Relaxation processes and propagation of ultrasound in nematic liquid crystals

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A study was made of the influence of relaxation processes on the velocity of ultrasound and the coefficient of its absorption in nematic liquid crystals. Allowance is made for the dependence not only of the pressure but also of the irreversible (viscous) stress tensor on the relaxing parameter, a particular consequence of which is the anisotropy of the velocity of ultrasound. A comparison is made of the calculated results with the experimental data on MBBA. Symmetry of the kinetic coefficients is used to obtain an additional constraint on the number of independent viscosity coefficients.

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Extensive experimental data are now available on the propagation of ultrasound in liquid crystals. In some cases the dependences of the velocity of ultrasound and its absorption coefficient on the acoustic frequency and temperature of a liquid crystal (see, for example, the reviews in Refs. 1 and 2) have been determined. However, difficulties have been encountered in the interpretation of these data. An attempt to provide a phenomenological description of the experimental data is made in Ref. 3 on the basis of Boltzmann-like representations of a "retarded" dependence of the stresses on strains (and other parameters describing the medium). Such a very general analysis makes it possible to describe any dispersion law of sound but specific information on the mechanism of the retardation in question is in practice ignored. However, the relaxation times typical of liquid crystals are fairly long.[2] Therefore, it would be desirable to interpret the experimental data in the spirit of the relaxation theory of Mandel'shtam and Leontovich.[4] This attempt, subject to some additional conditions associated with the anisotropy of liquid crystals, is made below. The temperature dependences of the ultrasonic characteristics are not discussed. It is assumed that the temperature of the system is constant and sufficiently far from a phase transition point. This justifies the neglect of fluctuations.

In accordance with the relaxation theory we shall assume that the state of a liquid crystal is described not only by the density ρ, temperature T, and director n, but by an additional parameter. In general, this parameter is not a scalar but a tensor. The dispersion of sound is in fact dependent on its actual structure and the changes affect not only the coefficients in the formulas but the nature of the functional dependence itself. In the case of sufficiently complex processes the relaxation approach adopted below and the more general approach mentioned above become essentially one and the same. However, we shall consider only one scalar relaxing parameter.

When a small-amplitude acoustic wave is propagating in a homogeneously oriented nematic liquid crystal, we can ignore the forces associated with distortions of the director field because the corresponding terms in the Euler equation are quadratic in the amplitudes of the director oscillations in an acoustic wave. Therefore, we can write down

$$t_{ik}=-p\delta_{ik}+t_{ik}'. \tag{1}$$

Here, t_{ik} is the stress tensor, p is the pressure, and t'_{ik} is the viscous (we prefer to call it irreversible) stress tensor. Since the velocity of sound in a nematic liquid crystal is anisotropic,[1] it is natural to assume that not only the pressure but the irreversible stress tensor depend on the relaxing parameter ξ. Among the many attempts to interpret acoustic experiments in nematic liquid crystals we can find also the assumption that the anisotropy of the velocity of sound is related to relaxation processes (see, for example, Ref. 5), but—to the best of the author's knowledge—this assumption has not been investigated in detail.

The irreversible corrections to the tensor of the moments of the forces M_{ij} are usually neglected (see, however, Ref. 6). Therefore, we shall assume[7]

$$M_{ij}=\varepsilon_{iqk}n_q\partial f/\partial n_{k,j}. \tag{2}$$

Here, f is the density of the free energy of a liquid crystal; $n_{k,j}=\partial n_k/\partial x_j$ (similar notation will be used later); ε_{iqk} is a unit antisymmetric tensor; the repeated indices indicate summation. The law of conservation of momentum in the presence of internal moments of the forces gives[8]

$$M_{ij,j}=\varepsilon_{ijk}t_{jk}. \tag{3}$$

The principle of symmetry of the kinetic coefficients and the assumption that the irreversible stress tensor is dependent on ξ yield the relationship between the expression for t'_{ik} and the law for relaxation of ξ. We can find this relationship if, in turn, we know the expression for the rate of rise of entropy because of irreversible processes. This expression is obtained in Ref. 7 but without allowance for the additional parameters. In the presence of an additional scalar parameter, it becomes

$$\rho T\dot{\sigma}=t'_{(ik)}V_{(i,k)}+\Gamma_i\Omega_i-\frac{\partial f}{\partial\xi}\dot{\xi}. \tag{4}$$

Here, σ is the entropy per unit mass; the point above a symbol denotes the total derivative with respect to time; V is the velocity vector; the indices in paren-

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theses imply symmetrization; and

$$\Gamma_i = e_{ipk} t_{pk}', \quad \Omega = [\mathbf{n}\dot{\mathbf{n}}] - {}^1/_2 \operatorname{curl} \mathbf{V}.$$

We note that Eqs. (2) and (3) give

$$\Gamma_i n_i = 0. \tag{5}$$

We must bear in mind that the free energy $f = f(\rho, T, n_i, n_{i,k})$ is a scalar and, consequently, it is invariant under rotation.

In addition to the parameter ξ, we shall consider its equilibrium value $\bar{\xi} = \bar{\xi}(\rho, T, n_i, n_{i,k})$. The equilibrium value of ξ corresponds to a free energy minimum

$$\partial f / \partial \xi |_{\xi = \bar{\xi}} = 0.$$

Therefore, for low values of $\zeta = \xi - \bar{\xi}$ we can assume approximately that

$$\frac{\partial f}{\partial \xi} = A\zeta; \quad A = \frac{\partial^2 f}{\partial \xi^2}\Big|_{\xi = \bar{\xi}}.$$

We shall now find the expressions for t_{ik}' and ξ'. The arguments in these expressions are the quantities $V_{(i,k)}$, Ω_i, and ζ. In the application of the principle of symmetry of the kinetic coefficients the important feature is the behavior of these quantities under time reversal: $V_{(i,k)}$ and Ω_i are multiplied by (-1), whereas in the case of the parameter ξ it is natural to assume that it does not change.[1)] Bearing this point in mind, we can write down (compare with Ref. 7)

$$t_{(ik)}' = B_{ikpq} V_{(p,q)} + \gamma_2 e_{pj(i} n_{k)} n_j \Omega_p + (a\delta_{ik} + b n_i n_k)\zeta; \tag{6}$$

$$\Gamma_p = g_{pk}\Omega_k + \gamma_2 e_{pj(i} n_{k)} n_j V_{(i,k)}; \tag{7}$$

$$\dot{\xi} = -\frac{\zeta}{\tau} + \frac{1}{A}(a\delta_{ik} + b n_i n_k) V_{(i,k)}. \tag{8}$$

We can easily show that these equations represent the most general linear equations compatible with the tensor structure of the parameters and the principle of symmetry of the kinetic coefficients[2)] and they relate the forces and fluxes (see Ref. 9) in the situation under discussion. However, the structure of the tensors g_{pk} and B_{ikpq} can be specified more closely. It follows from Eqs. (5) and (7) that

$$g_{pk} = \gamma_1(\delta_{pk} - n_p n_k)$$

(γ_i is a constant). The tensor B_{ikpq} can be written in the form

$$B_{ikpq} = \mu_1 \delta_{ik}\delta_{pq} + \mu_2 n_i n_k \delta_{pq} + \mu_3 \delta_{ik} n_p n_q + \mu_4 n_i n_k n_p n_q + \mu_5 \delta_{i(p}\delta_{q)k} + \mu_6 n_{(i}\delta_{k)(p} n_{q)} \tag{9}$$

(μ_i are constants). Again, it follows from the principle of symmetry of the kinetic coefficients that

$$B_{ikpq} = B_{pqik}. \tag{10}$$

Hence, we obtain

$$\mu_2 = \mu_3. \tag{11}$$

If we ignore the additional relaxing parameter, we find that the coefficients μ_i are identical with the corresponding viscosity coefficients of Ref. 7.[3)] However, explicit allowance for the parameter ξ makes its own contribution to the viscosity coefficients. This follows directly from Eqs. (8) and (9), because of low frequencies we can ignore the derivative $\dot{\xi}$ in Eq. (8) and express ζ directly in terms of $V_{(i,k)}$. Nevertheless, Eq. (11) still applies in the case of the true viscosity coefficients because its derivation is independent of whether we are considering or ignoring the additional relaxing parameter. It follows that the number of independent viscosity coefficients is seven and not eight (compare with Ref. 7):

$$\mu_1,\ \mu_2 = \mu_3,\ \mu_4,\ \mu_5,\ \mu_6,\ \gamma_1,\ \gamma_2$$

(one must however bear in mind the renormalization of μ_i mentioned above). We shall point out also that Eq. (8) describing relaxation of the parameter ξ is more complex than that in the simple theory of Mandel'shtam and Leontovich.[4]

We shall now consider the propagation of a small-amplitude acoustic wave in a nematic liquid crystal. As usual, we shall go over to a linearized version of the equations of motion and seek a solution in the form of a monochromatic wave. We now have to include Eq. (8) among the equations under discussion. Since the series of operations required is relatively simple and well known (see Refs. 10 and 4), we can give the results directly. However, we must first make the following comments.

As in the usual relaxation theory of isotropic liquids, the pressure p should be regarded as a function of the variables ρ and ξ. The amplitudes of oscillations of the parameter ξ, of the density, and of the director components are easily eliminated from the equations of motion. This yields for an acoustic wave an equation containing only the amplitudes of the mechanical vibrations u_i. It represents a linear homogeneous equation for u_i and, because of the anisotropy of a liquid crystal, the acoustic wave is strictly speaking no longer purely longitudinal. We shall ignore this aspect and assume that the acoustic wave is approximately longitudinal.

Consequently, the velocity of sound c is described by the following equation:

$$c^2 = c_0^2 + \frac{i\omega\tau}{1 - i\omega\tau}\left[\left(\frac{H}{A\rho} - N - \frac{a + b\cos^2\theta}{A\rho}\right)(a + b\cos^2\theta) + HN\right] - i\omega(q_1 + q_2\cos^2\theta + q_3\cos^4\theta), \quad H = \frac{\partial p}{\partial \xi}\Big|_{\rho,\sigma}. \tag{12}$$

Here, $\omega = 2\pi\nu$ is the angular frequency; $c = c_0$ in the limit $\omega \to 0$; θ is the angle between the director n and the acoustic wave vector k; $N = \bar{\xi}/\bar{\rho}$ is the ratio of the amplitude of oscillations of the equilibrium value of the parameter ξ to the amplitude of oscillations of the density in an acoustic wave; finally, q_1, q_2, and q_3 can be expressed in terms of the coefficients μ_i exactly as in the usual allowance for the viscosity of a nematic liquid crystal (see Ref. 10), but we must allow for Eq. (11).

We shall introduce $z = (c/c_0)^2$. The absorption coefficient of sound can be described approximately by

$$\varkappa = 2\operatorname{Im}(k) = \frac{2\omega}{c_0}\operatorname{Im}(z^{-1/2}) \approx -\frac{\omega}{c_0}\operatorname{Im}(z). \tag{13}$$

We have made allowance here for the fact that the inequality $|1 - z| \ll 1$, usually applies. The absorption coefficient describes the intensity and, therefore, $\operatorname{Im}(k)$ is multiplied by 2. Measurements of the value of

$\Delta\varkappa = \varkappa(\theta, \nu) - \varkappa(90°, \nu)$ were made on MBBA in Ref. 11 for different values of θ and ν. It follows from Eqs. (12) and (13) that

$$\Delta\varkappa = \frac{\omega^2}{c_0}\left[\frac{\tau(\alpha_1\cos^2\theta+\alpha_2\cos^4\theta)}{1+\omega^2\tau^2} + \beta_1\cos^2\theta+\beta_2\cos^4\theta\right],$$

where α_1, α_2, β_1, and β_2 are related by simple expressions to the coefficients of Eq. (12). These coefficients and also the values of τ were determined numerically on a computer to obtain the best fit with the experimental data of Ref. 11. This gave $\tau = 18.3$ nsec, $\alpha_1 = 0.506$, $\alpha_2 = 0.044$, $\beta_1 = -0.55$ nsec, $\beta_2 = 0.953$ nsec. The number of decimal points in these constants does not represent the true precision. It is difficult to estimate the precision because the determination of the constants is essentially a solution of the inverse problem.

In the case of α_2 an independent estimate can be obtained as follows. If the coefficient of viscosity μ_4 (the true, i.e., the renormalized coefficient) is governed entirely by relaxation of the parameter ξ, we can readily show that $\alpha_2 = \mu_4/c_0^2\rho\tau$. Using the known value of $\mu_4 = 6.4$ cP (Ref. 7), we find that $\alpha_2 = 1.5\times10^{-4}$, which is far outside the limits of error of the above method for the determination of the constants. In the case of the other four quantities the error is not as large. In particular, the value of τ is in satisfactory agreement with the available estimates of the acoustic relaxation time of MBBA (values of 10–20 nsec are given in Refs. 1, 4, and 12).

Figures 1 and 2 show the dependences of $\Delta\varkappa$ on the frequency and angle θ as well as the experimental results. The attenuation was determined in Ref. 13 in units of decibel per second. These quantities were converted to reciprocal centimeters by assuming that the velocity of sound was 1.55 km/sec (Refs. 1 and 14). The absorption coefficients in Refs. 13 and 15 were doubled in order to convert them into the intensity absorption coefficients. The temperatures of MBBA at which measurements were made in Refs. 11, 12, and 13 were not exactly equal but similar. We can see from Figs. 1 and 2 that Eq. (12) provides generally a satisfactory description of the experimental data in a fairly wide range of frequencies, although some points de-

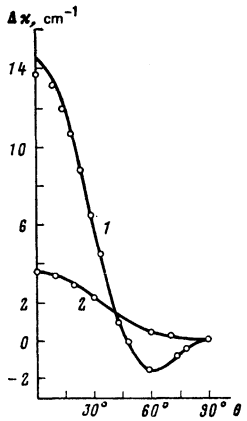

FIG. 2. Dependences of $\Delta\varkappa$ on the angle between the direction of propagation of the acoustic wave and the director. The continuous curves are calculated for two frequencies (MHz): 1) 85; 2) 25. The experimental results (○) are taken from Ref. 11.

viate from the calculated curves by amounts exceeding the errors estimated in the cited papers.

Knowing the values of τ, α_i and β_i and also assuming that $c_0 = 1.55$ km/sec, we find that

$$\Delta c = c(\theta, \nu) - c(90°, \nu)$$

(here c denotes the real part of the velocity). This quantity was measured in Refs. 5 and 15. Figure 3 gives the results of calculations and the experimental data.[15] The discrepancy from the experimental results is now greater and the shapes of the curves are different. The measurements in Ref. 5 were made at lower frequencies, precisely in the range where the influence of relaxation processes is strong. The results of measurements of Δc at the frequency of 10 MHz (Ref. 5) were approximately half those found by calculation, but in this case the shapes of the dependences of Δc on θ were approximated satisfactorily.

It is difficult to say why these discrepancies occur. It is possible that the real relaxation processes are more complex (for example, the relaxing parameter may be a tensor or there may be several relaxing para-

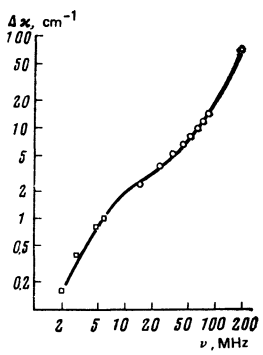

FIG. 1. Frequency dependence of $\Delta\varkappa$ for the propagation of sound parallel to the director. The continuous curve is calculated and the experimental results (denoted by □, ○, and Δ) are taken from Refs. 13, 11, and 15, respectively.

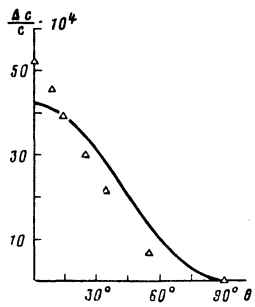

FIG. 3. Dependence of the relative difference between the velocities of sound on the angle between the direction of propagation of the acoustic wave and the director at 200 MHz. The continuous curve is calculated. The experimental results (Δ) are taken from Ref. 15.

meters with similar relaxation times—see Ref. 16). However, we must make the following comment. The quantity Δc is usually small (in the case of MBBA it is of the order of a tenth of a percent) and it is related to dispersion. However, if dispersion and absorption do exist, the very concept of the velocity of sound requires refinement and the velocity may depend on the measurement method (see Ref. 17). This aspect is not discussed in Refs. 5 and 15.

Different points of view are held on the physical nature of the relaxing parameter ξ. We prefer to assume (as is done in Ref. 7) that in the investigated range of frequencies the relaxing quantity is the order parameter, i.e., a quantity representing the local degree of order of the mutual orientation of molecules. This point of view is suggested by the results of an investigation of the temperature dependence of the acoustic relaxation. According to Ref. 12, the absorption coefficient of sound of the isotropic phase of MBBA can be described by the usual relaxation formula

$$\varkappa=\omega^2\left[\frac{A}{1+\omega^2\tau^2}+B\right]$$

(A and B are constants). The coefficient A decreases rapidly on increase in temperature and at 70 °C (approximately 30 °C above the transition point) the relaxation is practically undetectable. In this range of temperatures the relaxation time decreases rapidly on increase in T, whereas in the nematic phase the value of τ is practically constant. On the other hand, the pretransition range of temperatures of the isotropic phase of nematics is characterized by a strong tendency for the ordering of the molecular orientation. This is manifested by a large coherence length (orientation-correlation radius), by anomalously high values of the Kerr constant, and by other phenomena.[7] A comparison of these results confirms the above hypothesis of the physical nature of the relaxing parameter.

[1)] The physical nature of the parameter ξ is discussed in greater detail below.

[2)] It should be noted that Γ is independent of ξ. If instead of the scalar ξ we consider the tensor relaxing parameter ξ_{ik}, such a dependence is obtained. The complication of the equations due to this dependence gives rise to a more complex dispersion law of sound.

[3)] The designations of the coefficients have been altered here.

[1]A. P. Kapustin, Éksperimental'nye issledovaniya zhidkikh kristallov (Experimental Investigations of Liquid Crystals), Nauka, M., 1978, Chaps. V-VII.

[2]G. G. Natale, J. Acoust. Soc. Am. **63**, 1265 (1978).

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

[4]L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred, Gostekhizdat, M., 1944 (Fluid Mechanics, Pergamon Press, Oxford, 1959), §§ 59, 60.

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

[6]É. L. Aéro and A. N. Bulygin, Zh. Tekh. Fiz. **42**, 880 (1972) [Sov. Phys. Tech. Phys. **17**, 694 (1972)].

[7]P. G. de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford, 1974 (Russ. Transl., Mir, M., 1977), Chaps. 3 and 5.

[8]Yu. I. Sirotin and M. P. Shaskol'skaya, Osnovy kristallogiziki (Fundamentals of Crystal Physics), Nauka, M., 1975, §50.

[9]S. R. de Groot and P. Mazur, Nonequilibrium Thermodynamics, North-Holland, Amsterdam, 1962 (Russ. Transl. Mir, M., 1964).

[10]D. Forster, T. C. Lubensky, P. C. Martin, J. Swift, and P. S. Pershan, Phys. Rev. Lett. **26**, 1016 (1971).

[11]G. C. Wetsel Jr, R. S. Speer, B. A. Lowry, and M. R. Woodard, J. Appl. Phys. **43**, 1495 (1972).

[12]P. Martinoty and S. Candau, C. R. Acad. Sci. Ser. B **271**, 107 (1970).

[13]A. E. Lord Jr and M. M. Labes, Phys. Rev. Lett. **25**, 570 (1970).

[14]D. Eden, C. W. Garland, and R. C. Williamson, J. Chem. Phys. **58**, 1861 (1973).

[15]J. C. Bacri, J. Phys. (Paris) **35**, 601 (1974).

[16]K. Miyano and J. B. Ketterson, in: Physical Acoustics: Principles and Methods (ed. by W. P. Mason and R. N. Thurston), Vol. 14, Academic Press, New York, 1979, p. 93.

[17]M. Élices and F. Garcia-Moliner, in: Physical Acoustics: Principles and Methods (ed. by W. P. Mason), Vol. 5, Academic Press, New York, 1968, p. 163 (Russ. Transl. Mir, M., 1973, p. 192).

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