GENERALIZATION OF THE EQUATIONS OF CLASSICAL HYDRODYNAMICS
AND THE THEORY OF ELASTICITY AND THEIR USE TO DESCRIBE
THE KINETICS OF VITRIFICATION OF A LIQUID

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Liquids and amorphous solids simultaneously exhibit both viscous and elastic properties and are separated only by a quantitative difference characterized by relaxation time [1-4]. Thus, the behavior of a substance in the liquid and amorphous (glassy) state can be described by the same equations. At high and low temperatures, these equations become the equations of hydrodynamics and the theory of elasticity of anisotropic bodies, respectively [3]. The need for such equations has recently been increasing in connection with the development of methods of using ultrafast quenching from a melt to obtain new amorphous materials — especially amorphous metals [5, 6] — whose mechanical, magnetic, and other properties are to a large extent determined by viscoelastic processes occurring during their formation [6-8]. Maxwell was the first to propose equations to simultaneously describe the viscous and elastic behavior of a liquid for uniform shear deformation [2, 3]. Maxwell's theory was subsequently generalized in [3, 7-10] in the case of simple amorphous solids and liquids.

Here, we generalize the equations of hydrodynamics of a liquid and the theory of elasticity of isotropic bodies for arbitrary motion and a change in the temperature of the viscoelastic material. The equations are generalized without separating motion into purely shear and dilatational components. The resulting equations uniquely describe basic features of the viscoelastic behavior of ordinary liquids and amorphous solids, as well as the kinetics of the transformation of supercooled liquids to the glassy state with a decrease in temperature. The equations are solved for a uniform change in the volume of the liquid under the influence of the changing temperature in the region of the glass point and the propagation of an elastic transverse wave into a semiinfinite viscoelastic material.

We will examine the deformation of a liquid in which the strain tensor can be represented in the form $u_{ik} = (\partial u_i/\partial x_k + \partial u_k/\partial x_i)/2$ (u is the strain vector). The given strain depends on the elastic change in the distance between atoms, characterized by the parameter ψ, and on rearrangement of the liquid atoms. The deformation of the liquid will be characterized by the parameter φ (if some of the strains cannot be described by one parameter, then the corresponding quantity should be regarded as representing the aggregate of the necessary parameters).

Thus we assume that the strain tensor u_{ik} is a function of the variables φ and ψ. These variables can be formally regarded as being independent of each other. At the same time, each is a function of time. Thus, the tensor of strain rate $v_{ik} = (\partial v_i/\partial x_k + \partial v_k/\partial x_i)/2$ (v is the strain-rate vector) can be represented in the form

$$v_{ik} = \frac{du_{ik}}{dt} = \frac{du_{ik}}{dt}\bigg|_{\varphi=\text{const}} + \frac{du_{ik}}{dt}\bigg|_{\psi=\text{const}} = v_{ik}' + v_{ik}'', \tag{1}$$

where v_{ik}' corresponds to the elastic strain-rate tensor; v_{ik}'' is connected with restructuring of the liquid and thus corresponds to the viscous strain-rate tensor. This is equivalent to combining viscous and elastic strain, in accordance with Maxwell. Such a combination was used in [3, 9] for nondiagonal components of the tensors u_{ik} and v_{ik} and their deviators. We will assume, in accordance with previous discussions, that Eq. (1) is valid for all components of the tensor v_{ik}.

Let us examine the motion of a viscoelastic substance. The general equation of continuum mechanics has the form [11]

$$\rho \frac{d^2 u_i}{dt^2} = \rho \frac{dv_i}{dt} = \frac{\partial \sigma_{ik}}{\partial x_k} + f_i. \tag{2}$$

Here, ρ is the density of the material; f_i is a component of the vector of the body force; σ_{ik} is the stress tensor. Equation (2) is usually augmented by the continuity equation

$$\partial \rho / \partial t + \operatorname{div} \rho \mathbf{v} = 0. \tag{3}$$

We assume that the stresses acting on the substance are not very great. In this case, Hooke's law is satisfied for elastic deformation. In the theory of elasticity, with allowance for a temperature change [11], the stress tensor of an isotropic body has the form

$$\sigma_{ik} = -k'\beta'(T - T_0)\delta_{ik} + 2M'u'_{ik} + L'u'_{ll}\delta_{ik} + \lambda'v'_{ll}\delta_{ik} + 2\eta'_s v'_{ik}, \tag{4}$$

where L' and M' are the Lamé constants; T_0 is the initial temperature; $k' = L' + 2M'/3$ is the bulk compression modulus; β' is the coefficient of cubical expansion of glass; λ' and η_s' are coefficients characterizing the bulk and shear viscosity (internal friction) of the substance as a solid [11, p. 781].

The stress tensor of a viscous compressible liquid [11]

$$\sigma_{ik} = -p_\alpha \delta_{ik} + \lambda''v''_{ll}\delta_{ik} + 2\eta''_s v''_{ik} \tag{5}$$

(p_α is pressure; λ'' and η_s'' are coefficients characterizing the bulk and shear viscosity of the liquid). To obtain equations linking the stress and strain-rate tensors of a viscoelastic material, we combine Eqs. (4) and (5) in accordance with Eq. (1). To do this, we find from (5) that

$$v''_{ik} = \frac{\sigma_{ik}}{2\eta''_s} - \frac{\lambda''}{2\eta''_s}\left(\frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta''_s}\right)\delta_{ik} + \frac{p_\alpha}{2\eta''_s}\delta_{ik}. \tag{6}$$

We then differentiate (4) with respect to time. For most actual processes, an insignificant role is played by the last two terms in this equation — which account for the fact that the process occurs at a finite rate. Thus, we will henceforth ignore them. It should be noted that allowing for them only leads to somewhat more complicated formulas. The coefficients L', M', and β' change relatively slightly in relation to temperature and pressure. We will therefore consider them to be independent of time. As a result,

$$\frac{d\sigma_{ik}}{dt} = -k'\beta'\frac{dT}{dt}\delta_{ik} + L'v'_{ll}\delta_{ik} + 2M'v'_{ik}. \tag{7}$$

Replacing v_{ik}' in (7) by $v_{ik} - v_{ik}''$ and replacing v_{ik}'' by its value from (6), we obtain a system of differential equations to connect the tensors σ_{ik} and v_{ik}:

$$\frac{d\sigma_{ik}}{dt} = -k'\beta'\frac{dT}{dt}\delta_{ik} + L'\left(v_{ll} - \frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta''_s}\right)\delta_{ik} +$$
$$+ 2M'\left[v_{ik} - \frac{\sigma_{ik}}{2\eta''_s} - \frac{p_\alpha}{2\eta''_s}\delta_{ik} + \frac{\lambda''}{2\eta''_s}\left(\frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta''_s}\right)\delta_{ik}\right]. \tag{8}$$

System (2), (3), (8) is composed of ten independent equations (since $\sigma_{ik} = \sigma_{ki}$, $v_{ik} = v_{ki}$), which in the general case have twelve unknowns: six components of the tensor σ_{ik}, three components of the vector $\mathbf{v}$, pressure p_α, density ρ, and temperature T. If it is necessary to determine the strain, then the system is augmented by the equation $\mathbf{v} = d\mathbf{u}/dt$. This equation can be solved in the case when the problem turns out to be closed for a specific condition. Otherwise, as in hydrodynamics, it is necessary to solve a resolvent system augmented by the energy equation $\rho d\vartheta/dt = \sigma_{ik}v_{ik} - \partial q/\partial x_i$ (q and ϑ are the heat-flux vector and the specific internal energy of the medium), the equation of state of the liquid, etc.

Using system (1), (2), (8), we obtain the following for an incompressible liquid ($v_{ll}' = v_{ll}'' = v_{ll} = 0$) and a constant temperature

$$\frac{1}{\eta''_s}\frac{\partial p_\alpha}{\partial x_i} + \left(\frac{1}{M'}\frac{d}{dt} + \frac{1}{\eta''_s}\right)\left(\rho\frac{dv_i}{dt} - f_i\right) = \nabla^2 v_i \tag{9}$$

(∇^2 is the Laplace operator). Equation (9) differs from the corresponding equation in [10], p. 234] in the fact that it does not contain the term $(1/M')[d(\partial p_\alpha/\partial x_i)/dt]$. This is connected with the fact that here we generalized the equations of hydrodynamics and the theory

of elasticity in accordance with Eq. (1), while in [10] they were generalized by replacing the multiplier $1/\eta_s''$ in the Navier–Stokes equation by the Maxwell operator $1/\eta_s'' + (1/M')\cdot(d/dt)$. The solution of system (2)-(3), (8) in the general case poses formidable difficulties, but in certain cases it can be solved easily.

Let us examine the stress and strain distribution in a semiinfinite viscoelastic material whose surface is acted upon by a sinusoidal shear stress $\sigma_{yx} = \sigma_{yx}{}^0 \exp(i\omega t)$ (with the y axis being directed along the surface and x being directed inside the material, where x = 0 on the surface). We assume that ρ, η_s'', and T are constant. We seek the solution in the form $\sigma_{yx} = \sigma_{yx}{}^0 \exp[i(\omega t - \nu x) - \mu x]$, $v_y = v_y{}^0 \exp[i(\omega t - \nu x) - \mu x]$ ($\sigma_{yx}{}^0$, $v_y{}^0$, ν, and μ are constants). In the given case, two equations in system (2)-(3), (8) are nontrivial. Their solution has the form

$$\mu, \nu = \sqrt{\frac{\sqrt{\alpha^2 + \gamma^2} \mp \alpha}{2}}, \quad v_y^0 = \sigma_{yx}^0 (\nu - i\mu)/\rho\omega$$

$$(\alpha = \rho\omega^2/M', \gamma = -\rho\omega/\eta_s'').$$

With η_s'' approaching infinity, $\mu = 0$, while $\nu = \sqrt{\rho\omega^2/M'}$, i.e., the substance behaves as an ideally elastic body. At η_s'' approaching zero, $\mu = \nu = \sqrt{\rho\omega/2\eta_s''} \to \infty$. Thus, as in a moving liquid, the wave decays rapidly near the surface. With a decrease in temperature, the viscosity of the liquid rapidly increases from small to very large values (near the glass point T_g), while the Lamé constants change relatively slowly in relation to temperature. Thus, as can be seen from (1) and (6), system (2)-(3), (8) describes a viscous fluid above the glass point and an elastic solid (glass) below it. It should therefore reflect the process of vitrification of the liquid.

Let us now examine the change in volume under the influence of temperature in the vitrification region. For a uniform change in volume, the nondiagonal components of the tensors σ_{ik} and v_{ik} vanish, and Eq. (8) takes the form

$$\frac{d\sigma_{ll}}{dt} = -3k'\beta'\frac{dT}{dt} + (3L' + 2M')\left(v_{ll} - \frac{3p_\alpha + \sigma_{ll}}{3\lambda'' + 2\eta_s''}\right). \tag{10}$$

We will assume that bulk flow takes place fairly slowly. Then we can set $\rho dv/dt = 0$ in Eq. (2), so that (henceforth assuming $f \equiv 0$) $\partial\sigma_{ik}/\partial x_k = 0$ as well. Thus, the diagonal components of the tensor σ_{ik} are independent of the coordinate. Since they must be equal to the external pressure $-p$ at the boundary, we find that over the entire volume $\sigma_{11} = \sigma_{22} = \sigma_{33} = -p$. It can be shown that for a uniform change in volume $v_{ll} = \text{div } v = (1/w)\cdot(dw/dt)$ (w is the volume of the liquid). Making the substitutions $\sigma_{ll} = -3p$, $v_{ll} = (1/w)(dw/dt)$, $k' = L' + 2M'/3$ in Eq. (10), we have

$$\frac{1}{w}\frac{dw}{dt} = \beta'\frac{dT}{dt} - \chi'\frac{dp}{dt} + \frac{p_\alpha - p}{\eta_v''} = \beta'\frac{dT}{dt} - \chi'\frac{dp}{dt} - \frac{w - w_e}{w\tau}. \tag{11}$$

Here $\chi' = 1/k'$ is the instantaneous coefficient of compressibility (the coefficient of compressibility of glass); $\eta_v'' = \lambda'' + 2\eta_s''/3$ is the bulk viscosity of the liquid. In the last equality, we replaced the difference $p_\alpha - p$ by $w - w_e$ by introducing a coefficient expressing the structural (due to viscous flow) compressibility of the liquid $\Delta\chi = \chi - \chi' = -(w - w_e)/w(p_\alpha - p)$, where χ is the statistical coefficient of compressibility of the liquid; w, volume of the liquid after its elastic deformation; w_e, equilibrium value of volume; and $\tau = \Delta\chi\eta_v''$. The coefficient of structural compressibility is introduced because the term $(p_\alpha - p)/\eta_v''$ in (11) describes only viscous flow of the liquid.

Let the liquid be cooled at a constant rate $\dot{T} = dT/dt$ under conditions of a constant external pressure p = const. If we change over to the variable T in Eq. (11), then

$$\frac{1}{w}\frac{dw}{dT} = \beta' - \frac{w - w_e}{w\tau\dot{T}}. \tag{12}$$

With a decrease in temperature, η_s'' and thus τ ($\Delta\chi$ changes relatively slightly with temperature) increase from a small value to a very large value. As a result, in accordance with (12), at high temperatures the volume of the liquid is nearly equal to the equilibrium volume. At low temperatures, the volume changes (similarly to glass) in accordance with the equation

$$\frac{1}{w}\frac{dw}{dT} = \beta'. \tag{13}$$

Thus, (12) describes the transition from the supercooled liquid state to the glassy state. Equations (11) and (12) reflect the main features of the vitrification of the liquid. Compared to existing theories of vitrification, here the proportionality of relaxation time and the viscosity of the liquid are a consequence rather than a postulate. The bulk and shear viscosities have identical or similar temperature dependences and can thus be linked with one another through a proportionality factor [12].

However, these equations lead to a simple exponential law of change in the volume of the liquid with isothermal relaxation in the case of a small change in its temperature. This does not fully reflect the actual situation regarding relaxation of the liquid [4, 6]. Also, the "memory" effect is seen in glasses, this effect being manifest in a certain increase in the volume of glass with an increase in temperature as the glass point is approached. This occurs despite the fact that the equilibrium value of volume is usually smaller than the volume of the glass. This fact also cannot be described by the given equations. However, the "memory" effect is small. Thus, as a first approximation, Eqs. (11) and (12) make it possible to correctly describe the vitrification of a liquid. They can be used to study the kinetics of vitrification of rapidly-quenched amorphous metals. They also more systematically and more completely describe the vitrification of a melt than do the theories [13, 14] used for this case, since Eqs. (11) and (12) not only consider elastic as well as structural deformation, but also place a certain value on relaxation time.

In deriving (8), we consider only elastic and viscous strains. However, delayed-elastic strain [3, 6, 15] also occurs in a liquid near the glass point T_g during shear. We will attempt to generalize the equations of viscoelastic motion with allowance for this type of strain.

When the shear stress σ_{12} is applied to an amorphous substance, this strain increase in accordance with the formula $u_{12}''' = (\sigma_{12}/2M''')\Phi(t)$ [3, 6, 15] [$\Phi(t)$ is a function which changes from zero to unity, M''' is the shear modulus associated with delayed-elastic strain). This strain completely disappears when the stress is removed. In experiments, it is seen only near T_g, since its relaxation time becomes very short above T_g and very long below T_g [3]. In the simplest case, it has the form [9, 3]

$$\sigma_{12} = 2M''' u_{12}''' + 2\eta_s''' v_{12}''' \tag{14}$$

(η_s''' is shear viscosity associated with delayed-elastic strain). This formula makes it possible to satisfactorily describe experimental data on vitrification [16]. We will assume that along with elastic and viscous strain, delayed-elastic strain occurs analogously to shear for volumetric flow. Since viscous strain also behaves as delayed-elastic strain in this case, then two forms of delayed-elastic strain accumulate here. It is difficult to empirically observe them separately, but their existence can be checked by indirect means. As will be shown below, this hypothesis makes it possible to explain the nonexponential law of relaxation of the volume of a liquid and the presence of the "memory" effect in an amorphous material.

Equation (14) is analogous to (4) for the nondiagonal components of the stress tensor. It can be proposed that the tensor of delayed-elastic strain has a form analogous to (4):

$$\sigma_{ik} = -k'''\beta'''(T - T_0)\delta_{ik} + L''' u_{ll}''' \delta_{ik} + 2M''' u_{ik}''' + \lambda''' v_{ll}''' \delta_{ik} + 2\eta_s''' v_{ik}'''. \tag{15}$$

Here, the coefficients of elastic strain are analogous to the coefficients of Eq. (4); β''' is the coefficient of cubical expansion associated with delayed-elastic strain; $k''' = L''' + 2M'''/3$. According to [3, 15], elastic, viscous, and delayed-elastic strain are manifest independently. Thus, the total strain is equal to their sum: $v_{ik} = v_{ik}' + v_{ik}'' + v_{ik}'''$.

We will differentiate (15) with respect to time, assuming, as we did in deriving (7), that L''', M''' and β''' are independent of time. At the same time, η_s''' changes significantly with temperature [3]. Thus we will take the derivatives of η_s''' and λ''' with respect to time. Then, in the resulting equation, we replace v_{ik}''' by $v_{ik} - v_{ik}' - v_{ik}''$ and we replace v_{ik}' and v_{ik}'' by their values from (6) and (7). This gives us an equation linking the stress and strain-rate tensors for a medium having viscous, elastic, and delayed-elastic properties:

$$\frac{d\sigma_{ik}}{dt} = -k'''\beta'''\frac{dT}{dt}\delta_{ik} + \left(L''' + \frac{d\lambda'''}{dt}\right)\left[v_{ll} - \frac{d\sigma_{ll}/dt + 3k'\beta'dT/dt}{3L' + 2M'} - \right.$$

$$-\frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta_s''}\delta_{ik} + 2\left(M''' + \frac{d\eta_s'''}{dt}\right)\left\{v_{ik} - \frac{1}{2M'}\left[\frac{d\sigma_{ik}}{dt} + k'\beta'\frac{dT}{dt}\delta_{ik} - \right.\right.$$

$$-L'\frac{d\sigma_{ll}/dt + 3k'\beta'dT/dt}{3L' + 2M'}\delta_{ik}\right] - \frac{1}{2\eta_s''}\left[\sigma_{ik} + p_\alpha\delta_{ik} - \lambda''\left(\frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta_s''}\right)\delta_{ik}\right]\right\} +$$

$$+ \lambda'''\frac{d}{dt}\left[v_{ll} - \frac{d\sigma_{ll}/dt + 3k'\beta'dT/dt}{3L' + 2M'} - \frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta_s''}\right]\delta_{ik} + \tag{16}$$

$$+ 2\eta_s'''\frac{d}{dt}\left\{v_{ik} - \frac{1}{2M'}\left[\frac{d\sigma_{ik}}{dt} + k'\beta'\frac{dT}{dt}\delta_{ik} - L'\frac{d\sigma_{ll}/dt + 3k'\beta'dT/dt}{3L' + 2M'}\delta_{ik}\right] - \right.$$

$$-\frac{1}{2\eta_s''}\left[\sigma_{ik} + p_\alpha\delta_{ik} - \lambda''\left(\frac{\sigma_{ll} + 3p_\alpha}{3\lambda'' + 2\eta_s''}\right)\delta_{ik}\right]\right\}.$$

Similarly examining uniform volumetric flow for a constant external pressure, we find from (16) that

$$k'''\beta'''\frac{dT}{dt} = k'''g + \frac{d}{dt}\left(\eta_v'''g\right)$$

$$\left(\eta_v''' = \lambda''' + 2\eta_s'''/3, \quad g = (1/w)(dw/dt) - \beta'dT/dt - (p_\alpha - p)/\eta_v''\right). \tag{17}$$

If we put $\eta_V''' = 0$ into (17) and change over to the variable T, then

$$\frac{1}{w}\frac{dw}{dT} = \beta' + \beta''' - \frac{w - w_e}{w\tau\dot{T}}. \tag{18}$$

Here, $\tau = \Delta\chi\eta_V''$; $\Delta\chi$ is the coefficient of structural (due only to viscous flow) compressibility of the liquid.

The value of τ increases with a decrease in temperature, and the last term in (18) becomes negligibly small. As was noted in [3, 6, 10], the relaxation time for delayed-elastic strain $\tau_{el} = \eta_V'''/M'''$, being short at high temperatures, increases sharply with a decrease in temperature. This is due to an increase in η_V'''. Since $\eta_V''' = \lambda''' + 2\eta_s'''/3$, then the bulk viscosity associated with delayed-elastic strain exists even if $\lambda''' = 0$, and it changes similarly to shear viscosity η_s'''. Thus, since η_V'' and η_V''' increase appreciably with a decrease in temperature, at low temperatures the volume changes in accordance with (13). This change reflects the conditions of Eq. (17).

Thus a decrease in temperature should be accompanied by the freezing of two structural strains: viscous, which disappears with an increase in η_V''; delayed-elastic, which disappears with an increase in η_V'''. Since delayed-elastic strain is seen at lower temperatures than viscous strain [3, 6, 15], then heating is evidently at first accompanied by freezing of delayed-elastic strain. This is followed by the freezing of viscous strain. Such a pattern can explain the presence of the memory effect in glass. The deviations from an exponential return of the volume of the liquid to the equilibrium value even in the case of small deviations from equilibrium [4, 6] can also be attributed to the presence of delayed-elastic strain together with viscous strain.

Let us examine the process of relaxation of a liquid. Let the temperature of a melt at first "instantaneously" ($\dot{T} \to \infty$) change from T_1 to T_2 and then stay at $T = T_2$. We will assume that the temperature change is small enough so that the change in viscosity during the given process can be ignored ($\eta_V'' = $ const, $\eta_V''' = $ const). In this case, $\eta_V''' \neq 0$, so that in Eq. (17) we put $(p - p_\alpha)/\eta_V'' = (w - w_e - \Delta w_s)/\tau$, where $\tau = \Delta\chi\eta_V''$, $\Delta w_s = \Delta w_s^0\exp(-t/\tau_s)$ is that part of the volume change due to the action only of delayed-elastic strain. Here $\tau_s = \eta_V'''/k'''$, $\Delta w_s^0 \approx w_e\beta'''(T_1 - T_2)$. The value of Δw_s is obtained from the solution of Eq. (15). The solution of Eq. (17) for the given two-stage process has the form

$$w(t) = \Delta w_v^0\exp\left(-\frac{t}{\tau}\right) + \Delta w_s^0\exp\left(-\frac{t}{\tau_s}\right) + w_e$$

(Δw_V^0 is the initial deviation of the volume connected only with viscous flow). Thus, relaxation of the volume is expressed in the sum of two exponents. This can in principle explain the deviation of the relaxation law of the liquid from the exponential (describable by a single experiment) law seen empirically.
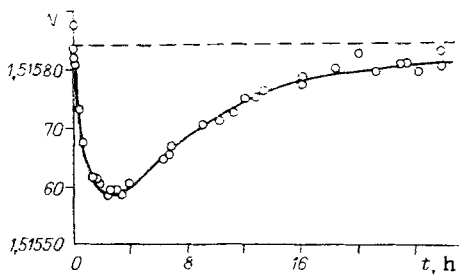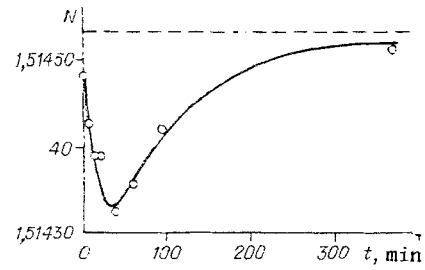
Fig. 1   Fig. 2

The presence of the thermal history of the glass, determining its structural state, is manifest in the following experiment [6, p. 123; 17]. At the temperature T_α, the liquid relaxes until the specific volume of the refractive index of the glass N reaches the values that would exist in the equilibrium material at T_β. Then the temperature changes sharply from T_α to T_β. As a result, we see the typical pattern of residual relaxation shown in Figs. 1 and 2. These figures show the dependence of refractive index on time for boron-silicate glass in an experiment with a sharp change in temperature [17] (the points denote experimental results). The solid line corresponds to Eq. (19) with $N_\infty = 1.51584$, $N_1 = 0.00094$, $N_2 = -0.00086$, $\tau_e = 75$ min, $\tau_g = 540$ min from Fig. 1. The dashed line corresponds to $N = N_\infty$ [N_∞ is the equilibrium value of the property $N(t)$]. For Fig. 2, $N_\infty = 1.51453$, $N_1 = 0.00064$, $N_2 = -0.00064$, $\tau_e = 12$ min, $\tau_g = 96$ min.

Curves of the type shown in Figs. 1 and 2 were analyzed with the assumption that slow and fast relaxation processes exist in the material [17]. The relaxation equation which describes the process for small deviations from equilibrium was expressed in the form of the sum of two exponents:

$$N(t) = N_\infty + [N_1 \exp(-t/\tau_e) + N_2 \exp(-t/\tau_g)]/2 \tag{19}$$

(N_1, N_2, τ_e, and τ_g are constants, with τ_e and τ_g having the significance of relaxation times).

Let us examine the given process, which has four stages. First the glass is in an equilibrium state at T_1. In the first stage, there is an abrupt transition to T_2, and the substance remains isothermally at this temperature. When the volume of the glass reaches the equilibrium value of volume at T_3 (lying between T_1 and T_2), the glass abruptly moves to T_3 and isothermal holding occurs again. We will assume that the temperature changes taking place are fairly small. Then, as before, $\eta_v'' \approx$ const, $\eta_v''' \approx$ const, and $d\eta_v'''/dt \approx 0$. The solution of Eq. (17) in this case has the form

$$w(t) = w_{3\infty} + A[\exp(-t/\tau) - \exp(-t/\tau_s)] + a\exp(-t/\tau), \tag{20}$$

where $A \approx w_{3,\infty}\beta'''\tau[(T_2 - T_1)\exp(-t_1/\tau_s) + (T_3 - T_2)]/(\tau_s - \tau)$; $a = w_{3,\infty}\beta'(T_3 - T_2)$; $w_{n,\infty}$ is the equilibrium volume at $T = T_n$ ($n = 1, 2, 3$). The value of the time t_1 can be calculated from the equation $w_{3,\infty} = w_{2,\infty} + \Delta w_v^0 \exp(-t_1/\tau) + \Delta w_s^0 \exp(-t_1/\tau_s)$ (Δw_v^0 and Δw_s^0 are the changes in volume due to viscous and delayed-elastic strains with the transition from the temperature T_1 to T_2 over an infinitely long period of time). It follows from this that relaxation of the volume for the given history of the process is expressed as the sum of two exponents — similarly to Eq. (19). The experimental values shown in Figs. 1 and 2 are described by Eq. (19). Here, N_1 and N_2 are close in absolute value but opposite in sign [17]. This is consistent with Eq. (20).

Thus, summing up the results obtained here, the Maxwell approach — making it possible to simultaneously describe the viscous and elastic behavior of liquids for uniform shear strain and generalized in [3, 7-9] to arbitrary but small strains of amorphous solids — has now been generalized to the arbitrary motion of a compressible viscoelastic medium with allowance for temperature change. The latter generalization was accomplished by combining the tensors for the rates of viscous and elastic strain without separating motion into shear and volumetric components. The equations that were obtained make it possible to simultaneously describe the viscous and elastic behavior of ordinary liquids and amorphous solids, as well as the kinetics of the transformation of a liquid to the glassy state under the influence of changing temperature.

Analogous to the case of shear strain, we assumed that for volumetric flow as well there exists not only elastic and viscous strains, but also delayed-elastic strain. The use of

this assumption makes it possible to explain the nonexponential law of relaxation of the volume of a liquid and the presence of the "memory" effect in an amorphous material.

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