Rayleigh scattering of light in glasses

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A comprehensive experimental study of the scattering of light in fused quartz showed that the relaxation theory of the Rayleigh scattering developed for equilibrium systems is inapplicable to glasses. This is because the equilibrium theory ignores the unlimited rise of the relaxation time as a glass forms from the melt. A modified theory allowing for this aspect is developed and it predicts a qualitative difference between the nature of the scattering in glasses from that in equilibrium solids and liquids, and provides a quantitative description of all the experimental results obtained by the authors.

In 1970 one of the present authors[1] developed a general relaxation theory of the Rayleigh scattering of light in isotropic bodies, relating the Rayleigh scattering coefficient to equilibrium thermodynamic properties of matter. The subsequent great improvement in the precision of the absolute measurements of the scattering coefficient[2,3] has made it possible to check the validity of this theory in the case of different scattering media.

It has been demonstrated experimentally[3,4] that in the case of low-viscosity liquids the theory of Ref. 1 describes experimental results to within better than 1–2%. In the case of solids this situation is much more complex. The existence of a static shear modulus has the effect that the number of parameters governing scattering is five, whereas in the case of liquid it is two. Verification of the theory requires independent determination of all these parameters. Moreover, the only type of isotropic solids is in the form of glasses. In spite of the many investigations of the scattering of light in such media, the attempts to describe these results within the framework of any theory have so far been unsuccessful.[5–7]

Our main task was to investigate experimentally the scattering of light in glasses. It should be pointed out immediately that our results (obtained for fused quartz) were in strong conflict with the predictions of the theory of Ref. 1. We shall show that this conflict is due to anomalous slowing down of relaxation on transition of a liquid to a glass.[8,9] Allowance for the anomalous increase in the relaxation time together with some additional assumptions makes it possible to modify the formulas of theory of Ref. 1. The results of such a modified theory will be found to be in quantitative agreement with our experimental data.

THEORETICAL SCHEME AND DESIGN OF EXPERIMENTS

We shall recount briefly the general scheme used in calculation of the coefficient representing the scattering of light in an isotropic medium based on the equations of hydrodynamics and on the fluctuation-dissipation theorem (for details see Ref. 1). The intensity of the scattered light is governed by fluctuations of the permittivity $\epsilon_{\alpha\beta}$, which in turn are related to deviations of macroscopic variables from their average values. We shall assume that, in addition to the quantities which are conserved (density, momentum, and energy), a medium is described by a set of relaxation parameters, some of which are symmetric zero-trace tensors. The introduction of such tensor parameters is necessary because they are responsible for the depolarized scattering, which always occurs in a liquid. On the other hand, relaxation of these parameters gives rise to a shear modulus which distinguishes a glass from a liquid.

A system of equations describing the dynamics of fluctuations in such a medium includes the Navier-Stokes equation, the equation of continuity, the heat conduction equation, and a set of equations describing relaxation parameters. Symbolically the system can be represented in the form

$$\hat{L}_{ij}\varphi_i = f_j^{(fl)}, \tag{1}$$

where $\hat{L}_{ij}$ is the operator matrix corresponding to the hydrodynamic and relaxation equations, i.e., $\hat{L}_{ij}$ represents operators which are linear in time t and in the coordinates x, y, and z; φ_i are the macroscopic variables; $f_j^{(fl)}$ are the Langevin fluctuation forces. The system (1) is complete if it is supplemented by the equation of state, i.e., by the dependence of the free energy of the medium on the investigated macroscopic variables.

The system of equations (1) allows us to express nonsimultaneous correlation functions of the variables $\langle\varphi_i(t)\varphi_j(t')\rangle$ in terms of hydrodynamic responses and correlation functions of the fluctuation forces, which in turn (according to the fluctuation-dissipation theorem) are proportional to k_BT and to the corresponding transport coefficients (k_B and T are the Boltzmann constant and the average temperature of the system).

Fluctuations of the permittivity $\epsilon_{\alpha\beta}$ can be expressed linearly in terms of deviations of macroscopic variables from their equilibrium values. In the spectral representation, i.e., as a result of the Fourier transformation with respect to x, y, z, and t, we find that $\varepsilon_{\alpha\beta}(\mathbf{q},\omega)$ can be described as follows in terms by the spectral amplitudes of these variables:

$$\varepsilon_{\alpha\beta}(\mathbf{q},\omega) = X_\infty\tilde{u}_{\alpha\beta} + \Big(Y_\infty u + Z_\infty T_1 + \sum_j m_j\xi^{(j)}\Big)\delta_{\alpha\beta} + \sum_k n_k\tilde{\zeta}_{\alpha\beta}^{(k)}. \tag{2}$$

Here, X_∞ and Y_∞ are the mechano-optic coefficients of spectral amplitudes of shear strains ($\tilde{u}_{\alpha\beta}$) and of fluctuations of isotropic compression ($u = -\delta\rho/\rho_0$, ρ_0 and $\delta\rho$ are the average value and fluctuations of the density); Z_∞ is the

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thermo-optic coefficient in the case of temperature fluctuations (T_1); $\xi^{(j)}$ and $\zeta^{(k)}_{\alpha\beta}$ are the sets of scalar and tensor relaxation parameters. The correlation function $\langle\varepsilon_{\alpha\beta}\varepsilon^*_{\gamma\delta}\rangle_\omega$ governing the light scattering coefficient is then [see Eq. (22) in Ref. 1]

$$\begin{aligned}\langle\varepsilon_{\alpha\beta}\varepsilon_{\gamma\delta}{}^*\rangle_\omega={}&M_1(\mathbf{q},\ \omega)\nu_{\alpha\beta\gamma\delta}+M_2(\mathbf{q},\ \omega)\pi_{\alpha\beta}\pi_{\gamma\delta}\\ &+M_3(\mathbf{q},\ \omega)(\delta_{\alpha\beta}\pi_{\gamma\delta}+\pi_{\alpha\beta}\delta_{\gamma\delta})\\ &+M_4(\mathbf{q},\ \omega)\mu_{\alpha\beta\gamma\delta}+M_5(\mathbf{q},\ \omega)\delta_{\alpha\beta}\delta_{\gamma\delta}.\end{aligned}\qquad(3)$$

Equation (3) contains five independent tensors composed of the components of the wave vector **q** and of the Kronecker deltas. The tensor structure of the correlation function (3) follows directly from the symmetry considerations.[10] The coefficients $M_i(\mathbf{q},\omega)$ are combinations of the correlation functions of macroscopic variables. The use of the equations of hydrodynamics and of the fluctuation-dissipation theorem makes it possible to determine the explicit form of $M_i(\mathbf{q},\omega)$ and, in particular, the dependence on the parameters of the scattering medium. For example, the expression for $M_1(\mathbf{q},\omega)$ has the form[1]

$$M_1(\mathbf{q},\ \omega)=-\frac{k_BT}{(2\pi)^4i\omega}\left\{\frac{X^2(\omega)}{\mu(\omega)q^2-\rho_0\omega^2}-\text{c.c.}\right\},\qquad(4)$$

where $X(\omega)$ and $\mu(\omega)$ are the values of the mechano-optic coefficient and of the shear modulus at the frequency ω.

Considered as a function of **q** and ω, the coefficients $M_i(\mathbf{q},\omega)$ represent the ratios of polynomials. Vanishing of the denominators, i.e., the complex poles $M_i(\mathbf{q},\omega)$ determine the positions of the components of the spectrum of the scattered light (Brillouin doublet, wings due to compression, shear, etc.).

The light-scattering coefficient $R^{p}_{p'}(\mathbf{q},\omega)$ is related directly to the correlation function of Eq. (3):

$$R_{\mathbf{p}'}{}^{\mathbf{p}}(\mathbf{q},\ \omega)=\frac{8\pi^5}{\lambda^4}\langle\varepsilon_{\alpha\beta}\varepsilon_{\gamma\delta}{}^*\rangle p_\alpha p_\beta{}'p_\gamma p_\delta{}',\qquad(5)$$

where λ is the wavelength of the incident light. Therefore, we are interested only in the convolutions of the tensors that occur in Eq. (3) and have the polarization unit vectors of the incident (**p**) and scattered (**p**′) light:

$$\begin{aligned}\nu=q^{-2}\nu_{\alpha\beta\gamma\delta}p_\alpha p_\beta{}'p_\gamma p_\delta{}'&=\frac{1}{4q^2}[(\mathbf{qp})^2+(\mathbf{qp}')^2+2\delta(\mathbf{qp})(\mathbf{qp}')]\\ -\frac{1}{q^4}(\mathbf{qp})^2(\mathbf{qp}')^2&=\frac{1+\cos\vartheta}{8}\sin^2(\varphi+\psi)\\ &=\frac{1+\cos\vartheta}{8}[1-(a-b)^2],\\ \Pi=\frac{1}{q^2}\pi_{\alpha\beta}p_\alpha p_\beta{}'&=\frac{1}{q^2}[(\mathbf{qp})(\mathbf{qp}')]-\frac{\delta}{3}\\ &=\frac{a}{2}\left(1+\frac{\cos\vartheta}{3}\right)-\frac{b}{3}\end{aligned}\qquad(6)$$

$$\mathrm{M}=\mu_{\alpha\beta\gamma\delta}p_\alpha p_\beta{}'p_\gamma p_\delta{}'=(1+\delta^2/3)/2,\quad\delta=\delta_{\alpha\beta}p_\alpha p_\beta{}'=a\cos\vartheta+b,$$

where

$$a=\sin\varphi\sin\psi,\quad b=\cos\varphi\cos\psi.\qquad(6a)$$

The angles ϑ, φ, and ψ occurring in Eqs. (6) and (6a) are related in the following way to the experimental geometry used in Ref. 5: the wave vector of the incident wave **K** is directed along the x axis and the corresponding vector of the scattered wave K' lies in the xy plane making a scattering angle ϑ with the x axis. The directions of the unit vectors p and p' are described by the angles φ and ψ relative to the vertical axis z. The components are therefore described by

$$\begin{aligned}\mathbf{q}&=\mathbf{K}'-\mathbf{K}=\{K(\cos\vartheta-1),\ K\sin\vartheta,\ 0\},\\ \mathbf{p}&=\{0,\ \sin\varphi,\ \cos\varphi\},\\ \mathbf{p}'&=\{-\sin\psi\sin\vartheta,\ \sin\psi\cos\vartheta,\ \cos\psi\}.\end{aligned}$$

Below we shall replace the vectors **q**, **p**, and **p**′ with the angular variables ϑ, φ, and ψ.

In the experiments under discussion the quantities which were measured directly were the integrated values of the scattering coefficient related to Eq. (4) by

$$R_\psi{}^\varphi(\vartheta)=\int_{-\infty}^{\infty}R_\psi{}^\varphi(\vartheta,\ \omega)\,d\omega.\qquad(7)$$

Using Eqs. (3)–(6) and the explicit form of the coefficients $M_i(\mathbf{q},\omega)$ given in Ref. 1, we obtain the integrated scattering coefficient

$$R_\psi{}^\varphi(\vartheta)=N_1\nu+N_2\Pi^2+2N_3\Pi\delta+N_4\mathrm{M}+N_5\delta^2,\qquad(8)$$

where[1]

$$\begin{aligned}&N_1=ATX_0{}^2/\mu_0,\quad N_2=ATX_0{}^2/(K_0+4\mu_0/3),\\ &N_3=ATX_0Y_0/(K_0+4\mu_0/3),\\ &N_4=AT\sum_k n_k{}^2,\\ &N_5=AT\left\{Y_0{}^2/(K_0+4\mu_0/3)+Z_\infty{}^2T/\rho_0C_{V\infty}+\sum_j m_j{}^2\right\}.\end{aligned}\qquad(9)$$

The quantities X_0 and Y_0 in Eq. (9) are the coefficients of the expansion of $\varepsilon_{\alpha\beta}$ in terms of $\tilde{u}_{\alpha\beta}$ and u in the case when all the other variables reach equilibrium at fluctuations $\tilde{u}_{\alpha\beta}$ and u (static values). However, X_∞ and Y_∞ in Eq. (2) are the coefficients in the expansion of the permittivity in terms of $\tilde{u}_{\alpha\beta}$ and u for fixed values of the remaining variable, i.e., they correspond to the case when the other variables do not reach equilibrium with fluctuations of the density and shear (high-frequency values). The quantities K_0 and u_0 are the static values of the bulk and shear moduli; $A=\pi^2k_B/\lambda^4$. Therefore, the integrated scattering coefficient of an isotropic medium can be expressed in terms of the set of angular functions ν, Π^2, $\Pi\delta$, M, and δ^2 [Eqs. (6) and (6a)] and a set of five invariants N_i, which are described by equilibrium properties of matter. The expressions for the integrated scattering coefficients of Eqs. (8) and (9) can be obtained also directly from thermodynamics allowing for the symmetry of the fluctuating parameters. In other words, these relationships do not depend on the actual system of the dynamic equations (1).

Liquids do not support static shear stresses, so that μ_0, K_0, and X^2_0/μ_0 vanish[1] and of all the nonzero invariants only two remain: N_4 and N_5. Equation (8) then reduces to the familiar Einstein-Cabannes formula[5] and the scattering coefficient depends only on δ, i.e., it depends only on the angle between the unit vectors **p** and **p**′ [see Eq. (6)].

In the case of a solid all the invariants N_i are generally different from zero, so that a comprehensive experimental investigation of the Rayleigh scattering in an isotropic solid should include determination of all these invariants. Equation (8) allows us, if we know a sufficient number of the measured scattering coefficients, to determine the whole set N_1–N_5. If the number of measured values $R^{\varphi}_{\psi}(\delta)$ is greater than five, we can then check the self-consistency of the main theoretical result, which is Eq. (8). On the other hand, some of the invariants N_i can be found independently from the data on elastic and elasto-optic properties of the investigated substance, which makes it possible to check the quantitative predictions of the theory.

Selection of the method of carrying out a comprehensive series of experiments is to some extent arbitrary. For example, we can determine five values of the scattering coefficient [the sets of angles that give a nondegenerate system of equations can be deduced from Eq. (6)]. However, this approach is subject to the influence of various distorting factors (glints, surface defects, etc.). It seems to us it is more reliable to determine the angular dependences of the scattering coefficient and to find the invariants N_i by approximation of the results obtained with Eq. (6). We shall use the following set of the angular dependences

$$
\begin{gathered}
R_V{}^H(\vartheta)=R_H{}^V(\vartheta)=[N_4/2+(N_1/4)\cos^2(\vartheta/2)],\\
R_\alpha{}^H(90^\circ)=R_H{}^\alpha(90^\circ)=[N_4/2+N_2/4+(N_1/8-N_2/4)\cos^2\alpha],\\
[R_H{}^H(\vartheta)-R_H{}^H(180^\circ-\vartheta)]/\cos\vartheta=N_3+N_2/6, \qquad (10)\\
R_V{}^V(\vartheta)=N_2/9-2N_3/3+2N_4/3+N_5.
\end{gathered}
$$

The first equation gives N_1 and N_4; the second gives N_2 and the ability to check the values of N_1 and N_4 by adding them; the third gives N_3 and the fourth gives N_5. The indices V and H in Eq. (10) correspond to the polarization angles of 0 and 90°, respectively. The second of the equations in the system (10) is derived on the assumption that either $\varphi=\alpha$ or $\psi=\alpha$.

The scattering of light in a solid described by Eq. (8) has the following qualitative features.

1. The indicatrix of the depolarized scattering $R^{H}_{V}(\vartheta)$ is extended in the forward direction $[R^{H}_{V}(0)>R^{H}_{V}(180^\circ)]$. This follows directly from the positive definite nature of the invariant N_1 and the explicit form of the angular function ν.

2. The Krishnan ratio obeys $\rho_h=R^{H}_{V}(90^\circ)/R^{H}_{H}(90^\circ)\geqslant 1$. This condition can be obtained by substituting, in the determination of the values of ρ_h, the explicit expressions for the scattering coefficients $R^{H}_{V}(90^\circ)$ and $R^{H}_{H}(90^\circ)$ and using the fact that the Poisson ratio is $0\leqslant\sigma\leqslant 1/2$. Hence, we find that $N_1-2N_2\geqslant 0$.

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3. All the invariants N_i, with the exception of N_3, are nonnegative.

We shall below that a comparison of the experimental results with just these qualitative features makes it necessary to modify the theory and, consequently, the expressions for the scattering invariants.

EXPERIMENTS

We investigated experimentally the Rayleigh scattering in fused quartz, which was selected for the following reasons. Samples of this glass can be of high optical quality with weak stray scattering by foreign inclusions.[5,6] Fused quartz is characterized by high values of the ratio X_0/Y_0 (Ref. 11), which results in a major relative contribution of the invariants N_1, N_2, and N_3 to the overall scattering and this in turn provides an opportunity for the experimental determination of these invariants at the precision level feasible at present. Finally, fused quartz has been investigated thoroughly: a sufficiently full set of data is available for this material when calculations and comparisons are made.

Our measurements were carried out on four samples of fused quartz of the *KV* grade both immersed in carbon tetrachloride and without such immersion. Measurements were made at wavelengths of 488 and 515 nm of an argon laser. An FÉU-79 photomultiplier, operating in the photon-counting regime, was used as the photodetector.[12] Apparatus was calibrated by scattering in benzene and the values of the scattering coefficient of this substance $R_V\equiv R^{V}_{V}(90^\circ)+R^{H}_{V}(90^\circ)=28.8\times10^{-6}\ \mathrm{cm}^{-1}$ ($\lambda=515$ nm) and $36.7\times10^{-6}\ \mathrm{cm}^{-1}$ ($\lambda=488$ nm) were taken from Ref. 3. Possible distortions due to luminescence and Raman scattering were avoided by the use of an interference filter. A contribution of stray scattering by the cell walls and the sample could reach 15% of the measured value. Such scattering was eliminated by a method similar to that described in Ref. 13 and based on the fact that the useful signal represented single scattering and the stray scattering was multiple. Measurements were made at room temperature of 20 ± 2°C.

In accordance with the system (10), we measured the dependences $R^{V}_{V}(\vartheta)$, $R^{H}_{V}(\vartheta)$, $R^{V}_{H}(\vartheta)$, $R^{\alpha}_{H}(90^\circ)$, $R^{H}_{\alpha}(90^\circ)$, and $R^{H}_{H}(90^\circ)$. The results of the measurements on all four samples in the range of scattering angles $\vartheta\geqslant 50^\circ$ agreed with one another to within 5%. The value of the scattering coefficient R_V at $\lambda=515$ nm was $(0.104\pm0.005)R^{b}_{V}=(3.0\pm0.15)\times10^{-6}\ \mathrm{cm}^{-1}$, where R^{b}_{V} is the scattering coefficient of benzene; the value of the depolarization coefficient was $\Delta_V\equiv R^{H}_{V}(90^\circ)/R^{V}_{V}(90^\circ)=(4.2\pm0.2)\cdot10^{-2}$. These values agreed with those reported elsewhere, namely with $R_V=(2.5\text{–}2.9)\times10^{-6}\ \mathrm{cm}^{-1}$ given in Refs. 5–7, 14, and 15 (reduced to the wavelength $\lambda=515$ nm) and $\Delta_V=0.04\text{–}0.05$ given in Refs. 5–7.

Our experimental results are plotted in Figs. 1–4. The graph $R^{V}_{V}(\vartheta)$ in Fig. 1 shows that for the scattering angles $\vartheta<50^\circ$ the scattering coefficient is independent of ϑ to within $\sim5\%$, which is in agreement with Eq. (8). Some increase in $R^{V}_{V}(\vartheta)$ in the range $\vartheta<50^\circ$, observed also in Ref. 6, is possible due to the large-scale structure of fused quartz observed earlier.[16] An estimate of the characteristic size of the homogeneities deduced from the scattering angles at which the effect was observed gave a value of ~1000 Å, in agreement with the results obtained in Ref. 16. Therefore, in the theoretical interpretation we decided to ignore the data for the scattering at angles $\vartheta<50^\circ$.

The curves plotted in Figs. 2 and 3 are in conflict with

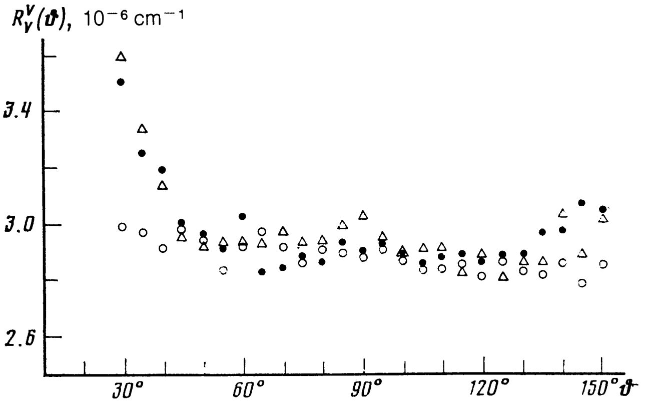

FIG. 1.

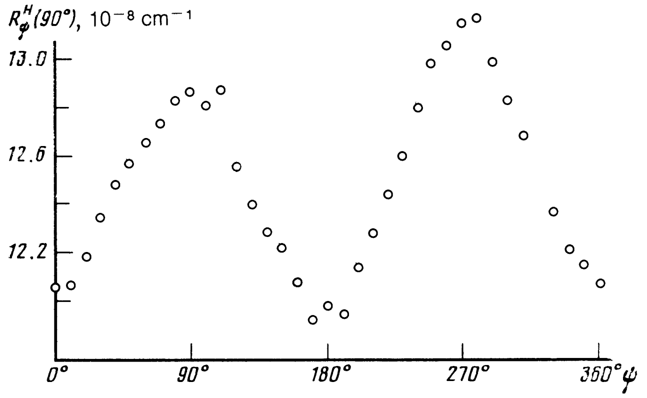

FIG. 3.

the above qualitative characteristics of the scattering in equilibrium solids in the following respects.

1. The indicatrix of the depolarized scattering is extended in the backward direction (Fig. 2), which is possible only in the case of a negative value of the invariant N_1.

2. The Krishnan ratio is less than unity (Fig. 3).

3. The invariant N_2 deduced from the experimental data is also negative.

It is clear from just these results that it is pointless to try to compare quantitatively the experimental results with the theory of Ref. 1.

MODIFICATION OF THE THEORY OF THE RAYLEIGH SCATTERING AND INTERPRETATION OF THE EXPERIMENTAL RESULTS

We shall assume that the most important property of glass samples resulting in such a major disagreement between the experimental data and the theory of Ref. 1 is the anomalous slowing down of the processes of establishment of an equilibrium on approach to the glass-formation region (see, for example, Refs. 8 and 9). The times needed to establish an equilibrium increase as a result of cooling in accordance with a nearly exponential law and in a narrow range of temperatures $\Delta T \ll T$ the values of these times may change from negligible, compared with the measurement time t_m, to values many times greater than a reasonable t_m. The glass-transition temperature is essentially the temperature at which the relaxation time of the system is of the same order of magnitude as the observation time. We can understand better the sense of the changes which we shall have to make in the equilibrium theory by considering, by way of illustration, the simplest model of a liquid, for which one relaxation time can be considerably greater not only than all the other characteristic times of the system but also than t_m.

For simplicity, we shall assume that the thermodynamic state of such a liquid is described by just two variables: the density ρ and the scalar relaxation parameter ξ, characterized by a relaxation time which rises anomalously. Following the general approach presented at the beginning of this paper, we shall write down the explicit system of equations (1) for this case:

$$\frac{\partial^2\delta\rho}{\partial t^2}=\Delta\delta P-\frac{1}{\rho_0}\zeta\Delta\frac{\partial\delta\rho}{\partial t}-\frac{\partial^2\Sigma_{ik}}{\partial x_i\,\partial x_k},\qquad \frac{\partial\xi}{\partial t}=-\alpha\frac{\partial\Psi}{\partial\xi}+\alpha\Xi, \tag{11}$$

where $\delta\rho$ and δP are the deviations of the density and pressure from the equilibrium values; ζ is the total viscosity of the liquid; α is a transport coefficient; Σ_{ik} is the tensor of fluctuation stresses; Ξ is a fluctuation force with is the conjugate of ξ; Ψ is the free energy of the system.

The pressure P and the quantity $h = \partial\Psi/\partial\xi$ considered in an approximation linear in fluctuations are

$$\delta P=P_\rho^{(\xi)}\,\delta\rho+P_\xi^{(\rho)}\,\xi,\qquad h=h_\rho^{(\xi)}\,\delta\rho+h_\xi^{(\rho)}\,\xi, \tag{12}$$

where $P_\rho^{(\xi)} = (\partial P/\partial\rho)_\xi$ etc. Substituting Eq. (12) into Eq.

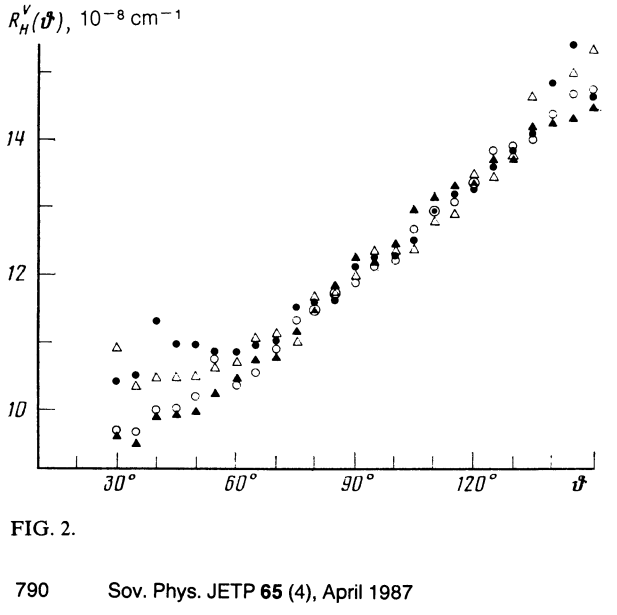

FIG. 2.

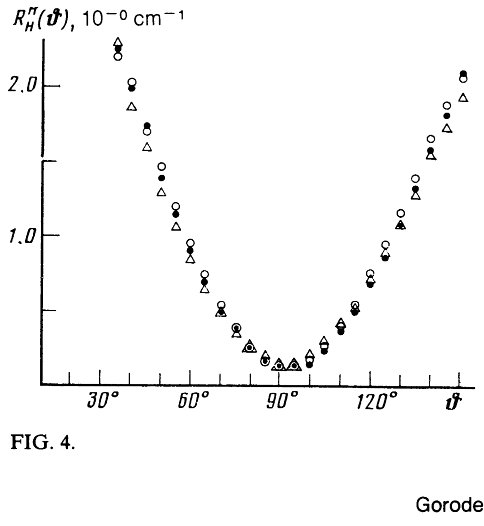

FIG. 4.

(11) and going over to the Fourier representation, we obtain a system of two linear algebraic equations:

$$G_{ac}\delta\rho(\mathbf{q},\omega)-P_{\xi}^{(\rho)}q^2\xi(\mathbf{q},\omega)=-q_iq_k\Sigma_{ik}, \tag{13}$$

$$-i\alpha(P_{\xi}^{(\rho)}/\rho_0)\delta\rho(\mathbf{q},\omega)+G_{\xi}\xi(\mathbf{q},\omega)=-i\alpha\Xi,$$

where

$$G_{ac}=\omega^2-i\omega\mathbf{q}^2\zeta/\rho_0-\omega_\infty{}^2,\ G_{\xi}=\omega-i\tau^{-1},$$

$$\omega_\infty{}^2=P_{\rho}^{(\xi)}\mathbf{q}^2,\ \tau^{-1}=\alpha h_{\xi}^{(\rho)}.$$

The solution of this system is

$$\delta\rho(\mathbf{q},\omega)=-\frac{1}{\Delta(\mathbf{q},\omega)}\{G_{\xi}q_iq_k\Sigma_{ik}+i\alpha P_{\xi}^{(\rho)}q^2\Xi\},$$

$$\xi(\mathbf{q},\omega)=-\frac{i\alpha}{\Delta(\mathbf{q},\omega)}\{(P_{\xi}^{(\rho)}/\rho_0)q_iq_k\Sigma_{ik}+G_{ac}\Xi\}, \tag{14}$$

where $\Delta(\mathbf{q},\omega)=G_{ac}G_{\xi}-i\alpha P_{\xi}^{(\rho)2}q^2/\rho_0^2$ is the determinant of the system (13).

The expressions in Eq. (14) allow us to find the spectral densities of macroscopic variables. For example, the spectral density of fluctuations $\delta\rho$ is given by

$$\langle|\delta\rho|^2\rangle=\frac{1}{|\Delta|^2}\{|G_{\xi}|^2q^4\langle|\Sigma|^2\rangle+\alpha^2P_{\xi}^{(\rho)2}q^4\langle|\Xi|^2\rangle\}, \tag{15}$$

where

$$q^4\langle|\Sigma|^2\rangle=\langle\Sigma_{ik}\Sigma_{lm}{}^*\rangle q_iq_kq_lq_m.$$

Equation (15) is derived on the assumption that $\langle\Sigma_{ik}\,\Xi^*\rangle$ is obeyed in the thermodynamic equilibrium state of a medium in the presence of random forces.

In a medium at equilibrium the mean-square value of fluctuations of the density is equal to the integral of Eq. (15) with respect to all the frequencies. An equilibrium then occurs when all the times for establishment of the equilibrium values are much shorter than the measurement time t_m. The time for the establishment of an equilibrium is governed by the imaginary parts of the roots of the equation $\Delta(\mathbf{q},\omega)=0$. This equation has three roots: two acoustic roots $\omega_{1,2}=\pm\omega_{ac}+i\gamma$, and one relaxation root $\omega_3=i\omega_r i\tau^{-1}$ (we shall assume that the absorption of sound is weak, $\omega_{ac}\gg\gamma$, which is normally true in the case of real systems). In the case of slow relaxation characterized by $\gamma\gg\tau^{-1}$, the quantities governing the roots of the equation $\Delta(\mathbf{q},\omega)=0$ are as follows

$$\omega_{ac}^2=P_{\rho}^{(\xi)}q^2,\qquad \gamma=\zeta q^2/2\rho_0,\qquad \omega_r=\tau^{-1}P_{\rho}^{(h)}/P_{\rho}^{(\xi)}\equiv\alpha h_{\xi}^{(P)}.$$

If the inequalities $\omega_{ac}\gg\gamma\gg\tau^{-1}$ are obeyed, Eq. (15) simplifies greatly. In the main approximation with respect to the parameters $1/\omega_{ac}\tau$ and $1/\gamma\tau$, it reduces to the following expression:

$$\langle|\delta\rho|^2\rangle_\omega=\frac{\langle|\Sigma|^2\rangle q^4}{|G_{ac}|^2}+\alpha^2\left(\frac{P_{\xi}^{(\rho)}}{P_{\rho}^{(\xi)}}\right)^2\frac{\langle|\Xi|^2\rangle}{\omega^2+\omega_r^2}. \tag{16}$$

The structure of Eq. (16), obtained from the theory of the equilibrium case, corresponds to the separation of fluctuations of macroscopic variables into two subsystems. The first subsystem, associated with a rapidly relaxing acoustic wave [or in the more general case, associated with all the modes of frequencies obeying $\mathrm{Im}(\omega_i)\gg\tau^{-1}$ is represented in Eq. (16) by a term proportional to $\langle|\Sigma|^2\rangle$. We shall call it the fast subsystem. The second (slow) subsystem is associated with a relaxation mode of frequency of the order of τ^{-1}. It is represented in Eq. (16) by the term with $\langle|\Xi|^2\rangle$. If fluctuations of the density are written down as the sum of the rapidly relaxing ($\delta\rho_1$) and slowly relaxing ($\delta\rho_2$) parts, then the spectral density $\delta\rho_1$ is equal to the first term in Eq. (15), whereas $\delta\rho_2$ is equal to the second term. In accordance with Eq. (16), the fast and slow contributions are uncorrelated, $\langle\delta\rho_1\delta\rho_2^*\rangle_\omega=0$, and this means that their fluctuations can be calculated independently.

In our model the fast subsystem is always in equilibrium ($t_m\gg\gamma^{-1}$), so that the mean-square value of the fluctuations in the fast subsystem can be found by integration of the first term in Eq. (16) with respect to all the frequencies:

$$\langle|\delta\rho_1|^2\rangle=\rho_0k_BT/P_{\rho}^{(\xi)}. \tag{17}$$

As long as the slow subsystem is also in equilibrium with the thermostat, the mean-square value of $\delta\rho_2$ can also be found in a similar manner:

$$\langle|\delta\rho_2|^2\rangle=\frac{k_BTP_{\xi}^{(\rho)2}}{P_{\rho}^{(\xi)2}h_{\xi}^{(P)}}\equiv\rho_0k_BT\left\{\frac{1}{P_{\rho}^{(h)}}-\frac{1}{P_{\rho}^{(\xi)}}\right\}. \tag{18}$$

[in the derivation of Eqs. (17) and (18) we have allowed for the fact that, in accordance with the fluctuation-dissipation theorem, we have $\langle|\Sigma|^2\rangle=\zeta k_BT/\pi$ and $\langle|\Xi|^2\rangle=k_BT/\pi\infty$]. The mean-square values of the density fluctuations can be described, as expected, by the thermodynamic expression

$$\langle|\delta\rho|^2\rangle=\langle|\delta\rho_1|^2\rangle+\langle|\delta\rho_2|^2\rangle=\rho_0k_BT/P_{\rho}^{(h)},$$

However, if the relaxation time τ rises without limit, we unavoidably reach a situation described by $\omega_r^{-1}\gg t_m$. We shall show later that this corresponds to the transition from the liquid to the glassy state. The slow subsystem cannot then attain equilibrium during the measurement time and the corresponding part of the density fluctuations $\delta\rho_2$ is found to be static (freezes), so that this part is not in equilibrium at lower temperatures.

Integration of the second term in Eq. (16) with respect to the frequency (equivalent to averaging with respect to time) does not, because the resultant nonergodicity, necessarily give the same result as averaging over an ensemble. Therefore, we cannot calculate $\langle|\delta\rho|^2\rangle$ rigorously.[2)] However, in view of the anomalous increase in the relaxation time as a result of cooling, we can assume that this quantity remains constant throughout the range $T<T_g$ and equal to its value at the glass-transition temperature $T=T_g$, i.e.,

$$\langle|\delta\rho_2|^2\rangle=\rho_0k_BT_g\left\{\frac{1}{P_{\rho}^{(h)}}-\frac{1}{P_{\rho}^{(\xi)}}\right\}_{T_g}.$$

The glass-transition temperature T_g is found from $\omega_r(T_g)=t_m^{-1}$ (Ref. 9). We thus see that if $T<T_g$, then

$$\langle|\delta\rho|^2\rangle=\rho_0k_BT\left[T\frac{1}{P_{\rho}^{(\xi)}}+T_g\left\{\frac{1}{P_{\rho}^{(h)}}-\frac{1}{P_{\rho}^{(\xi)}}\right\}_{T_g}\right]. \tag{19}$$

We stress once again that if $t_m\ll\tau$, then the rapidly relaxing subsystem remains in equilibrium. The thermodynamic description is valid for this system and the usual relationships between thermodynamic derivatives apply. The frozen subsystem makes no contribution to the thermodynamic derivatives because it is static. When such a division of the time scales is made, then Eqs. (17) and (18), like Eqs. (8) and (9), follow directly from thermodynamics and are independent of the nature of the system of equations (11) or the spectral representation (16). Equation (19) follows from Eqs. (17) and (18) if we additionally assume that the slow subsystem freezes and, therefore, it is also independent of the actual form of the initial system of equations (11). In the liquid range the low-frequency bulk modulus measured in a static experiment $K_0^{(l)}$ is governed by the thermodynamic derivative $P_\rho^{(h)}$: $K_0^{(l)}=\rho_0 P_\rho^{(h)}$. In the case of a glass the low-frequency bulk modulus $K_0^{(g)}$ measured in a similar experiment is now governed by the derivative $P_\rho^{(\xi)}$: $K_0^{(g)}=\rho_0 P_\rho^{(\xi)}$. On the other hand, the derivative $P_\rho^{(\xi)}$ gives the high-frequency value of the bulk modulus of a liquid ($K_\infty^{(l)}$), i.e.,

$$K_0^{(g)}=K_\infty^{(l)}.$$

Similar relationships apply also to the other parameters of the system. The relationship between the high-frequency characteristics of a liquid and the low-frequency characteristics of a glass is necessary in the interpretation of the experimental results.

We shall now turn from the above example to the more general situation when the state of a system is described by the full set of variables of Eq. (2). Once again, we shall make the separation into rapidly and slowly relaxing subsystems. The only thing that we need is a considerable difference between the scale of the characteristic times. Then, the expressions for the coefficients $M_i(\mathbf{q},\omega)$ in Eq. (3) [see also Eq. (22) in Ref. 1] split into two parts, one of which is associated only the fast subsystem and the other with the slow subsystem. The contribution of the fast subsystem to the integrated scattering intensity of Eq. (7) is governed, as pointed out above, by modes of frequencies which obey $\operatorname{Im}(\omega_i)\gg\tau^{-1}$. The contribution of the slow subsystem is related to the modes of frequencies $\omega_k\propto\tau^{-1}$, i.e., the expressions for the coefficient $M_i(\mathbf{q},\omega)$ have a structure similar to that of Eq. (16). For example, the quantity $M_1(\mathbf{q},\omega)$ [see Eq. (4)] considered in the same approximation as that used to derive Eq. (16) is

$$M_1(q,\omega)=\frac{1}{(2\pi)^3}\left\{\frac{X_\infty{}^2q^4\langle|\Sigma'|^2\rangle}{|G_{sh}|^2}+\left[-\frac{(X_\infty-X_0)^2}{\mu_\infty-\mu_0}\frac{\tau^{-2}}{\omega^2+\tau^{-2}}\right.\right.$$
$$\left.\left.+\frac{(X_\infty\mu_0-X_0\mu_\infty)^2}{(\mu_\infty-\mu_0)\mu_\infty{}^2}\frac{\tau^{-2}}{\omega^2+\omega_r^2}\right]\langle|Z|^2\rangle\right\},\tag{20}$$

where $\langle|\Sigma'|^2\rangle=k_BT\eta/\pi$ and $\langle|Z|^2\rangle=k_BT\tau/\pi$ are quantities obtained from the correlations of the fluctuation forces Σ_{ik} and $\widetilde{Z}_{ik}$, which are the conjugates of the strain tensor and of the slowly relaxing tensor parameter[1]; η is the shear viscosity;

$$G_{sh}=\omega^2-i\omega q^2\eta/\rho_0-\mu_\infty q^2/\rho_0,$$

$\omega_r=\tau^{-1}\mu_0/\mu_\infty$. As in Ref. 15, the term with $\langle|\Sigma'|^2\rangle$ represents the contribution of the fast subsystem and the term with $\langle|Z|^2\rangle$ represents the contribution of the slow system $M_1(\mathbf{q},\omega)$.

The equilibrium values of the fast ($N_1^{(1)}$ and slow ($N_1^{(2)}$) contributions to the invariant N_1 can be found by integration of the relevant terms in Eq. (20) with respect to all the frequencies:

$$N_1^{(1)}=ATX_\infty{}^2/\mu_\infty,$$
$$N_1^{(2)}=AT\left\{-\frac{(X_\infty-X_0)^2}{\mu_\infty-\mu_0}+\frac{(X_\infty\mu_0-X_0\mu_\infty)^2}{(\mu_\infty-\mu_0)\mu_0\mu_\infty}\right\};$$

hence, in full agreement with Eq. (9), we obtain

$$N_1\equiv N_1^{(1)}+N_1^{(2)}=ATX_0{}^2/\mu_0.$$

If $t_m\ll\tau$ and the assumptions of the simplified model apply, we obtain

$$N_1(T)=N_1^{(1)}(T)+N_1^{(2)}(T_g)\equiv N_1^{(1)}(T)+[N_1(T_g)-N_1^{(1)}(T_g)].$$

We must bear in mind that in the frozen contribution of the slow subsystem $N_1^{(2)}(T_g)$ we have to include not only an explicit temperature dependence in the form of the factor k_BT, which originates from the correlation function of the fluctuation forces, but also contributions due to possible temperature dependences of X_0, X_∞, μ_0, and μ_∞.

In this way we obtain expressions also for the other invariants:

$$N_i(T)=N_i^{(1)}(T)+N_i^{(2)}(T_g)\equiv N_i^{(1)}(T)+[N_i(T_g)-N_i^{(1)}(T_g)].$$

Since a system in the equilibrium region at temperatures $T>T_g$ represents a liquid for which the first three invariants vanish, it follows that in the glassy region, (i.e., at temperatures $T<T_g$), these invariants are of the form

$$N_i(T)=N_i^{(1)}(T)-N_i^{(1)}(T_g)\quad(i=1,2,3).$$

Neglecting temperature dependences of X_∞, Y_∞, K_0, K_∞, and μ_∞, we obtain

$$N_i(T)\approx N_i^{(1)}(T)(T-T_g)/T\quad(i=1,\ 2,\ 3).$$

Therefore, the sign of the first three invariants for glass is opposite to the sign of the invariant for the fast subsystem. Since in the case of the fast subsystem we find that the equilibrium expressions of Eq. (8) are valid, it follows that both $N_1^{(1)}$ and $N_1^{(2)}\leqslant 0$. Consequently, in the case of a glass the two invariants are N_1 and $N_2\geqslant 0$. We can readily show that the inequalities governing the values of N_1-2N_2 and ρ_h in the case of a glass are also opposite to those in the case of an equilibrium isotropic solid. These qualitative features of glasses, liquids, and equilibrium isotropic solids are listed in Table I.

In considering the general case corresponding to Eq. (1) with the full set of variables of Eq. (2), we were assuming that the slow variable is a tensor relaxation parameter of an arbitrary form. Relaxation of just this tensor parameter results, as is demonstrated by the equations of hydrodynamics (1), in the appearance of dynamic shear stresses in a system (representing high-frequency shear sound[17]). How-

TABLE I.

	Equilibrium solid	Liquid	Glass
N_1	$\geqslant 0$	0	$\leqslant 0$
N_2	$\geqslant 0$	0	$\leqslant 0$
N_1-2N_2	$\geqslant 0$	0	$\leqslant 0$
ρ_h	$\geqslant 1$	1	$\leqslant 1$

TABLE II.

i	Experiment	Calculation	
	$N_i\cdot 10^8$ cm	$N_i^{(1)}\cdot 10^8$ cm	$N_i\cdot 10^8$ cm
1	-26 ± 4	8.2 ± 1.4	-28 ± 5
2	-10 ± 2	$3{,}2\pm0.5$	-11 ± 2
3	24 ± 5	-4.9 ± 0.7	18 ± 4
4	31 ± 3	$\geqslant0$	$\geqslant36\pm5$
5	280 ± 20	$\geqslant7{,}5\pm1.0$	$\geqslant170\pm50$

ever, if $t_m \ll \tau$, these shear stresses are retained throughout the measurement period, i.e., a finite static shear modulus appears in the system. However, this implies the transition from a liquid to a solid (glass).

The relationship between the shear stresses and the slow tensor relaxation parameter gives the following relationship between the invariants N_1 and N_4:

$$N_1+N_4=N_1^{(1)}+N_4^{(1)}$$

(the contributions of the slow subsystem balance out in this expression).

It follows from the experimental results that qualitative characteristics of the scattering in fused quartz agree with those of glass obtained in our modified theory. We shall now carry out a quantitative comparison. Table II gives the experimental and calculated values of the invariants for fused quartz. The experimental values are obtained by approximation of the data (Figs. 1–4) with the dependences in Eq. (10). The errors listed in Table II include the confidence limit of the approximation as well as the error in the determination of the absolute values of the scattering coefficient using the selected apparatus. The contributions of the fast subsystem were calculated using the following values of the elastic and elasto-optic characteristics: $X_0 = 0.66 \pm 0.04$; $Y_0 = -1.01 \pm 0.06$; $\mu_0^{(g)} = (3.0 \pm 0.2)\times 10^{10}$ J/m^3; $K_0^{(g)} = (3.7 \pm 0.4)\times 10^{10}$ J/m^3. These values were obtained from the Pockels constants $p_{12} = 0.27 \pm 0.01$ and $p_{44} = -0.072 \pm 0.004$ (Refs. 11 and 18), from the refractive index $n = \varepsilon^{1/2} = 1.462$ (Ref. 19), from the velocities of longitudinal $V_L = 5900 \pm 50$ m/sec and transverse $V_T = 3700 \pm 100$ m/sec sound,[5,7,10] and from the density $\rho_0 = 2.206$ g/cm^3 (Ref. 19). All the values apply at room temperature $T = 293$ K at the wavelength of $\lambda = 515$ nm. The relationships between the initial values and those in Eq. (8) are as follows:

$$\mu_0^{(g)}=\rho_0 V_T^2,\quad K_0^{(g)}+4\mu_0^{(g)}/3=\rho_0 V_L^2,$$
$$X_0=-2n^4 p_{44},\quad Y_0=-n^4(p_{12}+2p_{44}/3).$$

Since the data on the contribution of rapidly relaxing parameters were not available in the interval corresponding to $N_4^{(1)}$ and $N_5^{(1)}$, only the inequalities could be given for these invariants.

In calculating the total values of the invariants we needed the values of the moduli and the glass-transition temperature and the temperature itself. Following the data presented in Fig. 7 of Ref. 20, we assumed that the elastic moduli increased in the interval between $T = 293$ K and $T_g = 1400$ K by 10%. This was in agreement with the studies of the hypersonic properties reported in Ref. 21. The glass-transition temperature T_g was taken to be the average value of those listed in various handbooks, namely 1350 ± 100 K (Refs. 7, 20, and 22).

Since in the liquid state (when $T > T_g$) the value of the invariant N_5 does not vanish (in contrast to N_1, N_2, N_3), we had to know the value of the modulus $K_0^{(l)}$ at temperatures $T \gtrsim T_g$. We took the value found by x-ray diffraction measurements[23]: $K_0^{(l)}$ $(T \gtrsim T_g) = (1.5 \pm 0.15)\times 10^{10}$ J/m^3.

It is clear from Table II that, within the limits of the total experimental error, the calculated and experimental values of the invariants are in agreement. Naturally, our modified theory is not based on general principles of statistical physics, but simply on physically reasonable assumptions. However, we must stress that the good (not only qualitative but also quantitative) agreement between our formulas and the experimental data, achieved without any fitting, supports strongly the assumptions and our description of the Rayleigh scattering of light in glasses.

It is worth pointing out an interesting observation which applies directly to fused quartz. It is clear from Table II that the inequality for N_4 can be replaced (within the limits of the experimental error) by the equality. This means that the only tensor parameter of fused quartz which experiences relaxation is that which is responsible for the formation of a glass. In this sense we can regard fused quartz as the "minimal" model of a glass.

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[1)] The term with Z_∞^2 in N_5 was omitted in Ref. 1 because of the incorrect statement that "for all the intensities of Eq. (24) we have $g(\infty)/f(\infty) = 0$." In fact, the term with Z_∞^2 which is a coefficient of $\langle T_1 T_1^* \rangle_\omega$ [see Eqs. (19) and (24) in Ref. 1] differs from zero in the limit $\omega \to 0$.

[2)] If $T < T_g$, we have a time-independent field of frozen inhomogeneities $\delta\rho_2(\mathbf{r})$, which contribute to the intensity of the unshifted component in the spectrum of scattered light in the form of the δ function of the frequency ω. The time averaging of this field simply does not alter anything. In this case it would have been natural to assume the existence of spatial ergodicity at which the statistical average is equal to the volume average. However, we cannot carry out the correct averaging of the volume, because we do not know the statistics of the field $\delta\rho_2(\mathbf{r})$.

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