

# Propagation of ultrasound near phase transitions in the liquid crystal working environment of technical devices

Alexey Larionov<sup>1\*</sup>, Sergey Dedov<sup>2</sup>, Valentin Mashin<sup>2</sup>, Ljubov Gorban<sup>1</sup>, Vladimir Chongin<sup>2</sup>, and Angelika Machina<sup>2</sup>

<sup>1</sup>Voronezh State Agrarian University after Emperor Peter the Great, 394087 Voronezh, Russia

<sup>2</sup>Military educational scientific center air force «Air force Academy named after Professor N.E. Zhykovsky and Y.A. Gagarin», 394064 Voronezh, Russia

**Abstract.** The results of measurements of the velocity and absorption coefficient of ultrasound in a nematic phase oriented by a magnetic field are presented. Within the framework of the hydrodynamics of the nematic phase, the coefficients of the bulk and shear viscosity of the nematic phase are calculated. The temperature dependence of the shear viscosity coefficients is exponential. The nature of the sharp increase in the bulk viscosity coefficients with an increase in the temperature of the nematic phase in the region of the phase transition nematic liquid crystal - isotropic phase is analyzed. The analysis of the temperature dependence of the ultrasound velocity in the nematic phase, carried out under the assumption of the existence of two processes responsible for the propagation of ultrasound, allowed us to identify the critical component and calculate the relaxation time of the critical contribution. In the vicinity to the phase transition, the dependence on the temperature of the relaxation time of the critical contribution increases sharply with a divergence index equal to 1.03. The relationship between the critical contribution to the absorption and the speed of ultrasound has been established. An array of data necessary for the calculation of liquid crystal technical devices has been obtained.

## 1 Introduction

Prospects for the wide practical application of liquid crystals (LC) as a working environment continuously adjustable delay lines of technical devices, optical shutters, sensors of pressure, temperature, magnetic field parameters, linear and angular displacement, optical shutters requires their comprehensive study. The thermodynamic parameters of the state have a significant effect on the speed of such devices, and this effect is especially noticeable in the vicinity of phase transition temperatures. The response time of the orientational structure of the nematic phase to the action of external electric and magnetic fields is characterized by the viscoelastic properties of the substance. Dissipative coefficients and elastic constants of

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\* Corresponding author: [larionovan@yandex.ru](mailto:larionovan@yandex.ru)

substances can be determined from the results of studies of the ultrasound absorption rate. The advantage of the acoustic research method is the ability to conduct experiments in autoclave conditions, which is associated with great difficulties when using other methods, for example, widely used optical methods, methods based on the use of nuclear magnetic resonance and electron paramagnetic resonance. Therefore, in this work, the propagation of ultrasound in the non-matic phase, including the region of the phase transition nematic liquid crystal - isotropic liquid, was studied by the fixed-distance pulse method.

## 2 Materials and methods

Researched relaxation properties mixtures nematic liquid crystals (N-96), consisting from pn-butyl-p-hexyloxyazoxybenzene), pn-butyl-p-hexyloxyazoxybenzolap-n-butyl-p-methoxyazoxybenzene, n-butyl-p-(hexyloxyphenoxy carbonyl)-phenylcarbonate and n-butyl-p-(n-ethoxyphenoxy carbonyl)-phenylcarbonate). The study of NLC mixtures is due to the fact that the expansion of the temperature range of the nematic phase relative to the mixture components, which is inherent in mixtures, makes it possible to study the dynamics of orientational processes in the region of states that are not affected by pretransition phenomena. This opens up the prospect of evaluating the effect of heterophase fluctuations on the kinetic properties of the mesophase [1, 2]. Along with the study of the nematic-isotropic phase transition, it is of interest to study the dynamics of critical phenomena in the region of the nematic-smectic liquid crystal phase transition.

The studies were performed by the fixed-distance pulse method, with an induction of 0.15 T and 0.29 T oriented by a magnetic field, which is much higher than the induction required for a uniform orientation of the sample, at an ultrasound frequency of 2.9 MHz. The double-circuit thermostating system ensured temperature stability of  $\pm 0.1$  K. The hydrostatic pressure varied in the range of  $10^5$  Pa  $\div$   $6 \cdot 10^7$  Pa. The relative error in determining the ultrasound absorption coefficient did not exceed 2%, and the orientational relaxation time did not exceed 3%. The temperature  $T_{c}$  phase transition nematic liquid crystal (NLC) - isotropic liquid (IL) in the studied mixture increases with increasing hydrostatic pressure

$$T_c(P) = T_{c0} * (1 + k_c \cdot P). \quad (1)$$

Here  $T_{c0} = 348.0$  K is the temperature at which the anisotropy of the absorption coefficient of ultrasound at atmospheric pressure disappears,  $k_c$  is the proportionality coefficient equal to

$$7.9 \cdot 10^{-10} \text{ Pa}^{-1} \text{ in the pressure range } 10^5 \text{ Pa} \div 6 \cdot 10^7 \text{ Pa} [3, 4].$$

## 3 Results and discussion

The experimentally found increase in the anisotropy of the ultrasound absorption coefficient ( $\Delta\alpha/f^2$ , where  $\Delta\alpha = \alpha_p - \alpha_n$ ,  $\alpha_p$  and  $\alpha_n$  - the absorption coefficient of ultrasound, respectively, with mutually parallel and perpendicular orientation of the induction vector of the orienting magnetic field and the wave vector,  $f$  - frequency ultrasound) in the nematic phase in the vicinity of phase transition temperatures [5, 6] indicates the existence of relaxation mechanisms responsible for the anisotropy of acoustic properties. Within the framework of generalized hydrodynamics, taking into account the frequency and dissipative parameters, the problem of ultrasound propagation in the nematic phase was solved [5, 7]. The temperature dependence of the velocity anisotropy can be represented by the sum of two components that take into account the normal  $(\Delta c/c_H)_n$  and critical  $(\Delta c/c_H)_K$  relaxation process

$$\frac{\Delta c(T)}{c_H(T)} = \left[ \frac{\Delta c(T)}{c_H(T)} \right]_n + \left[ \frac{\Delta c(T)}{c_H(T)} \right]_K, \quad (2)$$

where

$$\left[ \frac{\Delta c(T)}{c_H(T)} \right]_n = \frac{\Delta c_n(T) \cdot \tau_n^2(T) \cdot \omega^2}{1 + (\omega \cdot \tau_n)^2}, \quad (3)$$

$$\left[ \frac{\Delta c(T)}{c_H(T)} \right]_K = \frac{\Delta c_K(T) \cdot \tau_K^2(T) \cdot \omega^2}{1 + (\omega \cdot \tau_K)^2}, \quad (4)$$

$\Delta c = c_H - c_{\parallel}$ ,  $c_H$  and  $c_{\parallel}$  are the speeds of ultrasound, respectively, in the direction perpendicular (normal) and parallel to the wave vector,  $\Delta c_n(T) = A_1 \cdot S^2(T)$ ,  $S$  is the order parameter [4,8]. Here  $\tau_n$ , and  $\tau_K$  are the relaxation times of the normal and critical contributions, respectively [6, 9].

Assuming that the critical relaxation process dominates in the vicinity of the clearing temperature

$T_c$ , the values of the relaxation time are calculated (table 1).

**Table 1.** Relaxation time of the critical contribution at atmospheric pressure.

$\Delta T_c = T_c - T$ , K	2.4	3.7	4.2	5.6	7.2	10.6
$\tau_K \cdot 10^8$ , s	12.5	7.76	6.37	4.89	4.04	2.56

The value  $\tau_K$  increases by more than an order of magnitude near the clearing temperature. The temperature dependence of the relaxation time of the critical contribution is characterized by the relation

$$\tau_K(T) = \tau_{K0} \cdot \left( \frac{\Delta T_c}{T_c} \right)^{-\gamma}, \quad (5)$$

where  $\tau_{K0} = 7,25 \cdot 10^{-10}$  s,  $\gamma = 1,03$ . The values of the component  $\Delta c/c_H$  associated with the critical relaxation process decreases, and with the normal process it increases with increasing temperature (Table 2).

**Table 2.** Temperature dependence of critical and normal components at atmospheric pressure.

T, K	340.8	337.4	327.9	317.1	310.6	300.4
$(\Delta c/c_H)_K \cdot 10^4$	5.68	3.23	1.16	0.58	0.42	0.29
$(\Delta c/c_H)_n \cdot 10^4$	0.74	1.29	1.89	1.98	2.23	3.63

The value of the normal component  $(\Delta c/c_H)_n$ , due to conformational transformations in the terminal chains of molecules, is characterized by a weak temperature dependence. The values  $(\Delta c/c_H)_K$  were used to calculate the critical contribution to the anisotropy of the ultrasound absorption coefficient using the relation (Table 3).

$$\left(\frac{\Delta\alpha}{f^2}\right)_K = \frac{\left(\frac{\Delta c}{c \cdot f^2}\right)_K}{c \cdot \tau} \quad (6)$$

**Table 3.** Temperature dependence of critical and normal components of ultrasound anisotropy.

T, K	345.6	337.4	327.9	320.0	310.6	303.0
$(\Delta\alpha/f^2)_K \cdot 10^{14},$ $m^{-1} \cdot s^2$	2.30	1.08	0.77	0.62	0.51	0.46
$(\Delta c/f^2)_n \cdot 10^{14}, m^{-1} \cdot s^2$	0.45	0.63	0.90	1.13	1.52	1.94

The temperature dependence of the normal contribution is determined by the dependence of the order parameter and time  $\tau_n$  on temperature.

The asymmetry of the influence of the magnetic field on the absorption coefficient of ultrasound, found experimentally at low frequencies, makes it possible to calculate the absolute values of the ratio of the absorption coefficient of ultrasound to the second power of the frequency in a transverse and longitudinal magnetic field [1, 10]

$$\left(\frac{\alpha_{\Pi}}{f^2}\right)_{2,9} = \left(\frac{\alpha}{f^2}\right)_0 + \frac{2}{3} \cdot \left(\frac{\Delta\alpha}{f^2}\right); \quad (7)$$

$$\left(\frac{\alpha_H}{f^2}\right)_{2,9} = \left(\frac{\alpha}{f^2}\right)_0 - \frac{1}{3} \cdot \left(\frac{\Delta\alpha}{f^2}\right), \quad (8)$$

if the absorption of ultrasound in an unoriented sample  $(\alpha/f^2)_0$  and the anisotropy of the absorption coefficient are known  $(\Delta\alpha/f^2)$ . The absorption coefficient values calculated at an ultrasound frequency of 2.9 MHz in the longitudinal and transverse magnetic fields in H-96 at various temperatures and atmospheric pressure are given in Table 4.

**Table 4.** The values of the absorption coefficient of ultrasound at a frequency of 2.9 MHz in the longitudinal and transverse magnetic fields.

$\Delta TC=TC-T,$ K	35	30	25	20	15	7	5	2,3
$\left(\frac{\alpha_{\Pi}}{f^2}\right) \cdot 10^{14},$ $m^{-1} \cdot s^2$	370	367	371	430	562	1418	1840	3167
$\left(\frac{\alpha_H}{f^2}\right) \cdot 10^{14},$ $m^{-1} \cdot s^2$	175	191	205	265	394	1226	1630	2917

The hydrodynamic theory of anisotropic liquid media describes the dependence of the ultrasound absorption coefficient in the nematic phase on the angle  $\theta$  between the director and the wave vector by the relation [11]:

$$\frac{\Delta\alpha(\theta)}{f^2} = \frac{\alpha_{\Pi}}{f^2} \cdot \cos^2\theta + \frac{\alpha_H}{f^2} \cdot \cos^4\theta, \quad (9)$$

where the absorption coefficients  $\alpha_P / f^2$  and  $\alpha_N / f^2$  are related to the dissipative coefficients  $\nu_i$  by the relations

$$\frac{\alpha_{\parallel}}{f^2} = \left( \frac{2 \cdot \pi^2}{\rho \cdot c_0^3} \right) \cdot (2\nu_1 + \nu_2 - \nu_4 + 2\nu_5), \quad (10)$$

$$\frac{\alpha_H}{f^2} = \left( \frac{2 \cdot \pi^2}{\rho \cdot c_0^3} \right) \cdot (\nu_2 + \nu_4). \quad (11)$$

Here  $\nu_1$  and  $\nu_2$  are shear viscosity coefficients,  $\nu_4$  and  $\nu_5$  are bulk viscosity coefficients,  $\nu_1$  and  $\nu_2$  are a combination of bulk and shear viscosity coefficients,  $\rho$  is the sample density,  $c_0$  is the ultrasound velocity in the low-frequency limit. At high ultrasound frequencies (for example, at  $f = 560$  MHz), a nematic liquid crystal can be considered as a quasi-incompressible medium, which makes it possible to use the results of high-frequency measurements of the ultrasound absorption coefficient to calculate the shear viscosity coefficients [5, 12]:

$$\nu_1 = \frac{\left( \frac{\alpha_{\parallel}}{f^2} \right)_{560} \cdot c_0^3}{4\pi^2}; \quad (12)$$

$$\nu_2 = \frac{\left( \frac{\alpha_H}{f^2} \right)_{560} \cdot c_0^3}{4\pi^2}. \quad (13)$$

The temperature dependence of the shear viscosity coefficients is described by an exponential law (Table 5)

$$\nu_i(T) = C_i \cdot \exp\left(\frac{E_i}{RT}\right), \quad (14)$$

where  $i = 1, 2$ ;  $C_i$  is a constant factor, with  $C_1 = 2.74 \cdot 10^{-6}$  Pa·s and  $C_2 = 2.71 \cdot 10^{-6}$  Pa·s;  $E_i$  - activation energy  $E_1 = 23.5$  kJ/mol,  $E_2 = 2305$  kJ/mol.

**Table 5.** Values of shear viscosity coefficients at atmospheric pressure.

$\Delta T C = T C - T$ , K	2,3	5	7	10	12	15	20	25
$\nu_1 \cdot 102$ , Pa·s	0,95	1,02	1,09	1,18	1,24	1,33	1,49	1,68
$\nu_2 \cdot 102$ , Pa·s	0,81	0,86	0,92	0,99	1,04	1,11	1,24	1,40

The values of the ratios  $\alpha_P / f^2$  and  $\alpha_H / f^2$  obtained at low (2.9 MHz) and high (560 MHz) frequencies can be used to determine the coefficients of bulk viscosity [7]

$$\nu_4 = \frac{\frac{\rho \cdot c_0^3}{4\pi^2} \cdot \left[ \left( \frac{\alpha_H}{f^2} \right)_{2,9} - 0,5 \cdot \left( \frac{\alpha_H}{f^2} \right)_{560} \right]}{2\pi^2}; \quad (15)$$

$$\nu_5 = \frac{\frac{\rho \cdot c_0^3}{4\pi^2} \cdot \left[ \left( \frac{\alpha_{\parallel}}{f^2} \right)_{2,9} - 0,5 \cdot \left( \frac{\alpha_{\parallel}}{f^2} \right)_{560} \right]}{2\pi^2} + \frac{\nu_4}{2} - \frac{\nu_2}{2}. \quad (16)$$

The temperature dependence of the bulk viscosity coefficients (Table 6) is described by the expressions [6,10]

$$v_i(T) = C_i \cdot \left(\frac{\Delta T_c}{T}\right)^{-x}, \quad (17)$$

where  $i = 1, 2$ ;  $C_i$  - constant factor equal to  $C_4=9,54$  Pa·s;  $C_5=8,64$  Pa·s;  $x_4=1,02$ ,  $x_5=20,91$  - exponent.

**Table 6.** Values of shear viscosity coefficients at atmospheric pressure.

$\Delta T_c = T_c - T$ , K	2.3	5	7	10	12	15	20	25
$v_4 \cdot 102$ , Pa·s	3,51	2,03	1,55	1,02	0,77	0,54	0,38	0,31
$v_5 \cdot 102$ , Pa·s	3,67	2,17	1,58	1,20	0,88	0,65	0,48	0,41

The bulk viscosity is an order of magnitude higher than the shear viscosity at low temperatures of the nematic phase, and as the temperature rises, this difference increases, reaching a maximum at temperatures close to the phase transition temperature, the bulk viscosity exceeds the shear viscosity by more than 350 times. The coefficients  $v_4$  and  $v_5$  are due to the presence of phase shifts between volume, temperature, and pressure during periodic volumetric deformations in an ultrasonic wave and are a consequence of molecular relaxation processes with finite times for establishing equilibrium. Since these times are  $10^{-4} \div 10^{-10}$  s, then at the ultrasound frequency of 2.9 MHz used in the experiment, the coefficients  $v_4$  and  $v_5$  are frequency-dependent, that is, dynamic. An increase in the frequency of ultrasound leads to a decrease in the bulk viscosity coefficients.

The temperature dependence of the coefficient  $v_3$  has a complex character and increases as it approaches the phase transition temperature (Table 7).

**Table 7.** Viscosity values  $v_3$  at atmospheric pressure.

$\Delta T_c = T_c - T$ , K	2.3	5	7	10	12	15	20	25
$v_3 \cdot 102$ , Pa·s	1,78	1,03	1,01	0,83	0,68	0,57	0,51	0,35

## 4 Conclusion

Studies of the rate and absorption coefficient of ultrasound in nematic samples, oriented by a magnetic field, make it possible to calculate the coefficients of bulk and shear viscosity, as well as a combination of these coefficients. The temperature dependence of the shear viscosity coefficients is exponential. The temperature dependence of the bulk viscosity coefficients has a complex character, and in the region of the phase transition temperature of a nematic liquid crystal - an isotropic liquid, the bulk viscosity coefficients increase sharply with a decrease in temperature in the nematic phase or with an increase in pressure. An array of data necessary for calculating the parameters of liquid crystal technical devices has been obtained.

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