A distinctive feature of the phase transition from a nematic liquid crystal to an isotropic liquid

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A complex investigation of the elastic parameters of para-azoxyanisole is carried out in conjunction with observation of light scattering near the phase transition from the nematic liquid crystal to the isotropic liquid. Fine structure in the anomaly in the velocity of the elastic waves is detected. A new method for determining the constant in the quadratic term of the expansion of the thermodynamic potential in the order parameter is proposed. It is shown that in the nematic phase the contribution of nonuniform fluctuations to the anomalies in the elastic parameters is small compared with that of the well-known Landau–Khalatnikov relaxation mechanism. For the isotropic phase it is found that the correlation of nonuniform thermal fluctuations of the order parameter rapidly weakens with increase in temperature and is practically absent at 2–3° above the transition point.

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The problem of the phase transition in nematic liquid crystals (NLC) remains, as yet, insufficiently studied, although the main indications (experimental data for certain thermodynamic quantities) are that this transition is first-order. From a theoretical point of view the NLC–isotropic-liquid transition is a transition from a less symmetric to a more symmetric phase, in which the order parameter changes rather sharply, if not discontinuously. Therefore, the region of the metastable state is rather narrow here. In experimental studies of the phase transition this gives rise to the need for careful thermostatting of the volume of substance being studied, and also makes greater demands on the purity of the substance.

1. The following experimental investigations have been carried out with the aim of studying the mechanism of the NLC–isotropic-liquid phase transition. The phase transition was observed visually in a volume 2–3 cm³ of the substance, and measurements of the phase velocity C and absorption of ultrasonic waves in the range of frequencies 0.8–14 MHz were performed at the same time. The substance investigated, para-azoxyanisole (PAA), was carefully freed from mechanical and chemical impurities by the technique described in[1]. The data from an analysis showed the substance to be 99.9% pure. The phase-transition point in the first melting of the substance was 2–3° higher than the tabulated value (136 °C), and then decreased to 136 °C; this was connected with the oxidation of the substance on heating. There was practically no lowering of the phase-transition point below 136 °C. The substance was placed in a transparent quartz cell between ultrasonic buffers of annealed quartz. The cell was situated, in turn, in a thermostatted silvered vessel with double walls and double quartz windows. The phase transition in the substance was observed visually through the windows. A given temperature was maintained in the vessel by circulation of silicone oil from a "Vobzer" thermostat. In addition, the thermostat, pipes and cell were thermally isolated. The setup made it possible to maintain a constant temperature with accuracy ~0.1 °C. To excite longitudinal ultrasonic waves, resonance quartz X-cut transducers, glued to the buffers, were used. From measurement of the amplitude of the signal over a given length of the PAA sample the attenuation was determined with an accuracy of ~2%. The measurement of the phase velocity was performed by an interferometric method, with accuracy 0.1%. For convenience in comparing the data for α and C these measurements were performed one after the other at each temperature point. The NLC was not previously oriented, i.e., in the nematic phase it was a polycrystal.

The increased accuracy of the experimental measurement of the velocity, in conjunction with the data on the absorption of ultrasonic waves and the data from the visual observations, gave us the possibility of detecting a number of previously unobserved phenomena in the region of the phase transition. After the velocity discontinuity, which reached its maximum $C_{1\max}$ immediately after the maximum in the absorption at $T^{\alpha}_{\max}$, the velocity was observed to decrease to a minimum $C_{2\min}$ that did not exceed 6% of the discontinuity, at any frequency (Fig. 1). We note that the maxima of the absorption and of the velocity ($C_{1\max}$) did not, as a rule, coincide in temperature (see the table). The maximum of the absorption α coincided with the phase-transition point determined by the optical method while the second velocity minimum, on the average, moved into the region of higher temperatures with increase of the frequency.

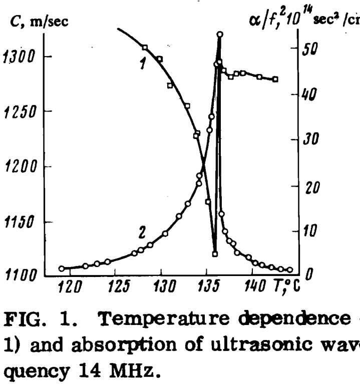

FIG. 1. Temperature dependence of the phase velocity (curve 1) and absorption of ultrasonic waves in PAA (curve 2) at frequency 14 MHz.

Substance	f, MHz	$T^C_{1\max}-T^\alpha_{\max}$, °C (experiment)	$T^\alpha_{\max}-T_c$, °C (classical theory)
PAA	0.8	0.2	0.01
	2.2	0	0.02
	6.2	0.5	0.06
	10	0.2	0.1
	14	0	0.15

Before proceeding to the theoretical explanation of the experimental facts, we give a comparison of the visual observations with the acoustic data obtained. As the isotropic melt cooled, the following picture was observed: Approximately 1° above the phase transition, nuclei of the liquid-crystalline phase, in the form of light points if they are observed in polarized light, began to appear in the isotropic bulk of the liquid. It was at this temperature $T^C_{2\max}$ that the second minimum $C_{2\min}$ in the velocity of the ultrasonic waves was observed. The number and size of the nuclei then increased as the phase-transition point was approached. It should be noted that if the temperature of the substance was kept constant, the two-phase state could be preserved for an arbitrarily long time; the transition of some nuclei to the isotropic phase and the appearance of other nuclei proceeded continuously. At 0.1–0.5 °C from the transition point coalescence of the nuclei occurred discontinuously (this corresponded to the maximum velocity), and then, on further lowering of the temperature by 0.1–0.5 °C, the minimum transparency was reached, the substance went over completely into the liquid-crystalline phase, and it was here that the maximum in the absorption and the principal minimum in the phase velocity were observed.

In view of this, the behavior of the velocity curve can be explained qualitatively in the following way. On lowering of the temperature of the melt the total order in the isotropic melt increases and the velocity increases. Then, because of the growth of the thermal fluctuations, the velocity increases sharply to a maximum at the moment of coalescence of the nuclei.

Taking into account what has been said above, it can be assumed that the NLC–isotropic-liquid phase transition possesses the symptoms of both a first- and a second-order transition. Our theoretical interpretation of the transition, undertaken from these standpoints and based on fluctuation theory,[2] is given below.

2. The anomalous variation in the parameters of ultrasonic waves at phase transitions is due to their interaction with the fluctuations of the order parameter. As the latter in a NLC one usually takes the tensor $Q_{\alpha\beta} = S[\bar{\mathbf{n}}_\alpha(\bar{\mathbf{r}})\cdot\bar{\mathbf{n}}_\beta(\bar{\mathbf{r}}) - \frac{1}{3}\delta_{\alpha\beta}]$, where S is the order parameter and $\bar{\mathbf{n}}_\alpha(\bar{\mathbf{r}})$ is the direction vector of a molecule of the NLC. In the region of the nematic phase, the average value of the order parameter $\bar{Q}\neq 0$. Consequently, here, as shown in[2], the principal mechanism will be the well-known Landau–Khalatnikov mechanism.[3] The interaction of ultrasonic waves with fluctuations of the order parameter occurs in both phases.

In view of the inadequacy of the theoretical treatment of the interaction of ultrasonic waves with the order-parameter fluctuations, especially in the nematic phase, we shall briefly describe our ideas on this question. Following the phenomenological description of[2,4], the density of the thermodynamic potential of the NLC in the absence of external fields can be represented in the form

$$\Phi = \Phi_0 + \frac{1}{2}AQ^2 - \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4 + \frac{1}{2}L\left(\frac{\partial Q}{\partial x}\right)^2. \tag{1}$$

For unoriented NLC's this expression will be valid in both the isotropic and the nematic phase. The introduction of the cubic term in (1) is equivalent to the assumption that the phase transition is first-order. For $B=0$ we have the well-known Landau–Khalatnikov theory. Putting, as usual,

$$A = a(T-T^*), \tag{2}$$

we obtain for the average value of the order parameter:

$$\bar{Q} = \begin{cases} 0, & T>T^*, \\ \sqrt{\dfrac{a}{C}}\left(\sqrt{T_1-T^*}+\sqrt{T_1-T}\right), & T<T_1. \end{cases} \tag{3}$$

Here the temperatures T^* and T_1 delimit the region of the metastable state ($T_1 > T^*$). Following[2,3], we find the following relation for the relaxation frequency f_c corresponding to the frequency for the maximum value $\alpha_{\max}$ of the absorption of ultrasonic waves at a given temperature ($\omega\tau = 1$):

$$f_c = \frac{1}{2\pi\tau} = \frac{a}{\pi b}\{T_1 - T + [(T_1-T^*)(T_1-T)]^{1/2}\}, \tag{4}$$

where b is a kinetic coefficient. In principle, it can be determined experimentally from the linear part of the temperature dependence of f_c:

$$\frac{\partial f_c}{\partial(T^\alpha_{\max}-T)} = \frac{a}{\pi b}\left(1+\frac{(T_1-T^*)^{1/2}}{2(T_1-T)^{1/2}}\right). \tag{5}$$

In the case of a second-order phase transition, $T_1 = T^* = T_c$.

In the immediate vicinity of the phase-transition point, besides the Landau–Khalatnikov mechanism we must take into account the order-parameter fluctuations. In this case, it is convenient to expand (1) in a Taylor series. For polycrystalline NLC's we can introduce an effective value of the elastic constant L:

$$L_{\text{eff}} \approx \bar{k}_{ij}/S^2, \tag{6}$$

where the k_{ij} are the Frank elastic constants.[5] Confining ourselves in the following to the model of[6], where it is assumed that the anomalies in the acoustic parameters are due principally to temperature fluctuations, we have for the velocity C and the product of the absorption α and wavelength λ:

$$C = C_{\text{ad}}\left[1-\frac{\gamma_0-1}{2c_p{}^0}\operatorname{Re}\delta\right], \tag{7}$$

$$\alpha\lambda = -\frac{\pi(\gamma_0-1)}{c_p{}^0}\operatorname{Im}\delta.$$

Here $\gamma_0 = c_p^0/c_V^0$, the specific heats $c_p = c_p^0 + \delta$ and $c_V = c_V^0$

$+\delta$, and δ is the change in the specific heat of the NLC near the phase transition. To determine δ we proceed by the classical method of[2,7], which is equivalent to the self-consistent field approximation. As a result, we obtain

$$\delta=\delta(T)\,[f_1(x)-if_2(x)], \tag{8}$$

where the reduced frequency

$$x=\frac{f_0}{f}=\begin{cases}-2A/b\omega, & T<T_c,\\ A/b\omega, & T>T_c,\end{cases}$$

$$\delta(T)=\frac{k_BT^2}{8\pi L_{\text{eff}}^2}\left(\frac{\partial A}{\partial T}\right)^2 r_c=\frac{k_BT^2}{32\pi T_c^2r_0^3(|T-T_c|/T_c)^{1/2}}. \tag{9}$$

In this expression, $r_c=r_0(|T-T_c|/T_c)^{-1/2}$ is the correlation length and k_B is the Boltzmann constant;

$$r_0=\begin{cases}(-L_{\text{eff}}/2aT_c)^{1/2}, & T<T_c\\ (L/aT_c)^{1/2}, & T>T_c\end{cases}.$$

The dispersion functions $f_1(x)$ and $f_2(x)$ coincide with the analogous functions introduced in[7].

In the classical solution, weak noninteracting fluctuations are considered. According to[8], this is valid in the temperature region

$$\left(\frac{\bar{r}}{r_0}\right)^6<\frac{|T-T_c|}{T_c}=t<1,$$

where $\bar{r}$ is the average distance between the particles. In the temperature region $t<(\bar{r}/r_0)^6$, where the fluctuations are no longer small, the scaling hypothesis gives the modern idea of the structure of the substance. In the dynamical case one assumes the existence of a characteristic critical frequency f_c, uniquely determined by the equilibrium correlation length $r_c=r_0(|T-T_c|/T_c)^{-\nu}$, where $f_c=k_BT/6\pi^2\eta r_c^3$, η is the shear viscosity, and ν is a critical index. For most simple nonconducting liquids, $\nu=0.63$.[8] It turns out that the complex bulk viscosity dependent on the external frequency f is determined by a universal function of the reduced frequency:

$$I\left(\frac{f}{f_c}\right)=\int_0^\infty\frac{y^2}{(1+y^2)^2}\,\frac{f/f_c}{K(y)-if/f_c}\,dy, \tag{10}$$

where the ratio of the frequency f_q of the relaxation of the order-parameter fluctuations, which depends on the wave-vector q, to f_c is a universal function of the argument $y=qr_c$:

$$f_q/f_c=K(y)={}^3/_4[1+y^2+(y^3-y^{-1})\operatorname{arctg}y]. \tag{11}$$

The excess ultrasonic absorption coefficient, due to the bulk-viscosity anomaly, is determined by the real part of (10):

$$\alpha\lambda=\frac{k_BT^2v^2g(T)}{\pi\rho T_c^2r_0^3}\left(\frac{|T-T_c|}{T_c}\right)^{-\alpha}\times\operatorname{Re}I\left(\frac{f}{f_c}\right), \tag{12}$$

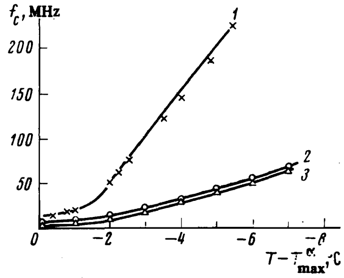

FIG. 2. Temperature dependence of the relaxation frequency: curve 1 is for PPA at $f=10$ MHz, $T_c=136\,°\text{C}$; curve 2 is for MBBA at $f=2$ MHz $T_c=44\,°\text{C}$; curve 3 is for EBBA at $f=2$ MHz, $T_c=73.5\,°\text{C}$.

where ρ is the density, $g(T)=1/c_V$ for simple liquids, and α is the critical exponent of the specific heat. According to scaling theory, $\alpha=2-3\nu$. We note that the expression (12) was obtained by invoking the correlation function in the Ornstein–Zernike approximation. Clearly, therefore, the classical solution and the scaling hypothesis give dependences for $\alpha\lambda$ that are similar in form.

3. All the theories cited give a decrease of the phase velocity as we move away from T_c in both directions. The experimentally observed steeper decay on the side of the NLC phase is clearly due to the marked dominance of the contribution of the Landau–Khalatnikov mechanism over that of the fluctuation mechanism.

Therefore, assuming that the principal contribution to the ultrasonic attenuation is determined by the Landau–Khalatnikov mechanism, we shall use the Mandel'shtam–Leontovich formula for the relaxational absorption, with allowance for a single relaxation time τ, to obtain the temperature dependence of the relaxation frequency in PAA in the nematic region (see Fig. 2). The necessary dispersion parameters can be determined from the graph of the phase velocity. In the same figure (Fig. 2), analogous curves, calculated from the results of[9], are given for MBBA (methoxybenzylidene-butylaniline) and EBBA (ethoxybenzylidene-butylaniline). From the slope of the linear part of the curve it is easy to determine the ratio a/b from formula (5). Estimating the kinetic coefficient η for PAA to be, according to[9], $\eta\approx0.03$ P, we find that $a=(6.8\pm1.5)\times10^5$ erg/cm³ · deg, i.e., practically the same as in MBBA, where $a=6.2\times10^5$ erg/cm³ · deg. The value of a that we have obtained is extremely close to the estimate given in[7]. Using the value of a for MBBA known from other experiments, we estimate the magnitude of the shear viscosity in this NLC to be $\eta=0.11$ P. According to[7], $\eta=0.15$ P, i.e., it coincides, within the limits of the experimental errors, with our calculations from the slope of the curve of $f_c(T)$. We note that the existence of a linear part on the curve of $f_c(T^{\alpha}_{\max}-T)$ does not yet prove the existence of a metastable region. There will also be an analogous dependence in the case of second-order phase transitions.

Analyzing the Mandel'shtam–Leontovich expression for the relaxational absorption and phase velocity, for $\alpha_{\max}\lambda$ we obtain $\omega\tau=f/f_c=1$, and for the velocity $C_{\max}$,

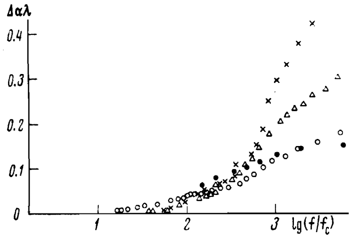

FIG. 3. Dependence of the product of the excess absorption coefficient and wavelength on the reduced frequency in the nematic phase; $r_0 = 9.5$ Å, $\nu = 0.5$; ●– for $f = 0.8$ MHz; ○—for $f = 2.2$ MHz; Δ – for $f = 6.2$ MHz; ×—for $f = 10$ MHz.

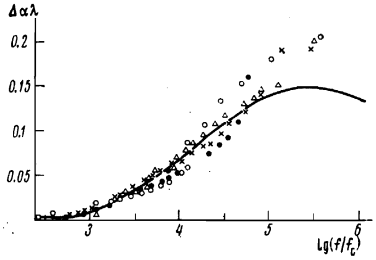

FIG. 4. Dependence of the product of the excess absorption coefficient and wavelength on the reduced frequency is the isotropic phase; $r_0 = 9.5$ Å, $\nu = 0.63$. The solid curve is calculated from formula (12); ○—for $f = 2.2$ MHz; ×—for $f = 6.2$ MHz; ●—for $f = 10$ MHz; Δ—for $f = 14$ MHz.

$\omega\tau = f/f_c \to \infty$. Comparing these results with (4), we find that the temperature $T^{\alpha}_{\max}$ at which the maximum damping of the ultrasonic waves occurs practically coincides with the phase-transition point T_c. In the general case the following inequality should be fulfilled: $T^* < T^{\alpha}_{\max} \leqslant T^{C}_{1\max} \leqslant T_1$. In the table, experimental values of the difference $T^{C}_{1\max} - T^{\alpha}_{\max}$ are given. Once again we note that in the experiment with PAA the value $T^{C}_{1\max}$ always lies above $T^{\alpha}_{\max}$, and $\overline{T^{C}_{1\max} - T^{\alpha}_{\max}} \approx 0.2$ K. From the estimates of[9], $T_1 - T_c \approx 0.1$ K for MBBA, i.e., is evidently of the same order as for PAA.

To analyze the results in the nematic region we shall estimate the range of applicability of the classical and scaling theories in our case. Assuming that the average distance between the molecules is approximately equal to their effective diameter, and using the expressions (6) and (9), we find that, by the classical theory, $r_0 = 9.5$ Å and $\bar{r}/r_0 \sim 1$, i.e., such an estimate is too crude. To estimate the actual contribution of the fluctuation mechanisms in the nematic phase we shall check the uniformity of the experimental results on the increment $\Delta\alpha\,\lambda$ in the ultrasonic absorption as a function of $\log(f/f_c)$ by varying the critical exponent ν. Coincident results are not obtained for the entire NLC region, inasmuch as the lowest scatter occurs for $\nu < 0.3$ near T_c, and for $\nu = 0.52 \pm 0.05$ when $T_c - T > 2$ K (Fig. 3). This, and also the data on the temperature dependence of the phase velocity, indicates that in the nematic phase, besides the Landau–Khalatnikov mechanism, fluctuations describable by the classical theory evidently also make their contribution. Apparently, the presence of order in the system hinders the development of strong fluctuations.

An analogous check on the uniformity in the isotropic region gives satisfactory agreement with scaling theory with $\nu = 0.65 \pm 0.05$ (Fig. 4). Here the quantity g was used as an additional fitting parameter and the data for the shear viscosity were used for η. Thus, no special measurement of the position of the curves along the abscissa was performed. The discrepancy between the calculation and the experimental data near T_c is due to the use of the Ornstein–Zernike approximation for the correlation function in the calculation. (The calculation of the dependence $I(f/f_c)$ from formula (10) was carried out on a MIR-2 computer.) The absence of a level of saturation in the experimental dependence of Fig. 4 is connected with the lack of reliable data for $T - T_c < 0.3$ K.

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