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PROPAGATION OF SOUND IN STRONGLY VISCOUS LIQUIDS

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Experimental data on anomalous absorption and dispersion of sonic, shear, and electromagnetic waves in strongly viscous liquids show that the relaxation theory of wave propagation is not applicable to these liquids. In particular, with increase of frequency, the absorption coefficient per wavelength and the departure of the propagation velocity from the limiting high frequency value tend to zero as $1/\sqrt{\omega}$ (ω is the frequency). Since such an asymptotic behavior is also characteristic of microinhomogeneous media with diffusion exchanges taking place between the components (for example, emulsions), it is suggested that a highly viscous liquid is a microinhomogeneous medium, one of the components of which is present in the form of inclusions with an ordered molecular arrangement in the second (disordered) component. It is assumed that in the passage of the wave, the ordered part undergoes a rearrangement and the equilibrium (relative to the second component) number of holes in it changes. The disturbed equilibrium with respect to the number of holes is restored by the diffusion between the components. The phase shift of this process relative to the incident wave results in anomalous absorption and dispersion.

In its simplest form, the theory for sound waves is formally identical with the theory of thermal dispersion and absorption of sound in emulsions. The theory is refined and the shear waves are considered by taking into account shear stresses due to the microinhomogeneities of the medium, it being assumed that the static displacement viscosity of the medium is due to the usual Maxwellian relaxation mechanism. In the analysis of electromagnetic waves, it is assumed that the mechanism related to the microinhomogeneity of the medium is superimposed on the usual Debye relaxation mechanism. In all cases, the velocity and the absorption of the waves can be expressed in terms of the limiting high frequency and low frequency velocity values, in terms of the absorption coefficient at low frequency, and in terms of the viscosity coefficient of the medium. No free parameters are employed in the calculations. Specific calculations of the wave velocity and absorption are performed for a number of highly viscous liquids for which the necessary data could be found in the literature (glycerine, butanediol, hexanetriol, 2-methylpentanediol-2,4); a spherical shape of the ordered inclusions is assumed. Good agreement has been obtained between the theory and experimental data for the indicated liquids throughout the dispersion region. The characteristic temperature for the appearance of ordered regions is presented. Some possible ways for determining the sizes of the ordered regions at various temperatures are indicated. According to a preliminary estimate, about six glycerine molecules fit into the linear dimensions of the ordered region at 22° C. The size of this region should increase with decrease in temperature.

1. INTRODUCTION

As is well known, in almost all liquids the ultrasonic absorption is larger and the hypersonic absorption is much smaller than follows from the Stokes theory of viscous absorption. About 30 years ago, a relaxation theory of sound absorption in liquids explaining this anomaly was set up by Mandel'shtam and Leontovich.[1] The theory also predicted dispersion of the sound velocity which was discovered later in some liquids (first by Shpakovskiĭ[2] in the ultrasonic frequency region and by Fabelinskiĭ and Shustin[3] in the hypersonic region). Attempts at the application of relaxation theory to a highly viscous liquid in which anomalous absorption and velocity dispersion are also observed, have not been successful. The aim of the present research was the construction of a theory of sound propagation in such liquids.

Let us sum up the results of the experimental investigation of the propagation of waves in highly viscous liquids. First we make the following note. In highly viscous liquids, the static shear viscosity η changes markedly (by several orders of magnitude) upon change in temperature by a few tens of degrees; the volume viscosity η' is proportional to the shear viscosity and has the same order of magnitude. It has been shown that the acoustical characteristics of highly viscous liquids (sound velocity v and the damping coefficient δ referred to the frequency) depend on the sound frequency ω and the viscosity in virtually exactly the same way: the frequency and temperature changes of v and δ/ω for a given liquid depend on the product $\omega\eta$ and not on the parameters separately. Consequently, these characteristics can be regarded as depending only on the nondimensional product $\omega\tau$, where τ is some characteristic time interval proportional to the viscosity; the physical meaning of this time interval is made clear in Sec. 3. In connection with this circumstance, the acoustic characteristics of highly viscous liquids are usually measured at a fixed frequency by varying only the temperature and thus at the same time changing the viscosity. It is more convenient to change the temperature than to carry out measurements at different frequencies, and the results that are obtained can be treated both as frequency dependences and viscosity (temperature) dependences. We note that a small departure from such a rule is still observed experimentally and consists in a slow growth of the limiting value of the sound velocity (at high and low frequencies) with decrease in temperature. This departure is taken into account in what follows both in the theory and in the comparison between theory and experiment.

In accord with the data found in the literature, the following characteristics of the dependence of the velocity and sound absorption on the value of $\omega\tau$ in a number of highly viscous liquids are typical.

a) For each temperature, there are limiting low-frequency and limiting high-frequency values of the sound velocity, v_0 and v_∞, in the given liquid. The difference between the high-frequency limiting value and the value v of the sound velocity at a certain frequency ω decreases asymptotically like $1/\sqrt{\omega\tau}$ with increase of the quantity $\omega\tau$. Relaxation theory gives a fall-off like law $1/(\omega\tau)^2$ for this difference.

b) At low frequencies the quantity δ/ω is proportional to $\omega\tau$, as in the relaxational case, but at high frequencies this quantity falls off like $1/\sqrt{\omega\tau}$, while relaxation theory leads to a fall off like $1/\omega\tau$.

c) The maximum value of δ lies close to the beginning of the dispersion curve, and not at its middle as follows for the relaxation case; a graph of the dependence of absorption on $\omega\tau$ is much broader than for the relaxational case.

d) In the entire dispersion region, the quantity $(v^2 - v_0^2)/(v_\infty^2 - v^2)$ is directly proportional to $\omega\tau$, while for the relaxational case (for small dispersion) this quantity is proportional to $(\omega\tau)^2$.

Thus, in spite of a certain qualitative agreement, the relaxation mechanism actually cannot explain the frequency and temperature dependence of the sound velocity and absorption in highly viscous liquids. It has been found by Fabelinskiĭ and Krivokhizha[4] that quantitative agreement with experiment for the dispersion of sound velocity could be materially improved if it was assumed that the relaxation time is not constant for a given material at a given temperature but is proportional to the square root of the frequency. It is clear that such an assumption is not compatible in principle with relaxation theory. This observation, which formulates the dependence of the acoustical characteristics of the medium on the square root of the frequency, is the starting point in the development of the theory set forth in the present research.

In highly viscous liquids, in addition to the longitudinal elastic (sonic) waves, there can also be propagated transverse elastic (shear) waves, for which there is also observed an anomalous absorption and dispersion. The same also holds for electromagnetic waves in strongly viscous liquids. In a given strongly viscous liquid, the regions of dispersion are identical for all these three types of waves; for a fixed frequency the temperatures at which the values of the absorption for sonic and electromagnetic waves reach a maximum are virtually identical (there are no data in the literature on the absorption of shear waves). Such an identical behavior allows us to assume that some common mechanism lies behind the observed behavior of viscous liquids. Relaxation theory, which has customarily been called upon up to the present time for an explanation of the anomalous absorption and dispersion in liquids, disagrees with experiment for each of these types of waves. The theory given below is in excellent agreement with experiment for all types of waves.

2. HYPOTHESIS ON THE MICROINHOMOGENEOUS STRUCTURE OF HIGHLY VISCOUS LIQUIDS

In the search for a mechanism which could explain the acoustic behavior of highly viscous liquids, we turned our attention to the well known characteristics of sound propagation in microinhomogeneous media. A medium is called microinhomogeneous if it contains two or more components and can be divided into regions which are small in comparison with the wavelength but which still contain many heterogeneous parts. With respect to the passage of a wave, such regions can be regarded as lying in a uniform pressure field. The features of the acoustic behavior of such media are determined by nonacoustic processes which take place between the components.

The first microinhomogeneous medium (a suspension of heavy particles in liquid) was investigated acoustically at the suggestion of L. I. Mandel'shtam by Rytov, Vladimirskiĭ and Galanin[5] as a model of a relaxing medium, admitting of a calculation in terms of the mechanics of continuous media. Actually, in such suspensions, there are also anomalous absorption and dispersion of sound, which are characteristic for relaxing media. But in the suspension the mechanism constitutes exchange of energy between different parts of the medium (between different components), and this exchange takes place by diffusion (viscous waves) in contrast with the mechanism of the relaxation process, where the exchange takes place between different degrees of freedom in each given particle. Therefore, the frequency dependences are different for velocity and sound absorption in the suspension than for a relaxing liquid. In particular, the asymptotic change of the velocity and sound absorption at high frequencies is described in a suspension by the same dependence on the half power of the frequency as for strongly viscous liquids. Such an asymptotic dependence also characterizes microinhomogeneous media, in which the exchange of energy between components takes place by means of the thermal conductivity: polycrystals, emulsions, liquids containing gas bubbles.1)

In connection with this formal identity between the acoustic behavior of viscous liquids on the one hand and microinhomogeneous media on the other (Mikhaĭlov was the first to note this property[7]) we introduce the following hypothesis on the structure of highly viscous liquids.[8, 9]

We assume that the highly viscous liquid is a microinhomogeneous two-component medium. We further assume that the condensation in the components is determined in an adiabatic process, in addition to the pressure or some quantity which takes into account ξ_1 in the first component and ξ_2 in the second.2) We assume that in the first component this quantity is one more independent thermodynamic variable (in addition to the entropy and the pressure); its equilibrium value in the absence of excitation we denote by ξ_1^{00}; for a change in pressure by a quantity p the equilibrium value will take on a changed value $\xi_1^0 = \xi_1^{00} + p\partial\xi_1^{00}/\partial p$. Following a rapid change in pressure, the actual value of ξ_1 will not take on the equilibrium value and will differ from it by the quantity $\xi_1' = \xi_1 - \xi_1^0$. We shall assume that in the first component the quantity ξ_2 is not an independent thermodynamic variable. Departure of the actual value of ξ_2 from the equilibrium value ξ_2^0 will be denoted by $\xi_2' = \xi_2 - \xi_2^0$. Finally, we shall assume that for different values of ξ_1' and ξ_2' equalization between the components of these quantities will begin, taking place according to the diffusion law. The delay of such an equilization relative to a change in the pressure leads to the anomalous absorption and dispersion of the sound velocity. The physical picture which holds for this phenomenological scheme will be given in Sec. 4.

On the basis of the assumed hypothesis of the microinhomogeneous structure of the liquid, we can give a phenomenological theory of the propagation of sound waves in it. In the next section, a simplified variant of the series is expounded; the simplification lies in the neglect of shear stresses in the passage of the sound wave. In the succeeding sections, a molecular treatment of the phenomenon is given and a more precise variant of the theory of sound propagation is set forth, which takes into account shear stresses, and a theory of shear and electromagnetic waves is also given. The results of calculation are compared with the experimental data found in the literature.

We note that in addition to the mentioned diffusion and exchange mechanism, which is brought about by the microinhomogeneities of the structure of the medium, local processes of the relaxation type can also take place in it, not connected with the inhomogeneity; the effects of the two types are additive (see Secs. 5 and 6 below).

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1) The asymptotic half-power dependences on the frequency were also obtained by Levanyuk [6] in the calculation of the thermal fluctuations of the transition parameter for the velocity and absorption of sound near the point of second order phase transition.

2) Here and below we shall denote by the indices 1 and 2 the quantities referring respectively to the first and to the second components; we shall omit the indices in writing the average quantities and in expressions which have the same form for each of the components.

3. SIMPLIFIED THEORY OF THE PROPAGATION OF SOUND WAVES

Upon neglect of shear stresses, we can assume that the equalization of the quantities ξ_1' and ξ_2' takes place in a way that is formally analogous to the equalization of temperatures in two component emulsions upon passage of the wave.[10, 11] 3) In the emulsion, an increase in the pressure produces a different adiabatic heating of the components, and the disrupted temperature equilibrium is restored by means of the thermal conductivity. Since the acoustic condensation in the medium for a given pressure depends on the temperature, such an equalization, taking place with a delay relative to the change in pressure, leads to an additional (thermal) damping and to dispersion of the sound velocity. Such a similarity of the mechanisms of absorption and dispersion allows us to perform a simplified calculation according to the model of calculation of acoustical properties of the emulsion by substituting the quantity ξ' in the corresponding formulas in place of the temperature increase. Such a calculation is carried out in the following way.

The quantities v and δ are determined by the relation

$$1/v + i\delta/\omega = \sqrt{\rho s/p}, \tag{1}$$

where p is the acoustic pressure, ρ is the density, and s the mean (complex) compression of the medium; the time dependence is chosen in the form $e^{-i\omega t}$. Averaging must be carried out over a section that is small in comparison with the wavelength but which still contains many different regions. The condensation of any component at each point is found from an equation of the form

$$s = p/K + f\xi'. \tag{2}$$

In these equations, the temperature does not appear, since the process of some propagation is assumed to take place without heat exchange; K is the adiabatic modulus of the bulk elasticity for the equilibrium value of ξ; $f = (\partial s/\partial\xi')_p$.

The averaged condensation is found from the formula

$$s = \frac{1}{V_1 + V_2}\left(\int_{V_1} s_1 dV_1 + \int_{V_2} s_2 dV_2\right), \tag{3}$$

where V_1 and V_2 are volumes filled respectively by the first and second components. The spatial distribution of the quantity ξ' is found from the corresponding diffusion equation

$$\frac{\partial\xi_1'}{\partial t} = D_1\Delta\xi_1' - \frac{\partial\xi_1^{00}}{\partial p}\frac{\partial p}{\partial t}, \qquad \frac{\partial\xi_2'}{\partial t} = D_2\Delta\xi_2', \tag{4}$$

where D_1 and D_2 are the diffusion coefficients. For a harmonic process, these equations take the form

$$\Delta\xi_1' + 2in_1^2\xi_1' + 2in_1^2\frac{\partial\xi_1^{00}}{\partial p}p = 0, \qquad \Delta\xi_2' + 2in_2^2\xi_2' = 0,$$

where $(1 + i)n = \sqrt{i\omega/D}$ is the (complex) wave number of the diffusion waves. The solutions must satisfy the boundary conditions: on the boundaries between different components, the following equalities must hold

$$\xi_1' = \xi_2', \qquad D_1\nabla\xi_1' = D_2\nabla\xi_2'. \tag{5}$$

In what follows we shall assume that the diffusion coefficients are identical for both components. We shall choose the specific model under the assumption that the first component is contained inside the second in the form of spherical inclusions of radius a, located sufficiently far from one another that one can neglect their diffusive interaction. It can be shown that in the dispersion region the shape of the inclusion has little effect on the result; this justifies the choice of the spherical shape, which is convenient for calculation. The desired solutions have the form*

$$\xi_1' = -\frac{\partial\xi_1^{00}}{\partial p}p + A\frac{\mathrm{sh}[(1-i)nr]}{r}, \qquad \xi_2' = B\frac{e^{-(1-i)nr}}{r}.$$

Eliminating the integration constants A and B by means of the boundary conditions, and substituting the results of the expression (2), we find, in accord with (3), the average modulus of volume elasticity in the form

$$K = \frac{p}{s} = \left[\Phi\left(\frac{1}{K_1} - f_1\frac{\partial\xi_1^{00}}{\partial p}\right) + (1-\Phi)\frac{1}{K_2} + i\Phi(f_1 - f_2)\frac{\partial\xi_1^{00}}{\partial p}F(\omega\tau)\right]^{-1}. \tag{6}$$

Here we have introduced the notation $\Phi = V_1/(V_1 + V_2)$, $\omega\tau = (na)^2$,

$$F(\omega\tau) = \frac{3}{2}\frac{1}{\omega\tau} \times \frac{[1 + (1-i)\sqrt{\omega\tau}]\{(1-i)\sqrt{\omega\tau} - \mathrm{th}[(1-i)\sqrt{\omega\tau}]\}}{(1-i)\sqrt{\omega\tau}\{1 + \mathrm{th}[(1-i)\sqrt{\omega\tau}]\}}. \tag{7}†$$

The physical meaning of the time interval $\tau = a^2/2D$ is the time of diffusion equalization of the quantity ξ' over a distance a. Since τ must be proportional to viscosity, then one can take D to be inversely proportional to the viscosity. This

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[3)] Corrections are given in [11] for certain errors in the formulas of [10].

*sh ≡ sinh.

†th ≡ tanh.

means that at constant frequency the length of the diffusion wave will be inversely proportional to the square root of the viscosity and therefore it will fall off rapidly upon decrease in temperature. Thus, at low temperatures, the diffusion interaction will be virtually absent for any values of Φ up to those very close to unity; for high temperatures, a sufficient smallness of the concentration Φ is required for this case.

The asymptotic values of the functions $F(\omega\tau)$ are given by the formulas

$$F(\omega\tau)={}^4/_5\omega\tau-{}^2/_3(\omega\tau)^{3/2}-i[1-{}^2/_3(\omega\tau)^{1/2}],\qquad \omega\tau\ll 1,$$

$$F(\omega\tau)={}^3/_4(1-i)\,/\sqrt{\omega\tau},\qquad \omega\tau\gg 1.$$

Limiting values of the elastic modulus of the medium for approach of the frequency to zero and to infinity are given in the form

$$K_0=\left[\Phi\left(\frac{1}{K_1}-f_2\frac{\partial\xi_1^{00}}{\partial p}\right)+(1-\Phi)\frac{1}{K_2}\right]^{-1},\tag{8}$$

$$K_\infty=\left[\Phi\left(\frac{1}{K_1}-f_1\frac{\partial\xi_1^{00}}{\partial p}\right)+(1-\Phi)\frac{1}{K_2}\right]^{-1}.\tag{9}$$

Consequently, (6) can be rewritten in the form

$$K=\left[\frac{1}{K_\infty}+i\left(\frac{1}{K_0}-\frac{1}{K_\infty}\right)F(\omega\tau)\right]^{-1}.\tag{10}$$

Then, in accordance with (1), we find

$$\frac{1}{v}+i\frac{\delta}{\omega}=\frac{1}{v_\infty}\left[1+i\frac{v_\infty^2-v_0^2}{v_0^2}F(\omega\tau)\right]^{1/2}.\tag{11}$$

For a given temperature, the quantity τ can be determined from the limiting value of the loss at low frequencies. Indeed, the asymptotic value of δ/ω for $\omega\tau\ll 1$ is equal to ${}^2/_5\,\omega\tau(v_\infty^2-v_0^2)/v_0v_\infty^2$. Equating this quantity to the Stokes value

$$\frac{\delta}{\omega}=\frac{2}{3}\frac{\omega}{\rho v_0^3}\left(\eta+\frac{3}{4}\eta'\right),$$

which takes both viscosity coefficients into account and is obtained directly from experiment at low frequencies, we find

$$\tau=\frac{5}{3}\frac{v_\infty^2}{\rho v_0^2}\frac{\eta+{}^3/_4\eta'}{v_\infty^2-v_0^2}.\tag{12}$$

At low frequencies, the correction to the limiting low frequency value of the velocity is of the order of $(\omega\tau)^{3/2}$;

$$v=v_0\left[1+\frac{1}{3}\frac{v_\infty^2-v_0^2}{v_\infty^2}(\omega\tau)^{3/2}\right].$$

We recall that for a relaxing mechanism, the corresponding correction is of the order of $(\omega\tau)^2$.

At high frequencies, we find the following asymptotic expressions for the sound velocity in the absorption coefficient:

$$v=v_\infty\left(1-\frac{3}{8}\frac{v_\infty^2-v_0^2}{v_0^2}\frac{1}{\sqrt{\omega\tau}}\right),$$

$$\frac{\delta}{\omega}=\frac{3}{8}\frac{v_\infty^2-v_0^2}{v_0^2v_\infty}\frac{1}{\sqrt{\omega\tau}}.$$

We thus see that items a) and b) of the summary of experimental data given in Sec. 1 are obtained automatically from the assumed theory. For a more detailed comparison of theory with experiment, the entire dispersion range was investigated. Here, the real and imaginary parts of the function $F(\omega\tau)$ were taken into account (Fig. 1) and the theoretical values of the sound absorption and velocity were computed for a number of liquids. We used in this case the experimental data available for these liquids on the asymptotic values of the sound velocity at low and high frequencies and on the values of the low frequency absorption coefficient of sound, and the viscometric data on the static viscosity of these liquids. In Figs. 2–6, the solid curves give the theoretical expressions for the velocity and the absorption coefficient in different liquids and the experimental points are plotted. The dashed lines in all figures denote the limiting values of the velocity of sound, v_0 and v_∞, obtained from the experiment. In addition to the fact that all four points of the summary of experimental data are shown to be satisfied, we see a very close agreement of theory with experiment throughout all the dispersion regions for the liquids investigated. In Figs. 7 and 8 the excellent agreement of the assumed theory with experiment is also illustrated; moreover, the disagreement of the relaxation theory with experiment is also demonstrated. Thus, in Fig. 7, a comparison is

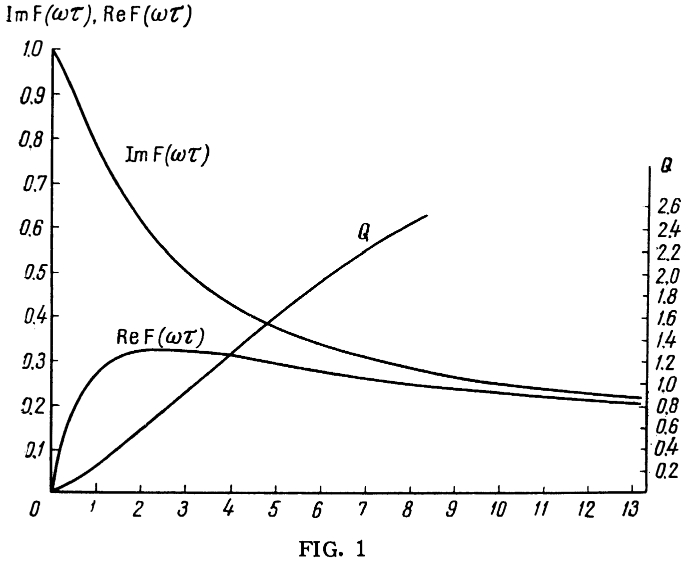

FIG. 1

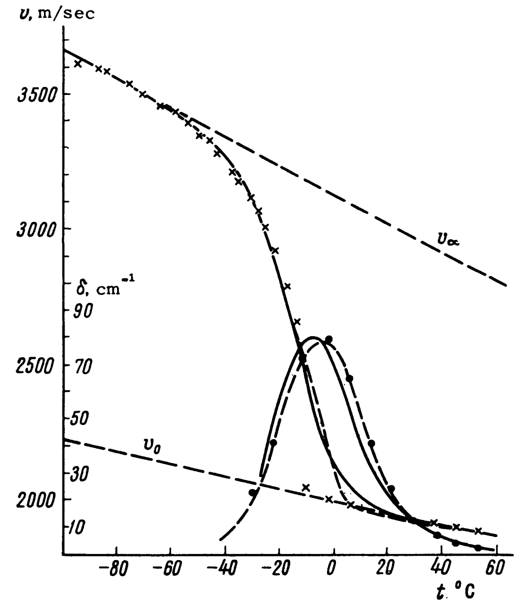

FIG. 2. Theoretical curves (solid lines – simplified theory, dashed lines – more exact theory) and experimental points of the temperature dependence of the sound velocity v(×) and absorption coefficient δ (●) for glycerin (water content 0.8%) at a frequency 22.3 MHz according to the data of [15].

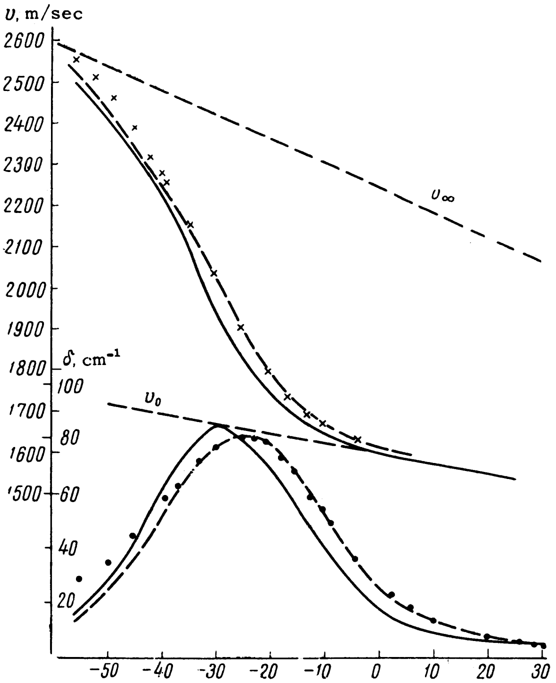

FIG. 3. The same for butanediol-1, 3 at a frequency of 22.5 MHz according to the data of [15].

given with experiment of the assumed theory (solid curve) and of relaxation theory (dashed curve) for the frequency dependence of the sound velocity in glycerin (water content 5%, η = 616 poise) at a temperature −14° C. The experimental points are taken from the book of Herzfeld and Litovitz.[12]

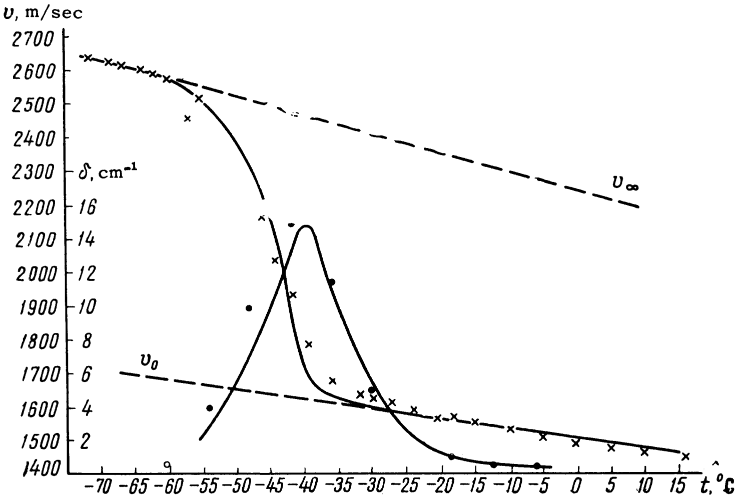

FIG. 4. The same for the triacetin at a frequency of 3 MHz according to the data of [4].

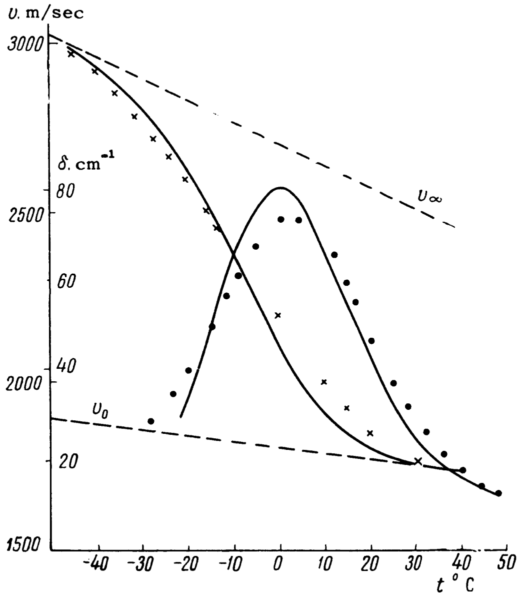

FIG. 5. The same for hexanetriol at 22 MHz according to the data of [16].

A similar comparison is shown in Fig. 8 for the temperature dependence of the damping coefficient in pentachlorobiphenyl,[13] where the relaxation curve is shown with a coincidence of the location of the maximum with the theoretical curve with the purpose of demonstrating a comparison of the curves in terms of width and height of the maximum.

Finally, Fig. 1 demonstrates the closeness to linearity in all of the dispersion regions of the dependence on $\omega\tau$ of the quantity

$$Q = \frac{v^2 - v_0^2}{v_\infty^2 - v^2}\frac{v_\infty^2}{v_0^2},$$

computed with account of Eq. (12). The experimental establishment of this fundamental fact is the main content of a paper by Fabelinskiĭ and Krivokhizha.[4]

In the conclusion of this section, we note that the limiting low frequency value of the elasticity modulus obtained in Eq. (8) does not agree with the static value of the modulus determined piezometrically. The piezometric value of the modulus is equal to $[\Phi/K_1' + (1 - \Phi)/K_2']^{-1}$, where K_1' and K_2' denote the isothermal values of the elasticity moduli of the components.

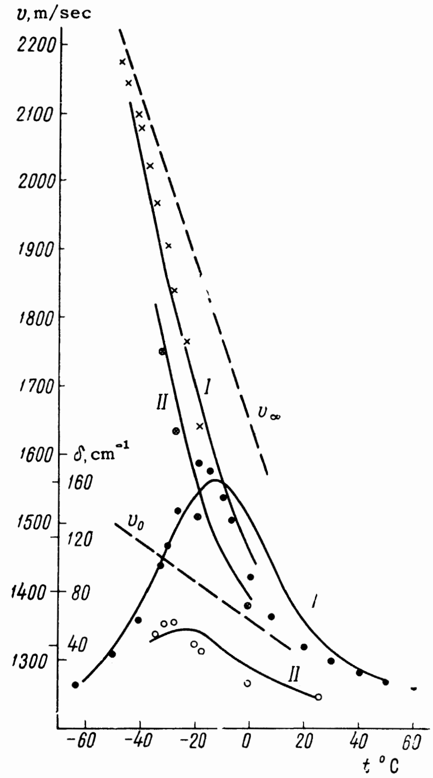

FIG. 6. Theoretical curves (simplified theory) and experimental points of the temperature dependence of the velocity and sound absorption for 2-methylpentanediol-2, 4 at frequencies 52.5 MHz (curves I, × – velocity, ● – absorption) and 15 MHz (curves II, ⊗ – velocity, ○ – absorption) according to the data of [16].

4. MOLECULAR PICTURE

The excellent agreement obtained between theory and experiment allows us to set forth the assumed hypothesis on the basis of the molecular picture of the structure of the highly viscous liquids. We shall assume that the highly viscous liquid is a microinhomogeneous medium consisting of two components—ordered regions situated in a disordered medium. The ordered and disordered components are respectively the first and second components of the phenomenological picture outlined above. No assumptions are made as to what sort of stability is possessed by the ordered regions, but only on the sufficiently long time of their existence in comparison with the period of the sound vibrations (fractions of microseconds).

We shall further assume that the quantity ξ is the concentration of holes, thus generalizing the well-known notions of Frenkel[14] to the case of a partially ordered and disordered but closely packed medium. To be precise, we shall consider the hole to be a free volume whose magnitude and shape of the potential of the self-consistent field are such that one molecule can jump over in it. It is natural also to assume that to each pressure there corresponds its own degree of ordering of the first component and an equilibrium concentration of holes characterizing it. Upon change in pressure, a reorganization will take place in the sections of the first component in a direction of

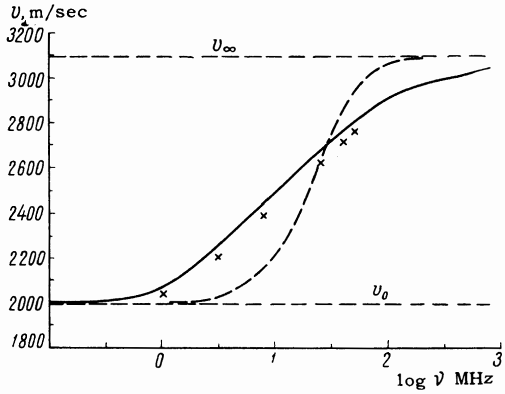

FIG. 7. Frequency dependence of the sound velocity for glycerin at t = -14°C. The dashed curve is from relaxation theory, the solid the simplified theory, the crosses the experimental points [12].

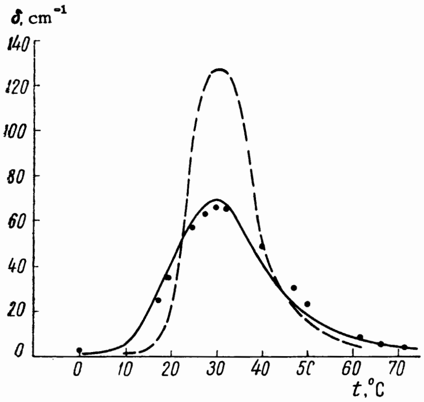

FIG. 8. Temperature dependence of the absorption coefficient for pentachlorobiphenyl at a frequency of 21.8 MHz. The dashed curve is the relaxation theory, the solid line, the simplified theory; the circles, the experimental points [13].

more or less ordering, that is, closer or less close approximation to the ideal crystalline order which is characteristic for the given liquid; the holes that are necessary for such a transition are drawn from the disordered component or are returned to it from the ordered portion by diffusion through the section boundaries.

The quantity ξ_1 can be considered as still one more thermodynamic variable (in addition to the pressure p and the entropy S in the description of the state of the ordered medium: this variable characterizes its structure. For the description of the equilibrium state of the disordered component, the variables p and S are sufficient, inasmuch as no change of structure takes place in them and the number of excess holes in their statistical disorder changes only as the result of diffusive exchange with the ordered component. Since such diffusion accompanies a pressure change, the equations which connect the variables S, p and ξ have the same form (2) for both components. In the phenomenological theory, the fact that ξ_2 is not an independent thermodynamic variable is expressed by the fact that the diffusion equation for ξ_2' is taken to be homogeneous.

The proposed molecular interpretation explains the generality of the character of the behavior of strongly viscous liquids relative to sound, shear, and electromagnetic waves, which up to now has had no explanation. Actually, in a similar medium shear, just as compression in a sound wave, can change the ordering of the first component; similarly, in view of the polarity of the molecules of a highly viscous liquid, the electric fields will also change the order by tending to rotate the molecules. As a result, upon passage of shear or electromagnetic waves, the same disruption of the thermodynamic equilibrium relative to the concentration of holes in the first component will take place, and the same mechanism of diffusion equalization as in the case of the sound wave will be brought into play. The generality of the mechanism also leads to an identity of the dispersion regions for all three types of waves and to correspondence of the character of the absorption for these waves.

The diffusion coefficient in the molecular interpretation is the coefficient of diffusion of holes, which can be regarded as identical with the coefficient of diffusion of molecules. The latter is connected with the mobility of the molecules z by the relation D = kTz (k is Boltzmann's constant and T the absolute temperature). On the other hand, the mobility is inversely proportional to the viscosity η, so that $z = 1/b\eta$, where b is a constant. Consequently, $D = kT/b\eta$, whence we find $\tau = a^2/2D = ba^2\eta/2kT$. We see that the molecular picture actually gives the assumed dependence of the characteristic time interval τ on the viscosity. By setting up the molecular interpretation of the mechanism of anomalous dispersion and absorption considered in Sec. 2, we now give a more accurate theory of dispersion and absorption for all three types of waves.

5. DISPERSION AND ABSORPTION OF SHEAR WAVES AND THE EXACT FORMULAS FOR THE SOUND WAVES

The shear stresses which we have neglected in Sec. 3 actually take place, and the experimental discovery of weakly damped shear waves showed that such stresses have not only a viscous, but also an elastic character and consequently can significantly affect the sound propagation. Therefore, we shall make more precise the calculation of Sec. 3, taking the stresses into account. However, it is convenient at first to consider the absorption and dispersion of shear waves and then, by using the result of this analysis, obtain corrections for the sound waves, too.

We shall assume that, for shear deformations, in addition to the diffusion mechanism considered in Sec. 2, there is also a mechanism of Maxwellian relaxation of shear stresses. Then the equation which connects the shear deformation u and the shear stress σ can be written in the following form

$$u_1 = \left(\frac{1}{\mu_1} - \frac{1}{i\omega\eta_1}\right)\sigma + g_1\xi_1', \qquad u_2 = \left(\frac{1}{\mu_2} - \frac{1}{i\omega\eta_2}\right)\sigma + g_2\xi_2',$$

where $g = (\partial u/\partial \xi')_\sigma$. Components of the shear modulus are consequently expressed by the formulas

$$G_1 = \left(\frac{1}{\mu_1} - \frac{1}{i\omega\eta_1} + g_1\frac{\xi_1'}{\sigma}\right)^{-1},$$

$$G_2 = \left(\frac{1}{\mu_2} - \frac{1}{i\omega\eta_2} + g_2\frac{\xi_2'}{\sigma}\right)^{-1}. \tag{13}$$

We shall assume that the viscous characteristics of both components are close to one another. Then the average elastic modulus of the medium G can be found from the formula

$$G = \left[\frac{1}{V_1 + V_2}\left(\int_{V_1}\frac{1}{G_1}dV_1 + \int_{V_2}\frac{1}{G_2}dV_2\right)\right]^{-1}. \tag{14}$$

The quantities ξ_1' and ξ_2' entering into these formulas are found from equations similar to (4):

$$\frac{\partial \xi_1'}{\partial t} = D_1\Delta\xi_1' - \frac{\partial \xi_1^{00}}{\partial\sigma}\frac{\partial\sigma}{\partial t}, \qquad \frac{\partial \xi_2'}{\partial t} = D_2\Delta\xi_2', \tag{15}$$

under the same boundary conditions (5). Taking it into account, as before, that $D_1 = D_2$, we find the solution (15) in the form

$$\xi_1' = -\frac{\partial \xi_1^{00}}{\partial \sigma}\sigma + A\frac{\operatorname{sh}[(1-i)nr]}{r}, \qquad \xi_2' = B\frac{e^{-(1-i)nr}}{r}.$$

Determining A and B from the boundary conditions and substituting the resultant values in (13), we get from (14), after integration:

$$G = \left[\Phi\left(\frac{1}{\mu_1} - \frac{1}{i\omega\eta_1} - g_1\frac{\partial \xi_1^{00}}{\partial \sigma}\right) + (1-\Phi)\left(\frac{1}{\mu_2} - \frac{1}{i\omega\eta_2}\right)\right.$$

$$\left. + i\Phi(g_1 - g_2)\frac{\partial \xi_1^{00}}{\partial \sigma}F(\omega\tau)\right]^{-1}. \tag{16}$$

Since the imaginary part of (16) must approach $1/i\omega\eta$ as the frequency approaches zero, we find, by using the asymptotic low frequency value of $F(\omega\tau)$, an expression for the static shear viscosity of the medium:

$$\eta = \left[\frac{\Phi}{\eta_1} + \frac{1-\Phi}{\eta_2}\right]^{-1}.$$

The low-frequency value of the shear modulus is found from the formula

$$G_0 = \left[\Phi\left(\frac{1}{\mu_1} - g_2\frac{\partial \xi_1^{00}}{\partial \sigma}\right) + (1-\Phi)\frac{1}{\mu_2}\right]^{-1}.$$

On the other hand, the high-frequency limiting value of the shear modulus is

$$G_\infty = \left[\Phi\left(\frac{1}{\mu_1} - g_1\frac{\partial \xi_1^{00}}{\partial \sigma}\right) + (1-\Phi)\frac{1}{\mu_2}\right]^{-1}.$$

Using the limiting values that have been found, we obtain a general expression for the shear modulus for any $\omega\tau$:

$$G = \left[\frac{1}{G_\infty} - \frac{1}{i\omega\eta} + i\left(\frac{1}{G_0} - \frac{1}{G_\infty}\right)F(\omega\tau)\right]^{-1}. \tag{17}$$

Finally, the velocity of shear wave w and the damping coefficient α for these waves are found from the formula

$$\frac{1}{w} + i\frac{\alpha}{\omega} = \sqrt{\frac{\rho}{G}} = \frac{1}{w_\infty}\left[1 - \frac{G_\infty}{i\omega\eta} + i\frac{G_\infty - G_0}{G_0}F(\omega\tau)\right]^{1/2}. \tag{18}$$

It is evident from the formulas that have been obtained that, in particular at low frequencies, the effect of reorganization of the ordered regions will be shunted by the viscosity; at high frequencies on the other hand the fundamental role will be played by the diffusion mechanism, which is connected with the realignment of the ordered regions.

Comparison of experimental data on the measurement of the velocity of shear waves with quantities calculated from Eq. (18) are shown in Fig. 9.

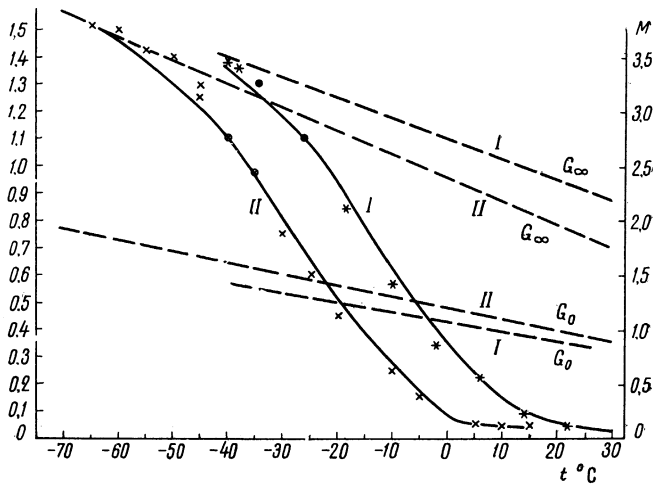

FIG. 9. Theoretical curves of experimental point to the temperature dependence of the quantity M(10^{10} dynes/cm²) for glycerin at a frequency of 34.4 MHz (curve I, scale to the right)[15] and for butanediol-1, 3, at a frequency 55 MHz (curve II, scale to the left)[16].

Along the ordinate are plotted values of the quantity

$$M = \operatorname{Re} G\frac{1 + [1 + (\operatorname{Im} G/\operatorname{Re} G)^2]^{1/2}}{2}$$

for glycerin (with a water content 0.8%) at a frequency 34.4 MHz[16] and for butanediol-1, 3 at a frequency 55 MHz.[16] The limiting values of G_0 and G_∞ are shown by the dashed lines. The line for G_0 was computed from the experimental points marked by circles on the graph. For glycerin, we used data on four different frequencies. The data of the theoretical calculations are shown by the solid lines.

We can now find the exact formulas for the velocity absorption of sound waves by taking the shear stresses into account. In fact, the elastic modulus for a longitudinal wave is equal to $K + {}^4/_3\,G$. The bulk elastic modulus K and the shear modulus G for the model of microinhomogeneity in this medium under consideration have already been found. Consequently, the elastic modulus of the longitudinal wave can be found by using (10) and (17) in the form

$$K + \frac{4}{3}G = \left(\frac{1/KG}{1/G + 4/3K}\right)^{-1}$$

$$= \left\{\frac{4}{3}\frac{1}{K_\infty} + \frac{1}{G_\infty} - \frac{1}{i\omega\eta}\right.$$

$$\left. + i\left(\frac{4}{3}\frac{1}{K_0} + \frac{1}{G_0} - \frac{4}{3}\frac{1}{K_\infty} - \frac{1}{G_\infty}\right)F(\omega\tau)\right\}$$

$$\times\left[\frac{1}{K_\infty} + i\left(\frac{1}{K_0} - \frac{1}{K_\infty}\right)F(\omega\tau)\right]^{-1}$$

$$\times\left[\frac{1}{G_\infty}-\frac{1}{i\omega\eta}+i\left(\frac{1}{G_0}-\frac{1}{G_\infty}\right)F(\omega\tau)\right]^{-1}. \qquad (19)$$

The exact expression for this velocity and absorption of the sound is found in the form

$$\frac{1}{v}+i\frac{\delta}{\omega}=\left(\frac{\rho}{K+{}^4/_3G}\right)^{1/2}. \qquad (20)$$

Formula (19) is valid only for elastic constants of the two components that are sufficiently close to one another. It can be shown that the criterion for this consists of the following conditions:

$$\left|\frac{G_0^{-1}-G_\infty^{-1}}{G^{-1}}F(\omega\tau)\right|\ll 1, \qquad \left|\frac{K_0^{-1}-K_\infty^{-1}}{K^{-1}}F(\omega\tau)\right|\ll 1.$$

For the specific materials considered, the first condition is always satisfied. For the temperature and frequency range in which the experiments were carried out, the results of which are shown in the present research, the second condition is also satisfied; it can be shown to be violated on going to much lower frequencies.

The asymptotic formulas for the velocity and dispersion for $\omega\tau \ll 1$ have the form

$$v=v_0\left[1+\frac{1}{3}\frac{K_\infty-K_0}{K_\infty}(\omega\tau)^{3/2}\right],$$

$$\frac{\delta}{\omega}=\frac{2}{3}\frac{\omega\eta}{\rho v_0^3}+\frac{2}{15}\frac{K_\infty-K_0}{v_0K_\infty}\omega\tau.$$

Comparing the last formula with the Stokes expression for the absorption coefficient, we find

$$\tau=\frac{5}{4}\frac{\eta'}{K_\infty-K_0}\frac{K_\infty}{K_0}. \qquad (21)$$

Thus the theory actually gives the experimentally obtained proportionality between η and η'.

The principal result of the more exact theory is that the time τ depends only on the volume losses; in the present model, the effect of realignment of the ordered regions leads asymptotically only to the volume viscosity.

The asymptotic values of the velocity and absorption coefficient for $\omega\tau \gg 1$ are given by the formulas

$$v=v_\infty\left[1-\frac{1}{4}\frac{(K_\infty-K_0)K_\infty G_0+{}^4/_3(G_\infty-G_0)G_\infty K_0}{K_0G_0(K_\infty+{}^4/_3G_\infty)}\frac{1}{\sqrt{\omega\tau}}\right],$$

$$\frac{\delta}{\omega}=\frac{1}{4}\frac{(K_\infty-K_0)K_\infty G_0+{}^4/_3(G_\infty-G_0)G_\infty K_0}{v_\infty K_0G_0(K_\infty+{}^4/_3G_\infty)}\frac{1}{\sqrt{\omega\tau}}.$$

Theoretically, the curves obtained for glycerin and butanediol by the more precise formulas (19) and (20) are shown in Figs. 2 and 3 by the dashed lines. We see that in the region of temperature where the exact solution differs materially from the solution obtained in the simplified theory, the agreement with experiment is still better, especially for the more sensitive indicator—the location and value of the maximum of the absorption coefficient.

Let us make some remarks on the features of the behavior of highly viscous liquids. Special interest attaches to the character of the temperature dependence of the limiting elastic modulus of the highly viscous liquid. Experiment shows that the values of K_0, K_∞, and G_∞ slowly increase upon decrease in temperature, following an approximately linear law. The slope of the straight line for K_∞ is greater than for K_0, so that the corresponding straight lines intersect at some temperature t_0. It is shown that for the same temperature the shear modulus of elasticity of the liquid vanishes. For glycerin, t_0 = 153° K. The temperature dependence of the elastic modulus for glycerin (containing 0.8% water) is given in Fig. 10. Above 50° K the graphs show an extrapolation of the experimental data obtained at much lower temperatures.[15]

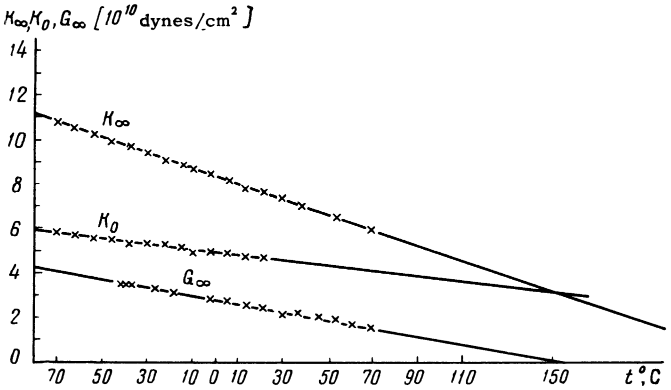

FIG. 10. Dependence of the limiting moduli K_∞, K_0 and G_∞ on the temperature for glycerin containing 0.8% water. The experimental points are taken from [15].

We recall that the boiling point of glycerin is 250° K. The physical separation of the temperature point t_0 can be explained by starting out from (8) and (9) and the assumption on the closeness of the elastic constants of the two components of the liquid, the dispersion jump $K_\infty - K_0$i is approximately proportional to Φ. The temperature at which the dispersion jump vanishes corresponds to the temperature for which the ordered regions vanish. This temperature should satisfy the condition $K(t_0 + 273) = U$, where U is the depth of the potential well of the self-consistent field of molecular interaction. Indeed, the ordered regions should disappear at a temperature above t_0 because in this case all the locations of the molecules become equally probable. Capture of molecules by the potential wells of the self-consistent field is made possible only at much lower temperatures. Only then can the locations of the molecules be fixed—if only for a certain time, and this means that only then is the appearance of ordered regions possible and, consequently, the appearance of the dispersion jump in the modulus of volume elasticity and, simultaneously, the appearance of of a shear modulus for the liquid.

It is consistent with the experimental facts and a consequence of the molecular picture considered that the depths of the potential wells are not large in comparison with the activation energy entering into the expression for the dependence of the viscosity on the temperature. Actually, the depth of the potential well is $kT_0 = k(t_0 + 273)$, which, for example, for glycerin, amounts to about 0.92 kcal/mole. The temperature effect on the viscosity of glycerin is described approximately by the exponential law $\eta \sim e^{-V/kT}$, where the energy V is of the order of 20–30 kcal/mole. Consequently, the deformation of the liquid particle is limited by the number of holes and not by the depth of the potential well, while the temperature dependence of the viscosity is determined by precisely this number. This result is in agreement with the empirical conclusion of Batchinski[17] on the role of the free volume in the viscosity of a liquid.

Upon increase in the frequency at which the investigation of the acoustical properties of the liquid is carried out, the dispersion region approaches the temperature t_0; here the dimensions and the concentrations of the ordered regions in it are decreased and the dispersion jump of the velocity and the elastic constants of the medium become small. Close to the temperature t_0, the diffusion character of the dispersion mechanism is therefore gradually lost and this mechanism must take on a relaxational character. It can be assumed that the acoustic behavior of certain highly viscous liquids (for example, oils) is connected with precisely this phenomenon; here one has not succeeded experimentally in finding the typical low temperature bend in the dispersion curve which would be produced in a transition from the dispersion region to the limiting value of the modulus.[18]

In connection with what has been pointed out above, this picture can be treated as a measurement at such high frequencies for which $\omega\tau$ is close to unity at the temperature t_0 for the given liquid. Then the dispersion jump must be very small and cannot generally be obtained by experiment, while the observed increase in the elastic modulus upon decrease in temperature is simply the temperature dependence of the limiting high frequency modulus and not the dispersion curve transition from the low frequency modulus to the high frequency as the experiments in [18] have confirmed. This assumption could be verified by investigation of the liquid at very low frequencies, where the dispersion region is moved to very low temperatures and where the dispersion jump has a very large value. Acoustic behavior of these liquids at high frequencies can be compared with the behavior of low viscosity liquids (such as benzene, carbon tetrachloride, acetic acid, and so forth), for which the dispersion jump is small and is excellently described by relaxation theory. In this connection, it would also be of interest to clarify the temperature dependence of the limiting high-frequency and low-frequency elastic moduli of these low-viscosity liquids (there are no published data at the present time).

The theory that has been set forth allows us to explain certain phenomena associated with the transition to the glass state, which is observed as a rule in highly viscous liquids. At the vitrification temperature, a break is noted at the temperature dependence of the density, in the curve for the sound velocity, and in the index of refraction. According to the hypothesis set forth, these phenomena can be explained by the fact that the vitrification temperature corresponds to the approach of the concentration of the ordered regions Φ to unity, where the ordered regions join together. Beginning at this temperature, it would be more correct to liken the glassy liquid not to an emulsion but to a polycrystal.

6. DISPERSION AND ABSORPTION OF ELECTROMAGNETIC WAVES IN HIGHLY VISCOUS LIQUIDS

In analogy to the investigation of elastic waves, we can, by starting out from the hypothesis that has been set forth, consider also theoretically the propagation of electromagnetic waves in highly viscous liquids. For this case it suffices to consider the real and imaginary parts of the dielectric constant of the medium ϵ.

We shall assume that in addition to the diffusion mechanism there is also the usual relaxation mechanism in the disordered component, associated with the viscous friction of molecules in their turning in an electric field. The total electric moment P per unit volume of the medium is expressed in terms of the electric moments per unit volume of the components P_1 and P_2 by the formula

$$P = \frac{1}{V_1 + V_2}\left(\int_{V_1} P_1\,dV_1 + \int_{V_2} P_2\,dV_2\right).$$

Following Onsager[19, 14] in the calculation of the actual field, and taking into account the fact that the highly viscous liquids possess a large dielectric constant, we find the following dependence of the electric moment of the components on the impressed electric field E:

$$P_1 = \chi_1 E + h_1 \xi_1', \qquad P_2 = \left(\chi_2 + \frac{L}{1 - i\omega\tau_D}\right) E + h_2 \xi_2'.$$

Here χ is the static dielectric constant, $\tau_D = 3\eta v/kT$ is the Debye relaxation time, v is the volume of the molecule

$$L = \frac{Nm^2}{2kT}\left(\frac{\varepsilon_\infty + 2}{3}\right)^2, \qquad h = \left(\frac{\partial p}{\partial \xi'}\right)_E$$

N is the number of molecules per unit volume, m the dipole moment of the molecule, ϵ_∞ the dielectric constant at infinite frequency. The values of ξ' are found from the equation

$$\frac{\partial \xi_1'}{\partial t} = D\Delta\xi_1' - \frac{\partial \xi_1^{00}}{\partial E}\frac{\partial E}{\partial t}, \qquad \frac{\partial \xi_2'}{\partial t} = D\Delta\xi_2'$$

and the boundary condition (5).

Carrying through the subsequent calculation in the manner used to compute acoustic quantities, we find the average (complex) dielectric constant of a liquid in the form

$$\chi = \Phi\left(\chi_1 - h_1\frac{\partial \xi_1^{00}}{\partial E}\right) + (1 - \Phi)\left(\chi_2 + \frac{L}{1 - i\omega\tau_D}\right) + i\Phi\frac{\partial \xi_1^{00}}{\partial E}(h_1 - h_2)F(\omega\tau).$$

The limiting low frequency and high frequency values of the dielectric constants are written in the form

$$\chi_0 = \Phi\left(\chi_1 - h_2\frac{\partial \xi_1^{00}}{\partial E}\right) + (1 - \Phi)(\chi_2 + L),$$

$$\chi_\infty = \Phi\left(\chi_1 - h_1\frac{\partial \xi_1^{00}}{\partial E}\right) + (1 - \Phi)\chi_2.$$

Consequently,

$$\chi = \chi_\infty + \frac{(1 - \Phi)L}{1 - i\omega\tau_D} + i[\chi_0 - \chi_\infty - (1 - \Phi)L]F(\omega\tau).$$

Finally, we find the (complex) dielectric constant of the medium:

$$\varepsilon = \varepsilon_\infty + \frac{(1 - \Phi)4\pi L}{1 - i\omega\tau_D} + i[\varepsilon_0 - \varepsilon_\infty - (1 - \Phi)4\pi L]F(\omega\tau). \tag{22}$$

Figure 11 gives the comparison of the theoretical curves computed by Eq. (22) for the real and imaginary parts of the dielectric constant (solid curves) and with the experimental values[20] for glycerin (with a water content of 5%) at a frequency of 30 MHz. The limiting values ϵ_0 and ϵ_∞ were taken from [21], where the measurements were carried out for water-free glycerin. The concentration of the ordered component was estimated in accord with the statements in Sec. 5, by starting from an assumption of a linear change of Φ with temperature over the entire temperature range between the point t_0 = 153° C and the glass point of glycerin (−89° C). The volume of the molecules was taken to be equal to 2.3×10^{-24} cm^3, in correspondence with the known bond lengths in the glycerin molecule.

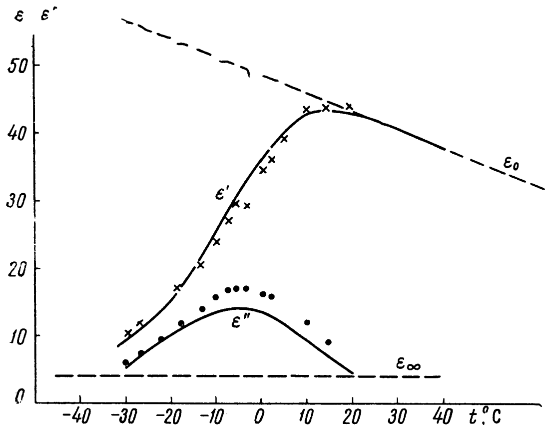

FIG. 11. Theoretical curves and experimental points [19,20] for the temperature dependence of the real (ϵ') and imaginary (ϵ'') parts of the dielectric constant of glycerin at a frequency of 30 MHz: × – ϵ', ● – ϵ''.

In conclusion, let us estimate the dimensions of the ordered regions. If the coefficient of self-diffusion D of the material were known, then these dimensions could be computed from the formula $a = \sqrt{2D\tau}$. If it is assumed that this coefficient is equal to the diffusion coefficient of glycerin in water, then one could use the handbook data given for a temperature 22° C: D = 10^{-5} cm^2 sec^{-1}. Equation (21) gives the value $\tau = 7.5 \times 10^{-10}$ sec for this temperature. Then $a = 1.22 \times 10^{-7}$ cm, which corresponds to approximately six molecules in the linear dimension of the ordered region. Upon decrease in temperature, the dimensions of the region must increase. It is curious to note that the resultant estimate is in order-of-magnitude agreement with the estimate of Khaĭkin,[22] who, to explain the observed dependence of the viscous stress on the velocity gradient, assumed the presence of crystals in a liquid.

Such small ordered regions cannot be observed directly by optical methods. However, their appearance upon cooling to a temperature below t_0

can be observed by the scattering of x-rays and neutrons. Up to now, no direct observation of these regions has been made; only indirect methods of their observation by studies of the microscopic behavior of the medium, for example those discussed in the present work, have been possible.

We take this occasion to express our thanks to V. P. Bazhnichkin for use of a number of calculations and for preparation of the graphs.

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