Sound propagation in the isotropic phase of a nematic liquid crystal

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Sound speed and absorption in PAA and MBBA crystals were investigated at ultra- and hypersound frequencies. The observed absorption peculiarities are discussed on the basis of the theory of interacting modes. The excess of hypersound absorption is substantially larger than predicted by the theory near the temperature of the transition from an isotropic crystal into a nematic.

It is known that sound-speed and sound-absorption anomalies are observed near an isotropic liquid–nematic liquid crystal (IL–NLC) phase transition and are due to interaction between the order-parameter fluctuations and the acoustic mode.[1] The order-parameter fluctuations in an IL–NLC transition are fluctuations in the distribution of the axes of the anisotropic molecules. The attenuation time of these fluctuations determine the half-width of the depolarized component of the scattering light—the Rayleigh-line wing (RLW). Imura and Okano[2] have predicted that the relation between the order-parameter relaxation-fluctuation time τ_r obtained from the RLW half-width and the acoustic relaxation time τ_0 is of the form

$$\tau_r=2\tau_0. \tag{1}$$

The anomalies in the absorption and speed of sound near the IL–NLC transition can be represented according to the theory of Ref. 2 by homogeneous functions of the reduced frequency $x=\omega_0/\omega$, where $\omega_0=1/\tau_0$, $\omega=2\pi f$, and f is the sound frequency.

We present here the frequency dependences of the speed and absorption of ultra- and hypersound near an IL–NLC transition, obtained by us for *n*-metoxybenzylidene-*n'*-*n*-butylanilin (MBBA) and *n*-para-azoxyanisol (PAA). The results are discussed on the basis of the theory of Imura and Okano,[2] using the relaxation times of the order-parameter fluctuations previously obtained by us[3] for the same PAA and MBBA samples.

THEORETICAL PART

Imura and Okano[2] calculated the excess absorption and the dispersion of the speed of sound near an IL–NLC transition using the de Gennes continuum statistical theory.[4] The theory yields the following expressions for the product $\alpha\lambda$ of the excess absorption and the sound wavelength and for the dispersion $\Delta V/V$ of the sound speed

$$(\alpha\lambda)_{\text{exc}}=\pi(\gamma_0-1)(c_p)^{-1}\,\text{Im}(\Delta c^*), \tag{2}$$

$$\frac{\Delta V}{V}=-\frac{1}{2}(\gamma_0-1)(c_p^0)^{-1}\,\text{Re}(\Delta c^*). \tag{3}$$

Here $\gamma_0=c_p^0/c_v^0$; c_p, and c_v^0 are the isobaric and isochoric heat capacities, respectively; $\text{Im}(\Delta c^*)$ and $\text{Re}(\Delta c^*)$ are the imaginary and real parts of the excess heat capacity. The frequency dependence of Δc^* given in Ref. 2 is

$$\Delta c^*(\omega)=\Delta c_p(T)[f_1(x)+if_2(x)], \tag{4}$$

where

$$f_i(x)=(2x)^{1/2}F_i(x),\quad i=1,2. \tag{5}$$

The functions $F_i(x)$ are given by

$$F_1(x)=[x+(x^2+1)^{1/2}]^{-1/2}, \tag{6}$$

$$F_2(x)=[x+(x^2+1)^{1/2}]^{-1/2}-(2x)^{1/2}. \tag{7}$$

Here $x=\omega_0/\omega$.

Using (4)–(7) we can rewrite (2) and (3) in the form

$$(\alpha\lambda)_{\text{exc}}=\pi B(T)f_2(x), \tag{8}$$

$$\Delta V/V=-(1/2)B(T)f_1(x). \tag{9}$$

Here $B(T)=(\gamma_0-1)\Delta c_p/c_p^0$.

As the transition temperature is approached and $\Delta T\to 0$, the value of Δc_p diverges[3] so that $B(T)$ increases continuously. As follows from Eqs. (5)–(7) and as shown in Ref. 2, the dependence of $f(x)$ on x^{-1} has a maximum at $x^{-1}=4.2$. The quantity $(\alpha\lambda)_{\text{exc}}$, which equals the product $B(T)f_2(x)$, is therefore larger for ultrasound.

In the hypersound region, the function $f_2(x)$ decreases substantially (owing to the decrease of d) and the expected excess absorption should depend weakly on the temperature and sometimes even decrease as $\Delta T\to 0$.

We analyzed our data by using the relaxation times of the fluctuations of the order parameter τ_r obtained by us earlier,[3] followed by estimating $\omega_0=1/\tau_0$ with the aid of relation (1). The values of $x=\omega_0/\omega$ we used to calculate the functions $f_1(x)$ and $f_2(x)$ and to estimate the excess absorption at hypersonic frequencies.

EXPERIMENTAL PART

To measure ultrasound speed and absorption in the isotropic phase of a liquid crystal we have assembled an acousto-optical facility of a known type,[5] based on diffraction of light by ultrasound. The distinguishing feature of this facility is that the measurements are in a pulsed regime. The video-pulse duration was 5 μs and the repetition frequency 100 Hz. Pulsed measurements lowered to a minimum the disturbances produced in the sample by the mea-

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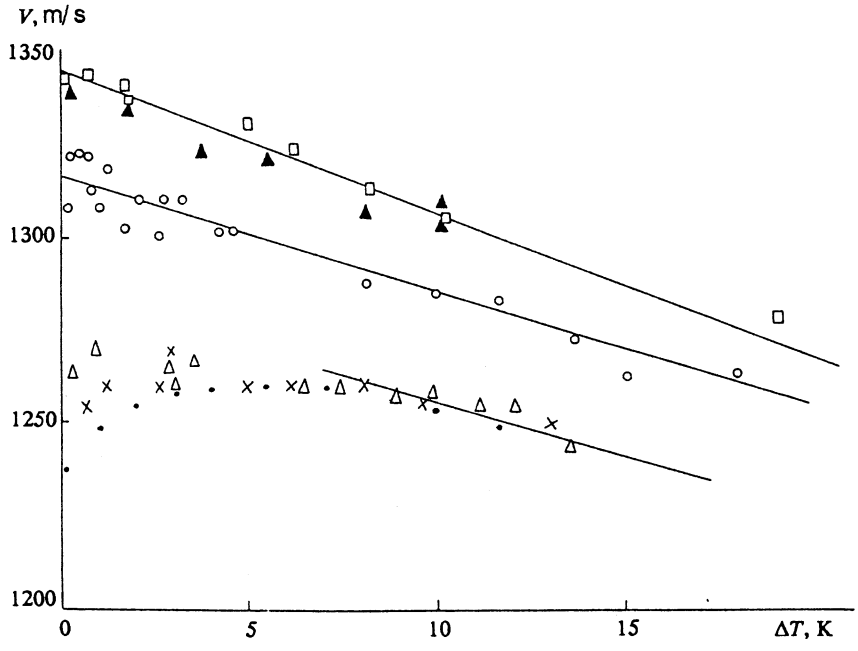

FIG. 1. Temperature dependence of the speed of sound in PAA at the frequencies: ●—5 MHz (Ref. 7), ×—14.4 MHz; △—29.9 MHz; ○—1.31 to 1.36 GHz; □—4.6 to 4.9 GHz; ▲—6.5 to 6.8 GHz; lines—results of data averaging.

surement process, a particularly important factor in the investigation of phase transitions. The measurement errors did not exceed 0.5% for the ultrasound speed and 10% for the absorption.

To investigate the propagation speed and absorption of hypersound by means of Brillouin-scattering spectra we used a spectral facility with a two-pass Fabry–Perot interferometer, previously described in detail in Ref. 6. The exciting-light wavelength was 632.8 nm, and the scattering angles were 20°, 60°, 90°, and 160° for MBBA and 23°, 90°, and 167° for PAA.

The sound propagation speed and absorption in PAA were measured acoustically at frequencies 29.9 and 14.4 MHz and using Rayleigh scattering at frequencies 1–7 GHz in a temperature interval $\Delta T = T - T_{tr}$ from 0 K to 20 K (T_{tr} is the IL–NLC transition temperature).

Figure 1 shows the temperature dependences of the sound propagation speed in PAA for all the investigated speeds, together with data taken from Ref. 7.

Figure 2 shows the temperature dependences of ultra- and hypersound speeds measured by us in the liquid crystal MBAA at 10.05 and 30.5 MHz and in the interval from 1 to 8 GHz, as well as data taken from Ref. 8.

We measured the absorption for all the investigated ultra- and hypersound frequencies. The results have shown that the absorption coefficient α increases as $\Delta T \to 0$ for all frequencies. The growth of the coefficient α at ultrasound frequencies begins long before the transition temperature is reached. The absorption at hypersound frequencies increases in a narrower temperature interval in the immediate vicinity of the transition.

Figure 3 shows plots of the product $\alpha\lambda$ of the absorption coefficient α and the wavelength λ for the frequencies 10.05 MHz, 30.5 MHz, and 7.3 to 8.2 GHz in MBBA.

DISCUSSION OF RESULTS

To evaluate the results from the standpoint of the theory of Imura and Okano[2] it is necessary to know the values

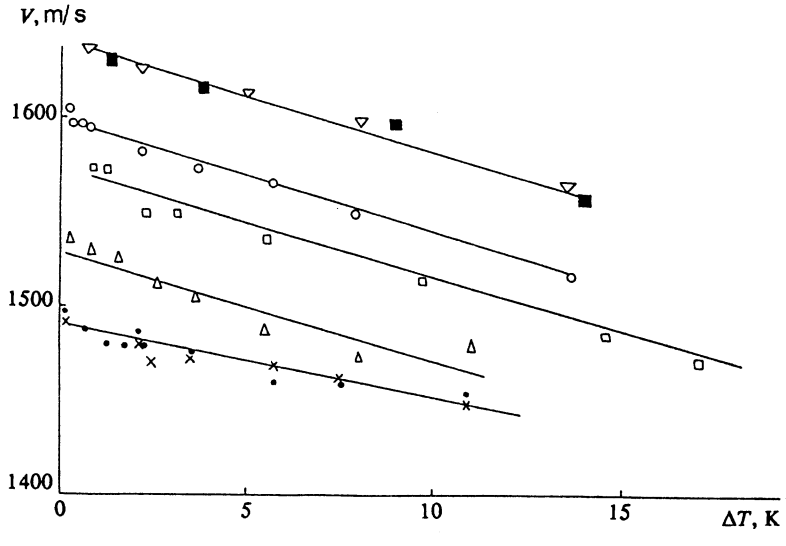

FIG. 2. Temperature dependence of the speed of sound in MBBA at the frequencies: ●—10.05 MHz; ×—30.3 MHz; △—1.23 to 1.37 GHz; □—3.57 to 4.0 GHz; ▽—7.3 to 8.8 GHz; ■—6 GHz; lines—averaging results.

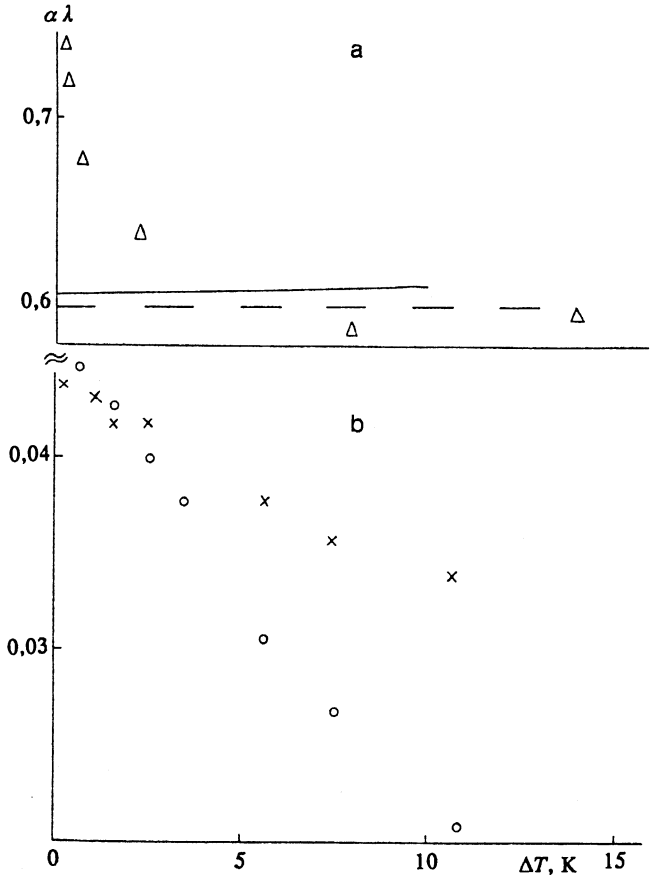

FIG. 3. Temperature dependence of $\alpha\lambda$ in MBBA: a) for frequencies 7.3 to 8.2 GHz; b) 10.05 MHz (○) and 30.3 MHz (×). Solid line—calculation using Eq. (9); dashed—Eq. (11).

of $B(T)$, $f_2(x)$, and $f_1(x)$. Calculation of $f_2(x)$ and $f_1(x)$ is easy if the reduced characteristic frequency $x=\omega_0/\omega$ is known. We have calculated the characteristic frequency ω_0 by using our results[3] for the half-widths of the depolarized component of scattered light. The values of ω_0 for MBAA and PAA for the temperature interval ΔT from 10 K to 1 K are listed in Tables I and II, which contain also the corresponding values of the functions $f_2(x)$ calculated from Eq. (5) for ultra- and hypersound (the frequencies are indicated in the tables) and also of $B(T)$. The functions $f_1(x)$ for MBBA and PAA for ultrasound frequencies are listed in Table III.

We determined the functions $f_2(x)$ and $f_1(x)$ by independent experiments in the Rayleigh line wing, and $B(T)$ from ultrasound absorption data. We calculated $B(T)$ under the assumption that, in accordance with the theory, ultrasound absorption occurs at frequencies 10 and 30 MHz, except in a small part due to bulk-viscosity relaxation, as a result of interaction of the acoustic mode with fluctuations of the order parameter. Using the function $f_2(x)$ one can calculate $B(T)$ from Eq. (8) taking $(\alpha\lambda)_{\text{exc}}$ to be the experimental value (after subtracting from it the non-critical part connected with bulk-viscosity relaxation). The estimate of $B(T)$ was reduced mainly to separation of the critical part of the absorption at ultrasound frequencies. We used for this purpose sound-speed frequency dependences obtained by us as well as by others.

The experimental results of Figs. 1 and 2 show an appreciable dispersion of the speed of sound in PAA and MBBA in the temperature interval ΔT from 15 K to 0 K. The dispersion in the liquid crystal MBAA reaches approximately 9% and is preserved in the entire temperature interval. The dispersion in PAA is about 4% for high ΔT and rises to approximately 7% as ΔT decreases. Such an order of magnitude of the dispersion, as well as its relative independence of temperature, are usually observed in low-viscosity liquids and is attributed to relaxation of the bulk viscosity.[9]

To calculate the absorption fraction due to bulk-viscosity relaxation one must know the relaxation time. It is easy to calculate this time for bulk viscosity when the investigated frequency range suffices to observe the total dispersion of the sound speed. It is perfectly obvious that the experimentally observed dispersion contains a part due to the proximity to the phase transition. Far from T_{tr} however, this part is itself small and furthermore its contribution to the total dispersion is altogether small. The error which we are sure to introduce in the calculations is thus not larger than that of the sound-speed measurement.

According to Ref. 9, the relaxation time τ is connected with the high- and low-frequency sound speeds V_∞ and V_0 by the relation

$$\frac{V^2-V_0^2}{V_\infty^2-V_0^2}=\frac{\omega^2\tau^2}{1+\omega^2\tau^2}. \tag{10}$$

Here V is the speed of sound at the frequency ω.

As seen from the presented temperature dependences of the speeds of sound, they are equal in both in MBBA

TABLE I.

ΔT, K	ω_0, MHz [Ref. 3]	30,3 MHz			(7,3 -- 8,2) GHz	
		$f_2(x)$	$(\alpha\lambda)_{\text{exp}}$	$B(T)$	$f_2(x)$	$(\alpha\lambda)_{\text{calc}}$
		MBBA				
10	64	0,300	0,034	0,036	0,102	0,0110
5	27	0,287	0,039	0,043	0,074	0,0100
4	24	0,282	0,040	0,045	0,070	0,0098
3	18	0.266	0,041	0,049	0,062	0,0095
2	14	0,250	0,042	0,054	0,054	0,0091
1	11	0,230	0,043	0,059	0,049	0,0090

TABLE II.

ΔT, K	ω_0, MHz [Ref. 3]	14,4 MHz			(4,6 – 4,9) GHz	
		$f_2(x)$	$(\alpha\lambda)_{exp}$	$B(T)$	$f_2(x)$	$(\alpha\lambda)_{calc}$
		PAA				
10	450	0,057	0,002	0,012	—	—
5	225	0,095	0,012	0,039	—	—
4	180	0,116	0,017	0,046	0,120	0,017
3	150	0,136	0,026	0,060	0,115	0,021
2	110	0,173	0,040	0,074	0,100	0,023
1	60	0,245	0,090	0,120	0,095	0,035

and in PAA at ultrasonic as well as hypersonic frequencies. In other words, the values of V_0 and V_∞ were contained in the frequency interval investigated by us.

Table IV lists the bulk-viscosity relaxation times τ calculated using Eq. (10). Our estimates of the relaxation times τ in MBBA from the value of the total sound speed dispersion agree with the estimates of τ in Ref. 7 on the basis of the observed excess absorption. It was found in Ref. 7 that in MBBA in the temperature interval ΔT from 24 K to 4 K the value of τ increases to 5×10^{-11} s to 6.6×10^{-11} s. As seen from Table IV, in both cases the bulk-viscosity relaxation frequency τ is in the gHz band and decreases slightly when the temperature is lowered.

Using the known equation for the frequency dependence of absorption in the case of a single relaxation process

$$\frac{\alpha}{f^2}=\frac{A}{1+(\omega\tau)^2}+C, \qquad (11)$$

one can estimate the values of A and C in MBBA and PAA by using ultrasound and hypersound absorption far from the phase transition. At hypersound frequencies, when $V=V_\infty$, the influence of the first term of (11) is weak and then $\alpha/f^2=C$. The value of C in both samples was determined from the absorption at frequencies $f\simeq7$ GHz. In ultrasound experiments $(\omega\tau)^2\leqslant10^{-5}$, and therefore A can be estimated as the difference between α/f^2 and C. The values of A and C determined in this manner are listed in Table IV. Since $\omega\tau$ is small, the temperature dependence of τ does not affect A and C. Knowing these coefficients we can calculate that part of the absorption which is connected with bulk-viscosity relaxation, at all sound speeds, and can therefore allow for it in the estimate of the critical part of the absorption. This part is regarded as redundant relative to the part estimated using Eq. (11).

The obtained ultrasound absorption due to relaxation of the bulk viscosity in MBBA was small enough to be able to determine the value of $B(T)$ using the entire experimentally observed absorption without incurring a significant error. In the case of PAA, the noncritical part of the absorption of ultrasound far from the transition point agreed with the experimentally observed value of $\alpha\lambda$, and amounted only 2.5% of this value near T_{tr}.

Having determined $B(T)$ in this manner, we calculated the excess absorption at 7–8 GHz for MBBA and 4–5 GHz for PAA (see Tables I and II).

In Table III we listed the values of the critical part of the dispersion as calculated using Eq. (9). As seen from this table, $\Delta V/V$ for MBBA equals 1.6% in the entire investigated temperature interval. It is quite obvious that the 1.6% dispersion is imperceptible against the background of the near 9% dispersion observed as a result of the bulk viscosity.

The value of $\Delta V/V$ increases as $T\to0$. The critical dispersion is small, of the order of 0.6%, far from T_{tr} but reaches 3.4% close to it, i.e., approximately 6 times larger. The temperature dependence of the speed of sound in PAA reflects this situation (see Fig. 1). At ultrasound frequencies one can readily see a decrease of the speed, which is easily explained by the influence of the critical part of the dispersion on the dispersion due to the bulk viscosity.

Thus, calculations using absorption data account well for the temperature kinetics of the speeds both in MBBA and in PAA. As to the excess absorption, it can be seen from Fig. 3 that the experimentally observed high-frequency sound absorption exceeds substantially the absorption level calculated with the equations of the theory.

To explain the growth of the absorption at hypersound frequencies, one can turn to our earlier results.[3] Orientational modes of the motion of a medium are usually iden-

TABLE III.

ΔT, K	MBBA (10,05 MHz)		PAA (14,4 MHz)	
	$f_1(x)$	$(\Delta V/V)_{calc}$	$f_1(x)$	$(\Delta V/V)_{calc}$
10	0,910	0,016	0,99	0,006
5	0,750	0,016	0,98	0,019
4	0,726	0,016	0,97	0,022
3	0,656	0,016	0,96	0,028
2	0,600	0,016	0,93	0,034
1	0,540	0,016	0,84	—

TABLE IV.

ΔT, K	τ, s	$f = 1/2\pi\tau$, GHz	A	C
		MBBA		
15	$4{,}7\times10^{-11}$	3,4		
10	$5{,}5\times10^{-11}$	2,9	7×10^{-16}	8×10^{-16}
5	$6{,}6\times10^{-11}$	2,4		
		PAA		
15	$1{,}6\times10^{-10}$	0,99		
10	$1{,}5\times10^{-10}$	1,00	45×10^{-16}	$3{,}5\times10^{-16}$
5	$1{,}3\times10^{-10}$	1,20		

tified by a viscosity coefficient ν. It was shown by us[3] that a singularity of the viscosity coefficient is observed both in PAA and in MBBA as the transition temperature is approached. It is natural to expect a corresponding contribution to the absorption. Obviously, this absorption contribution, which increases as $\Delta T \to 0$, is observed only at high frequencies, since it is masked in ultrasound by contribution from other relaxation processes.

Thus, for example, for ultrasound experiments in PAA at $\Delta T = 2$ K and $f = 14.4$ MHz this contribution to the observed value of $\alpha\lambda$ is approximately 2×10^{-4}, whereas the excess of $(\alpha\lambda)_{exp}$ at this frequency (see Table II) is 200 times larger. This contribution to absorption was estimated under the assumption that the exchange viscosity connected with the viscosity coefficient ν relaxes at frequencies $f > 10^{10}$ Hz. An exact value of the relaxation frequency of this process can be obtained only by a detailed analysis of the frequency dependence of the hypersound absorption.

Thus, investigations of the characteristics of sound distribution near an IL–NLC transition have shown that an excess-absorption growth, which cannot be explained by the theory,[2] is observed at high hypersound frequencies in a narrow temperature interval.

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