ACOUSTIC BEHAVIOR OF HIGHLY VISCOUS LIQUIDS AND THE THEORY OF LIQUIDS

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Abstract

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ACOUSTIC BEHAVIOR OF HIGHLY VISCOUS LIQUIDS AND THE THEORY OF LIQUIDS

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1. As is known, the acoustic behavior of highly viscous liquids cannot be explained by means of the usual relaxation theory with a single relaxation time. An attempt to modify the theory by introducing a continuous spectrum of relaxation times with the same temperature dependence (1–6) is arbitrary and cannot be considered satisfactory. Fabelinskii and Krivokhizha showed that if, in the formulas of relaxation theory, the relaxation time is formally taken to be proportional to the square root of the frequency ω, then for the value of the attenuation coefficient α and for the dispersion of the sound velocity c, data are obtained that are close to the experimental results of a number of authors and, at high frequencies, have a characteristic asymptotic dependence of the form $\sqrt{\omega}$ (5,7). It is clear, however, that such an assumption is in principle incompatible with relaxation theory. It can also be shown that, in a homogeneous relaxing liquid with a reaction equation in the form of any integro-differential polynomial, the dependence of the indicated quantities on frequency would have to be expressed asymptotically by an integral power of the frequency (for example, in the ordinary relaxation theory, by the zeroth power). Thus, local relaxation theories for this reason alone cannot explain the observed phenomena; there are also other discrepancies between relaxation theories and experiment.

Dispersion and absorption with a frequency dependence of the indicated character have been observed experimentally not only for longitudinal sound waves, but also for transverse waves, for which such liquids behave like a solid (1,4), and also for electromagnetic waves (8,9); moreover, the regions of dispersion and the temperature of maximum absorption coincide for all these types of waves.

2. In searching for a phenomenological picture describing the acoustic behavior of highly viscous liquids, we turned to the theory of microinhomogeneous media that we had studied earlier. In microinhomogeneous media, in which dispersion and attenuation are determined by one or another

Fig. 1

Figure 1: Fig. 1

exchange process occurring between the components of the medium and governed by a diffusion equation, the same characteristic asymptotic dependence of dispersion and absorption on $\sqrt{\omega}$ is obtained as for highly viscous liquids. In emulsions and polycrystals, this is heat exchange between components, arising as a result of the difference in the adiabatic heating of the components when the pressure changes in the sound wave ($^{10-12}$); in suspensions, it is the exchange of momentum between components of different density that acquire different velocities in the sound wave ($^{13-15}$), and so on. Proceeding from the indicated analogy in the acoustic behavior of microinhomogeneous media and highly viscous liquids, in the present work we give a phenomenological theory of such liquids, based on the assertion that they are microinhomogeneous media with diffusional exchange between components. Noti-

in that the similarity in the asymptotic dependence of sound absorption in polycrystals and in such substances as rosin and polymethyl methacrylate was first pointed out by I. G. Mikhailov (^{7}), while attempts to regard liquids as microinhomogeneous media have been made repeatedly, and quite independently of acoustic questions (^{16}-^{19}).

3. Thus, it is assumed that a liquid is a two-phase microinhomogeneous medium of the emulsion type, whose components, in addition to pressure and temperature, are characterized by a certain quantity ξ, the equilibrium values of which change in different ways when the pressure is changed. When a sound wave passes, the equilibrium between the values of ξ in the two components is disturbed, and equalization of this quantity between the components begins; this proceeds by diffusion, analogous, for example, to the equalization of temperatures between the components in an emulsion. It is further assumed that, for a given degree of compression, the pressure in the medium depends linearly on the deviation of ξ from its equilibrium value. Under these assumptions, the calculation of the complex sound velocity in the medium can formally be carried out in the same way as the corresponding calculation for emulsions, provided that the quantities characterizing the components are replaced; for example, the thermal conductivity must be replaced by the diffusion coefficient D of the quantity ξ, etc. As usual, the diffusion coefficient will be taken to be inversely proportional to the shear viscosity of the medium η. For the case in which one of the components is represented by spheres of radius a, situated in a medium consisting of the second component, like grains in an emulsion, the calculation gives, for the complex sound velocity, the equation

Fig. 1

Fig. 2

Figure 2: Fig. 2

$$\frac{1}{c} + i\frac{\alpha}{\omega} = \frac{1}{c_\infty}\left[1 + \frac{c_\infty^2 - c_0^2}{c_0^2}\, iF(\omega\tau)\right]^{1/2}, \tag{1}$$

where c_0 and c_∞ are the sound velocities at $\omega \to 0$ and $\omega \to \infty$, and $\tau = a^2/2D$,

$$F(\omega\tau) = \frac{3}{2}\,\frac{1}{\omega\tau}\,\frac{\left[1 + (1-i)\sqrt{\omega\tau}\right]\left\{(1-i)\sqrt{\omega\tau} - \operatorname{th}\left[(1-i)\sqrt{\omega\tau}\right]\right\}}{(1-i)\sqrt{\omega\tau}\left\{1 + \operatorname{th}\left[(1-i)\sqrt{\omega\tau}\right]\right\}}.$$

Equating the sound absorption at $\omega \to 0$ to the usual expression for absorption, containing both viscosity coefficients η, ξ, we find an expression for the relaxation time τ:

$$\tau = \frac{5}{3}\,\frac{c_\infty^2}{\rho c_0^2\left(c_\infty^2 - c_0^2\right)}\left(\eta + \frac{3}{4}\xi\right).$$

Thus, the proposed theory has no adjustable parameters, and all quantities entering the calculation are obtained directly from experiment.

Comparison of the theory with experiment was carried out chiefly for experiments in which the frequency remained fixed, while the viscosity varied over wide limits (3–6 orders of magnitude). An increase in viscosity

was achieved by cooling the sample. Most of the literature data ($^{1-9,20}$) relate precisely to such measurements, since measurements over a wide frequency range are more difficult. Since frequency and viscosity enter the right-hand side of (1) only symmetrically, a change in viscosity is equivalent to a change in frequency (we recall that $\tau \sim \eta$).

The data of Fig. 1 show good agreement between the theoretical curves for the sound velocity c (curve I) and the absorption coefficient a (curve II) in glycerin containing 0.8% water (solid lines) and experiment (points and crosses) for a frequency of 28.3 MHz (^{1}). In Fig. 2 the solid line is the frequency dependence of the sound velocity in glycerin containing 5% water, at a temperature of $-14°$; the circles are experimental data (^{3}). In Fig. 3 the solid line and the points are theory and experiment for the absorption coefficient at a frequency of 21.8 MHz in pentachlorobiphenyl (^{20}). Similar good agreement of the proposed theory with experiment has also been established for certain other liquids for which the required data could be found in the literature (butanediol, hexanetriol, 2-methylpentanediol) (^{4}). For the same liquids, the usual relaxation theory gives results sharply at variance with experiment (dashed lines in Figs. 2 and 3).

Fig. 2

Fig. 3

Figure 3: Fig. 3

4. The discovered good agreement of the proposed phenomenological theory with experiment makes it possible, on its basis, to put forward a molecular theory of highly viscous liquids. We consider that the different components of a liquid are a disordered phase and regions of a more or less ordered phase immersed in it. At a given temperature and pressure, the ordered regions have a definite equilibrium degree of order. The quantity ξ is the concentration of holes (in the sense of Frenkel’ s theory (19)). At a given pressure and temperature there is a certain equilibrium concentration of holes in the crystallites and in the disordered phase, and this concentration will change differently when the change in pressure caused by the passage of a sound wave occurs, since the resulting deformation of the ordered regions will be associated with their restructuring and with a change in the degree of their order. The disturbed equilibrium between the concentrations of holes will be restored by their diffusional penetration from the ordered regions into the disordered phase and back. The proposed molecular picture is described, on the average, precisely by the phenomenological theory that was set forth in § 3.

Fig. 3

5. The proposed molecular theory naturally interprets a number of phenomena that until now have found no explanation. Thus, the experimentally observed linear change of the limiting, with respect to fre—

The constancy of the values of the elastic moduli (ρc_0^2 and ρc_∞^2) with changing temperature is explained by the change in the concentration of ordered regions as the viscosity increases. The temperature at which the straight lines representing the dependence of the limiting moduli on temperature intersect is, consequently, the temperature at which ordered regions originate within the disordered phase: above this temperature ordered regions are absent, while below it their concentration increases. As can be shown, this picture also explains the experimental fact that upon cooling, beginning precisely from this physically distinguished temperature point, a shear modulus appears in the liquid (1, 4). Since shear, like compression, must cause a rearrangement of the ordered regions, the same exchange-diffusion mechanism must also manifest itself in the propagation of shear waves. Indeed, the dispersion of these waves has the same character as in longitudinal waves (unfortunately, the attenuation of shear waves has not been measured)*.

Finally, owing to the polarity of the molecules of strongly viscous liquids, electric fields must also lead to a rearrangement of the ordered regions, after which the same exchange mechanism should come into play. This explains the experimentally observed dispersion of the dielectric constant and the frequency dependence of dielectric losses when samples are placed in an alternating electric field ([8], [9]).

The exact coincidence of the experimentally obtained dispersion regions for sound, shear, and electromagnetic waves and of the points of maximum absorption for sound and electromagnetic waves of the same frequency is explained by the common mechanism producing these phenomena: the diffusive exchange of excess holes that arise during the rearrangement of crystals, whatever may cause this rearrangement.

The close agreement of the proposed theory with experiment makes it desirable to carry out new experiments (both acoustic and of other kinds) to test the basic assumptions of the theory.

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* Let us note that the presence of a shear modulus leads to the tensor character

of the stresses in the medium, in connection with which the calculations of P. 3 must be refined.

Note: Figure translations are in progress. See original paper for figures.

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