carried out in the regime of cooling of the sample in a magnetic field having an induction 0.3 T. The temperature T_{NA}, which was determined by an optical method, amounted to 43.5°C and was equal within 0.1° to the temperature at which reorientation of the magnetic field with respect to the wave vector ceases to produce changes in the acoustic parameters. The measurements were made at frequencies of 3 and 15 MHz by an pulse-phase method at variable frequency, based on interference of the continuous sinusoidal signal with a radio pulse is coherent with it and passing through the investigated medium. The error in measurement of $\Delta c/c_{\perp}$ amounted to 0.3×10^{-4}.

Figure 1 shows the angular dependence of the relative change in the ultrasonic velocity at various temperatures at the frequency 15 MHz. As the temperature T_{NA} is approached, the form of the angular dependence changes materially, as reflected in the appearance of a minimum in the value of $\theta<90°$ (curve 3). This singularity also occurs at the frequency of 3 MHz, as illustrated by curve 4. The curves shown in Fig. 1 were obtained as a result of a least-squares approximation of the experimental data to a relation of the form

$$\Delta c(\theta)/c_{\perp}=a\cos^2\theta+b\cos^4\theta. \tag{10}$$

The values of the coefficients a and b are given in the Table I. The coefficient a decreases with decrease in the temperature, changing sign in the neighborhood of T_{NA}; in particular, at $T=64.9$ °C the value of the coefficients b is equal to zero within the limits of error and, consequently, the angular dependence is described by a function of the form

$$\Delta c(\theta)/c_{\perp}=a\cos^2\theta \tag{11}$$

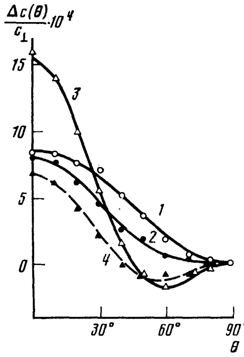

FIG. 1. Angular dependence of the quantity $\Delta c(\theta)/c_{\perp}$ at ultrasound frequencies 15 MHz (curves 1–3) and 3 MHz (curve 4) and at different T (in degrees C): 1—64.9, 2—48.7, 3—43.6, 4—43.8.

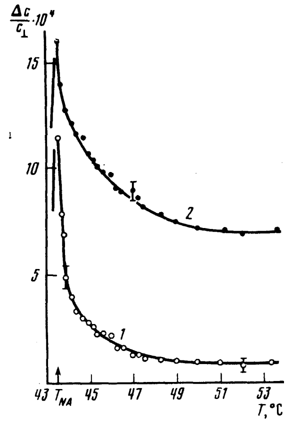

FIG. 2. Temperature dependence of the relative anisotropy of the ultrasound velocity at frequencies 3 MHz (curve 1) and 15 MHz (curve 2).

which corresponds with the results obtained in nematic phases of other materials.

Figure 2 shows the temperature dependence of the relative anisotropy of the ultrasound velocity:

$$\Delta c/c_\perp=(c_\parallel-c_\perp)/c_\perp$$

($c_\parallel$ is the ultrasound velocity at $\theta=0°$) at the frequencies 2 and 15 MHz. Upon approach to T_{NA}, an increase is observed in the indicated quantity. At $T>50$ °C, the quantity $\Delta c/c_\perp$ becomes temperature independent and takes on values equal to 1×10^{-4} and 7×10^{-4} at 3 and 15 MHz, respectively. The existence of a non-vanishing normal component $[\Delta c/c_\perp]_N$ in the value of $\Delta c/c_\perp$ far from T_{NA} is probably connected with the relaxation of the terminal molecules of the groups possessing the same structure as the MBBA butyl chain. Extrapolation of the temperature dependence of the relaxation time τ_n of the normal contribution for MBBA[10] in the region $T>50$ °C yields values that are equal within 5% of the value $\tau_n\approx8\times10^{-8}$ s, estimated in correspondence with Ref. 11 from the given experimental data. The estimates that have been made show that in the temperature range 43.5 °C < T < 50 °C the change in the value of the normal contribution $[\Delta c/c_\perp]_N$ can be neglected in comparison with the experimentally determined changes in the quantity $\Delta c/c_\perp$.

We note that the data given in Table I indicate that the relaxation of the terminal molecular groups makes a contribution only to the values of the coefficient a.

DISCUSSION OF THE RESULTS

Analysis of the experimental data within the framework of the theories set forth above shows that not one of them individually describes the characteristic features of the represented dependences. In particular, the fluctuation mechanism,[2] which leads to the expression (2), does not explain the existence of a term proportional to $\cos^2\theta$ in the angular dependence of the quantity $\Delta c/c_\perp$ that is. The Landau-Khalatnikov mechanism, as will be shown below, explains only certain features of the experimental dependences. For example, the temperature dependence of the coefficient z (see Table I) is obviously governed by the relaxation contribution (6), which depends significantly on the temperature through the time τ in accordance with (7).

As a result of the approximation of the temperature-dependent part of the quantity a by expression for the proportionality coefficient of $\cos^2\theta$ in (6), with account of (7), we obtained the values $\tau_0=(1.50\pm0.05)\cdot10^{-11}$ s, and $z=-1.07\cdot10^{-10}$ s, where

$$z=\beta_\perp\Delta\beta/c^2\eta\rho. \qquad (12)$$

The approximations were carried out using the values of the coefficient a at $T=43.6$, 43.8, and 48.7 °C. The temperature-independent part here was taken to be equal to the value of $\Delta c/c_\perp$ at $T>50$ °C. Moreover, the value of z was assumed to be weakly dependent on the temperature near T_{NA}.

The analysis that has been carried out allowed us to estimate for the first time the value and sign of the combination of the material coefficients $\beta_\perp\Delta\beta/\eta\approx-23$ kg/ms, experimental data on which are lacking at the present time. The values of the ultrasound velocity and the density were taken from Refs. 12 and 13. We note that it is possible to establish the sign and magnitude of the difference $\Delta\beta$ directly in experiments on the flow.[3]

In spite of the fact that the relaxation mechanism describes the temperature dependence of the coefficient a, this mechanism is not sufficient for the explanation of the corresponding dependences of the relative anisotropy $\Delta c/c_\perp$ (see Fig. 2). Actually, it follows from expression (6) that the quantity K_1 does not depend on the frequency at the given temperature:

$$K_1=\left[\frac{\Delta c}{c_\perp}\right]_R\frac{1+\omega^2\tau^2}{\omega^2\tau}. \qquad (13)$$

At the same time, the calculated values of the quantity K_2 at the obtained τ_0 differ by about an order of magnitude at the frequencies 3 and 15 MHz. This is evidence of the existence of an additional contribution $[\Delta c/c_\perp]_x$ to the relative anisotropy $\Delta c/c_\perp$. Here

$$\left\{\frac{\Delta c}{c_\perp}-\left[\frac{\Delta c}{c_\perp}\right]_N\right\}\frac{1+\omega^2\tau^2}{\omega^2\tau}=K_2. \qquad (14)$$

An estimate of this contribution can be made in the following way:

$$\left[\frac{\Delta c}{c_\perp}\right]_x=\frac{\Delta c}{c_\perp}-\left[\frac{\Delta c}{c_\perp}\right]_R-\left[\frac{\Delta c}{c_\perp}\right]_N. \qquad (15)$$

The temperature dependence of the quantity $[\Delta c/c_\perp]_x$ for 3 and 15 MHz, determined from (15), is shown in Fig. 3. In the calculation of the relaxation contribution according to (6) it was assumed that $|\Delta\beta/\beta_{\parallel,\perp}|\ll1$. The values obtained for the temperature dependences of $[\Delta c/c_\perp]_x$ agree qualitatively with the conclusions of fluctuation theory [relations (2) and (3)]. At the frequencies 3 and 15 MHz, the values of $\Delta T_{NA}=0.1$ K and $\Delta T_{NA}=0.5$ K divide the range of change of the quantity $\omega\tau$ into two regions; $\omega\tau>1$ and $\omega\tau<1$.

As follows from Fig. 3, the quantity $[\Delta c/c_\perp]_x$ at 15 MHz, for the case $T_{NA}<0.5$ K does not depend on the temperature within the limits of error. This agrees with expression (3). For $\Delta T_{NA}>0.5$ K a monotonic increase is observed in the exponent of the power-law divergence to a value that is close to the theoretical (2). The dashed lines correspond, to within a constant factor, to the limiting dependences (2) and (3) for $\beta=-4/3$. The indicated value of β corresponds to the conclusions of similarity theory, which is confirmed by the experimental investigations of the divergence of a

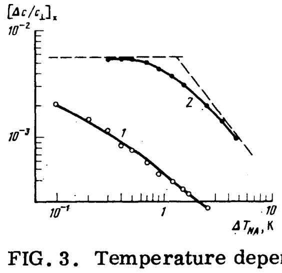

FIG. 3. Temperature dependence of the fluctuation contribution to the quantity $\Delta c/c_\perp$ at frequencies 3 MHz (curve 1) and 15 MHz (curve 2).

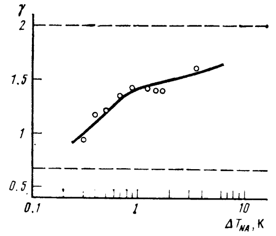

FIG. 4. Temperature dependence of the quantity γ (16).

number of physical quantities, in particular the elastic coefficients[14] and the viscosity.[15] At the frequency 3 MHz, a significant change should take place, in accord with the given estimate, in the exponent of the power-law divergence at $\Delta T_{NA} < 0.1$ K, which does not contradict the experimental data.

The relations (2) and (3) allow us to explain qualitatively the existing dependence of $[\Delta c/c_\perp]_x$ on the frequency. It follows from these expressions that the ratio of the fluctuation contributions at the two frequencies (15 and 3 MHz) decreases with increase in the quantity $\omega\tau$, which in turn depends on the temperature in correspondence with (7). The experimental dependence of the quantity γ on the temperature has a similar form. This is illustrated in Fig. 4 (the indices 15 and 3 refer to the corresponding ultrasound frequencies). Here γ denotes the quantity

$$\gamma=\left(\ln\frac{\omega_{15}}{\omega_3}\right)^{-1}\ln\left[\left(\frac{\Delta c}{c_\perp}\right)_{x15}\left(\frac{\Delta c}{c_\perp}\right)_{x3}^{-1}\right]. \tag{16}$$

The dashed lines on this figure correspond to the theoretical dependences of the fluctuation contribution on the ultrasound frequency for the two limiting cases: $\omega\tau \gg 1$ and $\omega\tau \ll 1$. As is seen from the figure, the most rapid change of this quantity takes place in the vicinity of the temperature $\Delta T_{NA} \sim 0.5$ K, at which $\omega\tau \approx 1$ (for 15 MHz), which is in agreement with the data on the temperature dependence of the quantity $[\Delta c/c_\perp]_x$. We also note that the experimental values given in Fig. 4 lie in the range predicted by the theory.

Thus the analysis presented shows that the aggregate of theoretical ideas concerning the anisotropic propagation of ultrasound in the neighborhood of T_{NA}, which have been considered above, describe qualitatively the given experimental results. For a quantitative comparison of the results of the experiment with the conclusions of theory, further acoustical study of this phase transition over a wide range of values of $\omega\tau$ is necessary.

[1] J. Swift and B. J. Mulvaney, J. de Phys. Lett. **40**, 287 (1979).

[2] H. J. Swift and B. J. Mulvaney, Phys. Rev. **B22**, 4523 (1980).

[3] M. Lui, Phys. Rev. **A19**, 2090 (1979).

[4] L. D. Landau and E. M. Lifshitz, Statistical Physics, Pergamon, 1980, Sec. 146.

[5] W. L. McMillan, Phys. Rev. **A4**, 1238 (1971).

[6] N. Doane, R. S. Parker, B. Cvikl, D. Johnson and D. Fishel, Phys. Rev. Lett. **28**, 1694 (1972).

[7] W. L. McMillan, Phys. Rev. **A7**, 1419 (1973).

[8] P. De Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford, 1974.

[9] M. E. Mullen, B. Lüthi and M. J. Stephen, Phys. Rev. Lett. **28**, 799 (1972).

[10] C. A. Castro, A. Hikata and C. Elbaum, Phys. Rev. **A17**, 353 (1978).

[11] F. Z. Jähnig, Z. Phys. **258**, 199 (1973).

[12] V. A. Balandin, and A. S. Lagunov, in: Primenenie ul'traakustiki k issledovaniyu veshchestva (Application of Ultrasonics to the Study of Matter), Moscow, VZMI, 1981, p. 41.

[13] J. V. Rao, N. V. S. Rao, V. G. K. M. Pisipati and S. R. K. Murty, Ber. Bunsenges, Phys. Chem. **84**, 1157 (1980).

[14] M. Delaye, R. Ribotta and G. Durand, Phys. Rev. Lett. **31**, 443 (1973).

[15] A. C. Diogo and A. F. Martins, Portgal. Phys. **10**, 167 (1979).

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