ULTRASOUND AT PHASE AND STRUCTURAL TRANSFORMATIONS IN LIQUID CRYSTALS

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ABSTRACT
The results of ultrasonic investigations of phase transitions and structural transformations in oriented liquid crystals are presented. The experimental data were obtained using the pulse-phase and the resonator methods in the frequency range 0.15…27 MHz. The critical anomalies of anisotropic ultrasonic parameters were studied for the phase transitions nematic – isotropic liquids, nematic – smectic A and smectic A – smectic C. The predictions of the fluctuation theories obtained in high and low frequency limits were confirmed experimentally. The possibility of usage of ultrasonic methods for an investigation of a slow orientation motion and structural transformations in liquid crystals is discussed.

INTRODUCTION
Among the different classes of condensed matter liquid crystals are of a special interest from the point of view of variety of dynamical processes [1]. Such processes take origin from both individual and collective motions of mesogenic molecules. Depending on a concrete liquid crystal phase (nematic, smectic A, smectic C (fig.1) and so on) there are different types of collective molecular motions. In the simplest case of nematic liquid crystals (NLC) these motions can be subdivided into very slow motion of local optical axe (director **n)** and relatively fast motions of long molecular axes which can be considered as changes of a degree of an orientation order parameter $S = 3/2\langle\cos^2\theta_i - 1/3\rangle$ **,** $\langle\ldots\rangle$ **-** a statistical average value. In a smectic A phase, where molecules are arranged in the system of equidistant layers there are the additional degreases of collective motions connected with distortions of smectic layers. These distortions can be described in terms of the vector of a layer displacement **u** , directed along the layer normal **n** . So in a smectic A phase the complex order parameter $\psi(z) = |\psi| e^{i\varphi}$ (analogous that for λ - transition in ^{4}He)is usually used [1] to take into account a modulation of a density $\rho(z)$ in the layer structure ($\rho(z) = \rho_0[1 + 2^{-1/2}|\psi| \cos(k_0 z - \phi)]$, $k_0 = 2\pi/l$, l – the mean distance between smectic layers, ϕ - the arbitrary phase).In a smectic C phase molecules are inclined relatively to the layer normal **n**. Thus to describe A-C transition the vector order parameter **y** = [**nn**] can be introduced [2] (its modulus is identically zero in a smectic A phase and differs from zero in smectic C).

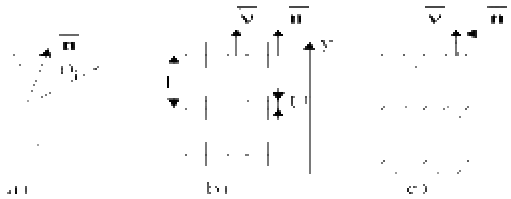
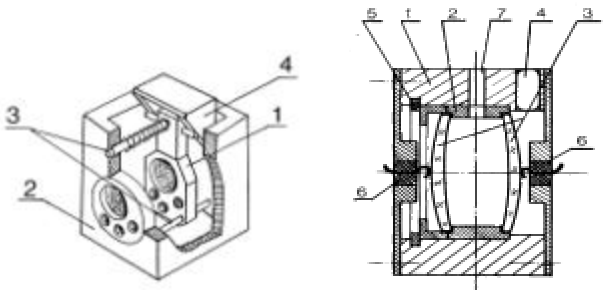


Fig.1. The structure of nematic (a), smectic A (b) and smectic C (c) phases.

In spite of a rather long history of acoustical studies of liquid crystals [3] there are some reasons which make such studies and the proper analysis of the obtained results a very complicated and actual problem. Firstly, liquid crystals are essentially anisotropic objects. It means that ultrasonic measurements, which can provide a detailed information about viscous and elastic properties of different liquid crystal phases have to be done in oriented samples. The most proper method of obtaining of such samples for ultrasonic experiments is the usage of a relatively strong magnetic fields (with induction of about 0.1…1T). Usually it leads to the relevant complications of the experimental set-up in the comparison with those, used for isotropic liquids. In particular, the linear sizes of acoustical cameras are limited, which makes difficult to carry out measurements at relatively low frequencies. Secondly, the phase transitions in liquid crystals can be of the weak first order (nematic – isotropic liquids (N-I), nematic – smectic C (N-C)), of the second order (smectic A –smectic C (A-C)) or show the intermediate behavior (nematic – smectic A (N-A)). In most cases the critical slowing down of order parameter time variations and the existing of critical fluctuations of order parameters play an essential role in the behavior of ultrasonic parameters at the transitions mentioned above. It is of importance that critical dynamic properties in the vicinities of phase transitions in liquid crystal are anisotropic too and even can be described (in the case of N-A) transition by different kinetic mechanisms for different orientations [4,5]. Moreover, in the case of the smectic A-smectic C phase transition one has to take into account the strong bare anisotropy of the layer structure. In this case the total universal behavior described by the universal models takes place in the temperature-frequency range, which is not achievable experimentally [6]. Thus the crossover behavior, which is rather complicated, makes difficult the comparison between the experimental and theoretical results [7,8].At last the situation is complicated by the mutual influence of different phase transitions, which usually takes place in liquid crystal compounds. It leads to difficulties in extracting of critical contributions in acoustical parameters, connected with the transition under consideration. In this report the most interesting results of experimental studies of phase and structural transformations in liquid crystals performed in Problem laboratory of molecular acoustics of Moscow State Academy of Instrument Engineering and Computer Science are presented. The measurements of anisotropic acoustical parameters were carried out using two experimental set-ups. The first one [7] shown in (fig.2 a), was based on a traditional pulse-phase method and allowed to perform measurements in the frequency range 3…27 MHz. The second one [9], which realized the acoustical resonator method was used to measure acoustical parameters at relatively low ultrasonic frequencies (0.15…1.2 MHz). The oriented liquid crystal samples were prepared by cooling mesogenic compounds from isotropic phase under a constant magnetic field of the induction equal to 0.3 T. The angle between the wave vector and the field direction could be varied by the rotation of magnetic field. In nematic and smectic C phases this rotation led to the changes both the ultrasonic velocity **c** and the attenuation coefficient **a**, connected with a director motion. In the last case such motion is restricted by the layer structure of a smectic phase, and results of acoustical measurements depend essentially on the geometry of the experiment. In nematic phase the changes of acoustical parameters induced by slow field rotation are in accordance with those, obtained by cooling of LC in the field $\mathbf{B_0}$ at different orientations between the wave vector **q** and the induction vector $\mathbf{B_0}$**.** In this report the results obtained for two liquid crystals – 4-*n*-butyloxybenzilidene-4′-*n*-butylaniline (BBBA) and 4-(n-hexyloxy)phenyl ester of 4-(n-decyloxy)benzoic acid (6010) showing the different phase transitions mentioned above are presented.



a) b)

Fig. 2. The constructions of the acoustic cameras for investigations of liquid crystals by the pulse-phase (a) and resonator (b) methods; a)1 – the cassettes with four pairs of piezo-transformers; 2 – the camera body; 3 and 4 – the director rails and the wedge needed to move one of the cassettes; b)1 – the duralumin casing; 2 – the stainless ring; 3 – the concave-convex quartz transducers, 4 - the quartz thermometer; 5 – the fixing nut; 6 – the contact electrodes; 7 – the filling hole.

LOW-FREQUENCY ATTENUATION AT PHASE TRANSITIONS

The low-frequency behavior of acoustical parameters at phase transitions mentioned above is of a special interest due to the critical slowing down of relaxation processes. The existing fluctuation theory of N-I [10] and N-A[11] transitions predicts the power low for $\alpha(\Delta T)$ dependence in the low frequency limit $\omega\tau<<1$ (τ - a characteristic relaxation time). Our measurements [12,13] show that this low indeed takes place at frequencies lower than 1 MHz (fig.3,4).

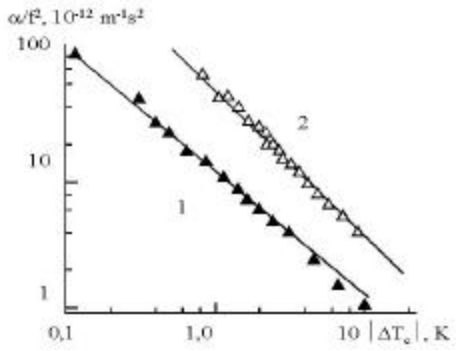


Fig.3.

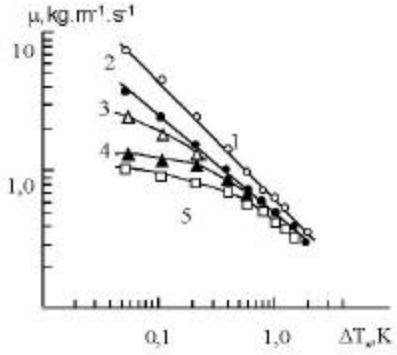


Fig.4.

Fig.3. The temperature dependence of the ultrasonic attenuation α (the wave vector is normal to the director) in the isotropic (1) and nematic (2) phases of BBBA in the vicinity of N-I transition (T_c) at frequency f = 0.15 MHz.

Fig.4. The temperature dependence of the combination of the viscosity coefficients $\mu = k\alpha$, calculated from the critical attenuation α in the nematic phase of BBBA in the vicinity of N-A transition (T_s) at frequencies f; 1 - f =0.15 MHz, 2 - 0.27, 3 - 0.51, 4 - 1.00, 5 - 1.25 MHz ($k = \rho c^3/2\pi^2$, ρ - the density, c - the ultrasonic velocity).

The value of critical index for α is close to 1 and is in accordance with theoretical predictions. It is worthwhile to point out, that a usage of data, obtained at higher frequencies may give a wrong conclusion about the character of the critical anomaly under consideration or about the value of the critical index. For example for N-I phase transition, which is of a weak first order the declination of experimental data on the simple power low can be interpreted as the existence of an essential difference between the virtual critical temperature and the real temperature of phase transition [10]. Indeed, our measurements [14] show that low frequency limit for A-C transition is not achieved even at very low frequencies used in our experiments (fig. 5).

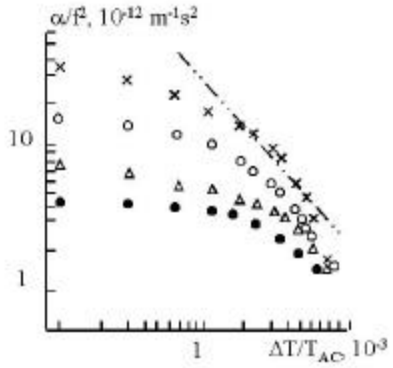


Fig.5. The temperature dependence of the critical part of the attenuation in the smectic A phase of 6010 in the vicinity of A-C transition(T_{AC}) at different frequencies f; x - 0.365 MHz, o - 0.46, Δ - 1.2, • - 3 MHz.

CRITICAL ULTRASONIC ATTENUATION IN HIGH-FREQUENCY LIMIT

A very interesting feature of the universal dynamic theories of phase transitions in liquid crystals is the connection between the temperature dependence of a critical ultrasonic attenuation and the frequency one. Namely, the same critical index has to describe the frequency dependence of **a** in the high-frequency limit and the temperature dependence of this parameter in the low-frequency limit. The data [13] presented in fig.6. confirm this conclusion (in this case high- frequency limit can be achieved at temperatures close to the phase transition).

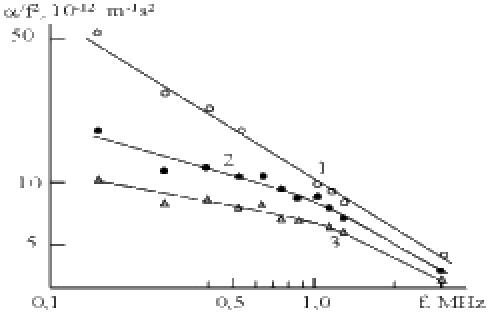


Fig.6. The frequency dependence of the critical attenuation α (the wave vector is normal to the director) in the nematic phase of BBBA in the vicinity of N-A transition (T_s) at different temperatures; 1) Δ T_s - 0.05 K, 2) T_s - 0.20 K, 3) T_s - 0.37 K.

CRITICAL BEHAVIOR OF THE PARAMETERS DESCRIBING THE ANGULAR DEPENDENCIES OF THE ULTRASONIC ATTENUATION AND THE ULTRASONIC VELOCITY

It is well known that acoustical parameters are anisotropic even for the simplest nematic phase[3] and can be described by the expressions:

$$c(\theta) = c(90^0) + a_c \cos^2\theta + b_c \cos^4\theta, \quad (1)$$

$$\alpha(\theta) = \alpha(90^0) + a_\alpha \cos^2\theta + b_\alpha \cos^4\theta, \quad (2)$$

The parameters $a_c, b_c, a_\alpha, b_\alpha$ of the presented angular dependencies contain additional information about dynamic processes in liquid crystals. The critical behavior of these parameters in the vicinity of N-A phase transition is of a special interest. Indeed, the parameter b_α does not contain the volume viscosity coefficients introduced at the description of nematic phase and so has to be independent on the frequency at temperatures far from the phase transition vicinities. The data [9] shown in fig.7 confirm this result. The critical increasing of b_α at approaching to N-A transition can be explained by a fluctuation contribution into the shear viscosity coefficient ν_1 (in the Forster

notation [15]). Indeed, the experimental value of the critical index of the frequency dependence of b_α obtained at the temperatures close to the transition temperature is approximately equal to the theoretical value (0.5), calculated in the high-frequency limit using mean field approximation for the coefficient ν_1[16]. The similar coincidence takes place relatively to the temperature dependence of b_α (fig.8) in low-frequency limit, for which a theoretical value of the critical index is also equal to 0.5 (it should be noticed that at temperatures far from N-A transition an effective value of the critical index exceeds the theoretical one, which shows the possible influence of the alternative dynamic mechanisms, a relaxation of the order parameter, for example [5]).

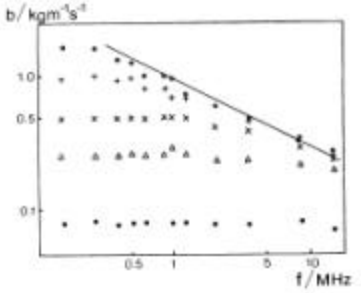


Fig.7.

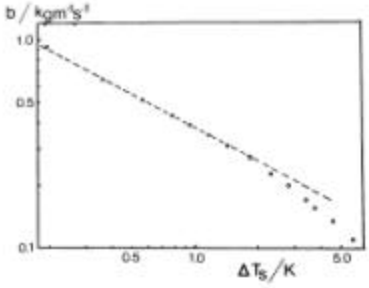


Fig.8.

Fig.7. The frequency dependence of the combination **b** of the viscosity coefficients ($b = 2(\nu_1 + \nu_2 - 2\nu_3)$) in a nematic phase of BBBA, calculated from $\alpha(\theta)$ dependence ($b = k^* b_\alpha$, $k = \rho c^3/2\pi^2$) at different values of ΔT_S: (• - 9.0 K, Δ - 1.8 K, x – 0.50 K, + - 0.20 K, o - 0.10 K).
Fig.8. The low-frequency temperature dependence of **b** in a nematic phase of BBBA.

The behavior of the parameter b_ε near N-A transition has a lot of common features with the critical variations of b_α parameter, discussed above. In particular, the low-frequency temperature dependence of this parameter is described by the critical index, which is close to the theoretical value 1.5, obtained in the framework of the fluctuation theory [11]. The temperature and frequency dependencies of the parameter a_α are more complicated and can be explained by taking into account a number of different dynamic mechanisms [9].It has to be noted that the anisotropic character of critical contributions into acoustical parameters [7] is very pronounced at A-C phase transition (fig.9). The detailed experimental investigations of such phenomena [7,8] confirmed that universal models are not applicable in this case.

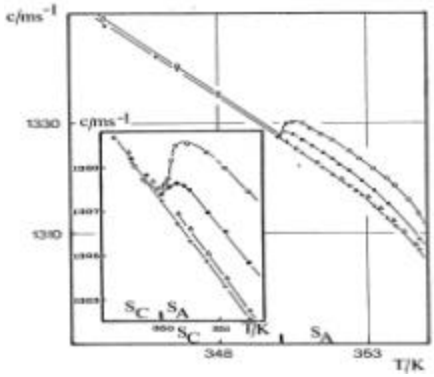


Fig.9. The temperature dependence of the longitudinal sound velocity (6010) in the vicinity of A-C phase transition for different angles θ between the wave vector and the normal to the smectic layers: o - $\theta = 0^0$; • - 30^0; Δ - 60^0; + - 90^0.

ULTRASOUND AND STRUCTURAL TRANSFORMATIONS IN LIQUID CRYSTALS

Ultrasonic methods can be effectively used to study slow orientation motions in liquid crystals, induced by magnetic fields[17] or flows [18]. For nematic liquid crystals a lot of new information was

obtained by usage of rotating magnetic field. In particular, such experiments are very useful at investigations of viscosity coefficients, including the rotational viscosity coefficient under variation of temperature and pressure [17,19]. The slow motion of a director in smectic C phase is more complicated (under this motion the angle between the director **n** and the local normal **n** to the smectic layer has to be constant). It leads to some new effects in the comparison with the case of nematic liquid crystals. In particular, there are two possible orientations of a director under the same orientation of magnetic field (the orientation bistability). This effect can be observed in the rotating magnetic field. Namely the angular dependencies of an attenuation coefficient have to be different under opposite directions of magnetic field rotation (acoustical hysteresis). Indeed, such behavior was observed [20] at the special experimental geometry (fig.10). This result and the investigations performed under different experimental geometries [21,22] confirms the conclusion that ultrasonic methods can be effectively used to study different structural transformations in liquid crystals, including field induced variations of a smectic C phase.

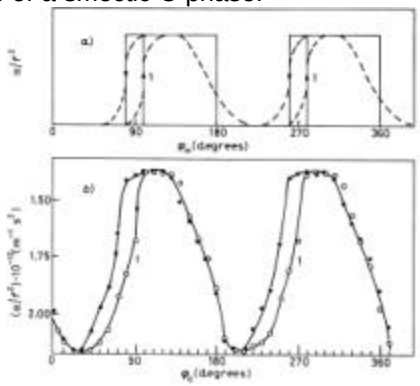


Fig.10. The angular dependence of an attenuation coefficient in the smectic C phase of 6010 for clockwise (1) and anticlockwise rotation of the magnetic field; a – the theoretical model; b – the experimental data.

LITERATURE

1. De Gennes P. Physics of liquid crystals, M. “Mir”, 1977.
2. Kats E.I., Lebedev V.V. Dynamics of liquid crystals, M. “Nauka”, 1988.
3. Natale G.G. J. Acoust. Soc. Amer. 1978, 63, 1265.
4. Swift J., Mulvaney B.J. J. Phys., 1979, 40, 287.
5. Liu M. Phys. Rev. A, 1979, 19, 2090.
6. Gurovich E.V., Kats E.I., Lebedev V.V. Sov. Phys. JETP, 1988, 94, 167.
7. Balandin V.A., Gurovich E.V., Kashitsin A.S., Pasechnik S.V. Liquid crystals, 1991, 9, 551.
8. Balandin V.A., Gurovich E.V., Kashitsin A.S., Pasechnik S.V., Tabidze A.A., Goldberg A.S. Sov. Phys. JETP, 1990, 96, 485.
9. Balandin V.A., Pasechnik S.V., Prokopjev V.I., Shmelyoff O..Ya. Liquid Crystals, 1988, 3, 1319.
10. Anisimov M.A. et al. Sov. Phys. JETP, 1984, 87, 1969.
11. Swift J., Mulvaney B.J., Phys. Rev. 1980, 22, 4523.
12. Pasechnik S.V., Balandin V.A., Prokopjev V.I., Shmelyoff O..Ya Z. Fizicheskoi Khimii (URSS), 1989, LXIII, 471.
13. Balandin V.A., Pasechnik S.V., Prokopjev V.I., Shmelyoff O.Ya. Akusticheskii Z. (USSR), 1987, XXXIII, 583.
14. Balandin V.A., Gurovich E.V., Kashitsin A.S., Pasechnik S.V, Shmelyoff O..Ya. Sov. JETP Lett., 1989, 49, 30.
15. Forster D. et al. Phys. Rev. Lett., 1971, 26, 1016.
16. Jahnig F. J. Phys., 1975, 36, 315.
17. Pasechnik S.V., Larionov A.N., Balandin V.A., Nozdrev V.F. J. Phys. , 1984, 45, 441.
18. A.S.Lagunov, V.F. Nozdrev, S.V. Pasechnik Sov. Phys.- Acoust. (USA), 1981, 27, 304.
19. V.A. Balandin, A.N. Larionov, S.V. Pasechnik Sov. Phys. – JETP (USA), 1982, 56, 1230.
20. Gevorkian E.V., Kashitsin A.S., Pasechnik S.V., Balandin V.A. Europhys. Lett., 1990, 12, 353.
21. Pasechnik S.V., Balandin V.A., Kashitsin A.S. Molec. cryst. liquid cryst., 1990, 192, 89.
22. Pasechnik S.V., Balandin V.A., Kashitsin A.S. Liquid crystals, 1989, 727.