

Intensity of the spectral components for Rayleigh scattering of light in glasses

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The results of a modified relaxation theory are generalized to the total intensities of the spectral components of the Rayleigh scattering of light in glasses. Expressions are obtained for the total scattering coefficients in terms of the spectral components. A comparison of the calculations on the basis of these expressions for molten quartz with the available experimental data has shown that they are in full agreement. The combined analysis of our earlier data on the total scattering coefficient with the data on the spectral scattering coefficients is used to obtain additional information on the investigated object (molten quartz). In particular, it is shown that tensor relaxation in the melt is related to more than one relaxation parameter. Moreover, it is shown that dispersion of the derivative $(\rho\delta\varepsilon/\delta\rho)_T$ should be exhibited by the melt.

INTRODUCTION AND FORMULATION OF THE PROBLEM

The problem of describing the Rayleigh scattering of light in glasses was largely solved in Ref. 1, where the standard scheme for the calculation of fluctuations² was modified to apply to the case of anomalous slowing down of the relaxation processes on transition from a liquid to a glass.¹⁾ Consequently, the results of experimental investigations of the total intensity of the Rayleigh scattering of light in fused quartz were found to be in qualitative and even quantitative agreement with the theoretical predictions. However, a description of the scattered-light spectrum was outside the scope of the treatment given in Ref. 1. On the other hand, a scheme for calculating the scattering coefficient of light in glasses developed in Ref. 1 makes it possible to go over in a natural way to the total intensities of the characteristic spectral components and thus widen the range of theoretical predictions. Moreover, the same calculation scheme provides additional opportunities for experimental determination of the parameters of the medium occurring in the theory. Since basically the calculation scheme of Ref. 1 does not include a model of the liquid–glass transition, but uses simply the familiar anomalous increase in the relaxation times as a result of this transition,^{3,4} the profiles of the spectral components (lines) can be obtained by this method for the transition region. However, as noted, we can find the total intensities of the spectral components expressed (sufficiently far from the temperature in the region of the transition) in terms of equilibrium (thermodynamic) properties of the liquid and glass.

The main idea introduced in Ref. 1 is that in a liquid approaching the glass-formation stage the fluctuations can be divided into two subsystems: “fast” when equilibrium with the thermostat is achieved after a short time and “slow” when the time needed to establish equilibrium increases without limit in the transition from the liquid to the glass. The various subsystems contribute very different components of the scattered-light spectrum. Information on the subsystems can therefore be obtained directly from the spectral data even without analysis of their symmetry properties, as was done in the full experiments.¹ Moreover, we can separate fluctuations of the same symmetry, particularly scalar fluctuations, which cannot be done in a full experiment involving the total intensities. The fast fluctuations shift and broaden the spectral components. They include the acoustic

modes, giving rise to corresponding doublets, a “heat-conduction” mode, and modes associated with fast relaxation processes that show no “freezing” and generally occur in glasses. Fluctuations of the slow subsystem are “frozen” in the glass from the statistical point of view and, hence, they contribute to the spectrum an unbroadened δ -like line at the unshifted frequency.

As already stressed, we shall consider only the total intensities of the spectral components which can be expressed in terms of the thermodynamic properties of the liquid and glass. These expressions can be obtained directly from the theoretical formulas given in Ref. 1. Before writing them down, we must make certain assumptions which are not of fundamental importance, but which describe the experimental situation and simplify greatly the final expressions. In the case of the majority of real systems the temperature fluctuations make a very small contribution to the scattering [in view of the smallness of the derivative $\partial\varepsilon/\partial T)_\rho$].^{1,7,8} Therefore, we shall ignore the temperature fluctuations and the deviation between the isothermal values of the moduli of glass and their adiabatic values. This is the usual approximation for solids⁹ and it relies on the smallness of the thermal expansion coefficient. We shall assume moreover that there are no relaxation processes with frequencies lower than or of the order of the acoustic mode frequencies, i.e., there is no dispersion of the moduli. This assumption is naturally disobeyed in some systems and then the description must be supplemented by a suitable relaxation model. This gives rise to cumbersome expressions but no fundamental difficulties are likely.

CALCULATIONS

The Rayleigh scattering of light is associated with fluctuations of the permittivity tensor $\varepsilon_{\alpha\beta}$. In our case these are not only the equilibrium thermal fluctuations, but also the fluctuations which are “frozen” on transition from the liquid to the glass. The light-scattering coefficient is obtained by convolving the correlation function of the fluctuations of $\varepsilon_{\alpha\beta}$ with the unit vectors representing the polarizations of the incident (\mathbf{p}) and the scattered (\mathbf{p}') light:

$$R(\theta, \varphi, \psi) \sim \langle \varepsilon_{\alpha\beta} \varepsilon_{\gamma\delta} \rangle p_\alpha p_\beta' p_\gamma p_\delta', \quad (1)$$

where ϑ is the scattering angle (i.e., the angle between the

wave vectors of the incident and scattered light), and φ and ψ are the corresponding polarization angles of the incident and scattered light. The total scattering coefficient is the sum of the total scattering coefficients of all the spectral components:

$$R = R_T + R_L + R_F + R_S, \quad (2)$$

where R_T and R_L denote the coefficients of the scattering by transverse and longitudinal acoustic waves, while R_F and R_S are the scattering coefficients associated with the existence of the fast and slow (resulting in the formation of a cluster) relaxation parameters. The dependence of these quantities on the scattering angle ϑ and on the angles of polarization of the incident and scattered light (φ and ψ) can be expressed in terms of the functions ν , Π , M , and δ . These functions, formed by convolution of the polarization vectors \mathbf{p} and \mathbf{p}' , are the tensors which are obtained in the calculation of the correlation functions $\langle \varepsilon_{\alpha\beta} \varepsilon_{\gamma\delta} \rangle$. The nature of the functions can be found in Ref. 1. The expressions for the total spectral scattering coefficients R_T , R_L , R_F , and R_S are as follows:

$$\begin{aligned} R_T &= AT X^2 \nu / \mu_0, \\ R_L &= AT (X\Pi + Y\delta)^2 / (K_0 + 4/3\mu_0), \\ R_F &= AT \left(M \sum_k n_k^{(F)2} + \delta^2 \sum_j m_j^{(F)2} \right), \\ R_S &= AT_g \left[M \sum_i n_i^{(S)2} + \left(Y_{i0}^2 / K_{i0} + \sum_i m_i^{(S)2} \right) \delta^2 - X^2 \nu / \mu_0 \right. \\ &\quad \left. - (X\Pi + Y\delta)^2 / (K_0 + 4/3\mu_0) \right]_{T_g}. \end{aligned} \quad (3)$$

Here $A = \pi^2 k_B / \lambda^4$, k_B is the Boltzmann constant, λ is the wavelength of light, μ_0 is the shear modulus of the investigated glass, K_0 and K_{i0} are, respectively, the static bulk moduli of the glass and melt (liquid), X_0 and Y_0 are the static elastooptic constants of the glass, Y_{i0} are the corresponding constants of the melt,^{1,2} and $n_k^{(F)}$, $n_i^{(S)}$, $m_j^{(F)}$, $m_i^{(S)}$ are the expansion coefficients in the expression for the permittivity $\varepsilon_{\alpha\beta}$ in terms of fluctuations of the scalar (m) and tensor (n) relaxation parameters, respectively. In the expression R_S , which is the coefficient of the scattering by "frozen" fluctuations

("frozen" slow subsystem) the values of all the parameters are taken at a temperature equal to the glass-transition temperature T_g (Ref. 1).

Table I gives the expressions for the spectral scattering coefficients of Eq. (1) calculated for the scattering angle $\vartheta = 90^\circ$ and the most widely used polarizations in experiments: VV ($\varphi = \psi = 0^\circ$), VH ($\varphi = 0^\circ$, $\psi = 90^\circ$), HV ($\varphi = 90^\circ$, $\psi = 0^\circ$) and HH ($\varphi = \psi = 90^\circ$). In the calculation of the scattering coefficients using the expressions derived above it is necessary to bear in mind a problem due to the fact that some of the parameters, namely n_k and m_j , cannot be determined experimentally. However, using the relationships for the dispersions of the elastic and elastooptic moduli [Eqs. (6) and (21) in the fundamental paper of Rytov²], we can write down inequalities for the relevant scattering coefficients (they are also included in Table I).

Experimental determination of the absolute values of the spectral scattering coefficients is difficult, but one can determine quite accurately the ratios of the intensities of the different spectral components. One of these ratios, defined as $(R_C^{VV} - 4/3 R_C^{VH}) / R_L^{HH}$ (R_C^{VV} and R_C^{VH} are the intensities of the central components for the VV and VH polarizations, respectively, whereas R_L^{VV} is the intensity of the scattering by longitudinal sound with the VV polarization), is known in the literature as the Landau-Placzek ratio. Measurements of this kind had been carried out on glasses on many occasions and those specifically on fused quartz are reported in Refs. 8 and 10. A calculation of the ratios of the intensities can be carried out in two ways. The first involves direct application of the system of equations (3) and of Table I. In the case of the majority of the ratios one can only obtain inequalities. The second way involves the use of independently determined experimental values of the integral scattering coefficient (for example, those taken from Ref. 1). Use is then made of the obvious [see Eq. (2)] relationship $R_C = R_F + R_S = R - R_T - R_L$. In this case the ratios of the spectral components yield equalities containing quantities that can be determined experimentally.

The use of the results of spectral measurements in combination with the results of integral measurements enables us, subject to the assumptions made above, to distinguish the contributions made to the central component by the fast and

TABLE I.

Polarization	R_T	R_L	R_F	R_S
VV	0	$\frac{AT(Y_0 - 1/3 X_0)^2}{K_0 + 4/3\mu_0}$	$AT \left[\sum_j m_j^{(F)2} + 2/3 \sum_k n_k^{(F)2} \right]$	$AT_g \left[2/3 \sum_k n_k^{(S)2} + \sum_j m_j^{(S)2} + \frac{Y_{i0}^2}{K_{i0}} - \frac{(Y_0 - 1/3 X_0)^2}{K_0 + 4/3\mu_0} \right]_{T_g}$ $\geq AT_g \left[\frac{X_0^2}{3\mu_0} + \frac{Y_{i0}^2}{K_{i0}} + \frac{(Y_0 - Y_{i0})^2}{K_0 - K_{i0}} - \frac{(Y_0 - 1/3 X_0)^2}{K_0 + 4/3\mu_0} \right]_{T_g}$
VH, HV	$\frac{AT X_0^2}{8\mu_0}$	0	$\frac{AT}{2} \sum_k n_k^{(F)2}$	$AT_g \left[1/2 \sum_k n_k^{(S)2} - \frac{X_0^2}{8\mu_0} \right]_{T_g} \geq AT_g \left[\frac{X_0^2}{8\mu_0} \right]_{T_g}$
HH	0	$\frac{AT X_0^2}{4(K_0 + 4/3\mu_0)}$	$\frac{AT}{2} \sum_k n_k^{(F)2}$	$AT_g \left[1/2 \sum_k n_k^{(S)2} - \frac{X_0^2}{4(K_0 + 4/3\mu_0)} \right]_{T_g}$ $\geq AT_g \left[\frac{X_0^2 (K_0 + 1/3\mu_0)}{4\mu_0 (K_0 + 4/3\mu_0)} \right]_{T_g}$

slow relaxing parameters, i.e., of R_F and R_S . In the case of sufficiently fast equilibrium relaxation processes discussed here, the width of a spectral line corresponding to the coefficient R_F is much greater than the shifts of the acoustic spectral lines, so that employing the existing techniques of recording the spectrum of scattered light^{8,10} it can be obtained as a general background with a low spectral density, which is difficult to separate from the other background sources. Therefore, the experimental value of the intensity of the central component includes contributions of just the slow fluctuations: $R_C^{\text{exp}} = R_S \ll R_C$. Then the experimental intensities of the spectral components will differ from those calculated by the second way to the extent that there is a deviation from zero of the component representing the scattering by fast fluctuations. Similar differences appear also in the ratios of the intensities of the spectral components. This makes it possible to determine the value of R_F .

EXPERIMENTAL DATA

We now consider the experimental situation. The most thoroughly investigated glass for which there is a comprehensive set of data is fused quartz. This material satisfies the assumptions made above and in particular it does not exhibit dispersion of the velocity of sound (and, consequently, it does not exhibit relaxation processes) up to hypersonic frequencies.¹¹ Table II gives some ratios of the spectral intensities found experimentally and those calculated by the first and second methods. The data used in these calculations were the same as in Ref. 1 and they represented the experimental values²⁾ of the ratios of the spectral components taken from Ref. 8, apart from the last two rows which were taken from Ref. 10. All the ratios were obtained at room temperature, apart from the Landau-Placzek ratio (last row) determined at 1400 K. Clearly, the measured and calculated values of the ratios are in agreement within the limits of the combined experimental errors. Since all the necessary data needed in the calculation of the coefficients R_T and R_L representing the scattering by the acoustic modes are available, we can find the absolute values of the scattering coefficients corresponding to the central component. The agreement between the experimental values of the ratios and those calculated by the second way [using Eq. (2)] means that the contributions of the fast relaxing parameters to the scattering process are less than the experimental error. Within these limits of precision, the central component is thus en-

tirely due to the slow fluctuations. As in Ref. 1, the calculations were carried out for the wavelength $\lambda = 515$ nm:

$$AT \sum_j m_j^{(F)2} \leq 30 \cdot 10^{-8} \text{ cm}^{-1}, \quad (4)$$

$$AT \sum_k n_k^{(F)2} \leq 3 \cdot 10^{-8} \text{ cm}^{-1}, \quad (5)$$

$$AT_g \sum_i n_i^{(S)2} = (30 \pm 3) \cdot 10^{-8} \text{ cm}^{-1}, \quad (6)$$

$$AT_g \left(Y_{10}^2 / K_{10} + \sum_i m_i^{(S)2} \right) = (240 \pm 30) \cdot 10^{-8} \text{ cm}^{-1}. \quad (7)$$

Unfortunately, we cannot find separately the contribution of the slow variables $\sum_i m_i^{(S)2}$, because there are no experimental data for Y_{10} . However, some estimates can be obtained if we start with the relationship between Y_1 and m_j (Refs. 1 and 2):

$$-Y_{10} \leq 1,24 \pm 0,1, \quad (8)$$

$$(5,7 \pm 0,6) \cdot 10^{-8} \text{ cm}^{-1} < AT_g \sum_i m_i^{(S)2}. \quad (9)$$

It therefore follows from Eq. (9) that a description of the scattering in glasses, particularly in molten quartz, requires an allowance for the scalar relaxation parameters. The inequality (9) also implies that the melt should exhibit dispersion of the derivative $Y_1 = -(\rho \partial \epsilon / \partial \rho)_T$, which distinguishes molten quartz from the usual liquids which do not exhibit such dispersion (within the limits of experimental error).⁷ The inequality (8) suggests also another difference. In the case of the usual liquids the derivative $(\rho \partial \epsilon / \partial \rho)_T$ is frequently obtained by making estimates based on the average field approximation,¹³ i.e., on the assumption of a single-valued relationship between the permittivity and the density or the molecular polarizability. It follows from these estimates (based on the Lorentz-Lorentz, Rocard, Vuks, and other relations) that $(\rho \partial \epsilon / \partial \rho)_T$ depends only on ϵ , i.e., that liquids with similar refractive indices ($\sqrt{\epsilon}$) have similar values of $(\rho \partial \epsilon / \partial \rho)_T$. This is confirmed by the experimental results (see Table II.5 in Ref. 13). Molten quartz does not belong to this group of materials. Carbon tetrachloride,

TABLE II.

Ratio	Experiment	Calculation 1	Calculation 2
$(R_C^{HH} + R_C^{VH})/R_L^{HH}$	27,0±2,7	≥ 12,3±1,8	26,2±3,0
$(R_C^{HH} + R_C^{VH})/R_T^{VH}$	19,7±2,0	≥ 9,6±1,4	21,6±2,5
R_L^{HH}/R_T^{VH}	1,37±0,14	1,27±0,08	—
R_L^{VV}/R_T^{VH}	11,0±2,0	11,0±2,0	—
$(R_C^{VV} + R_C^{VH})/R_L^{VV}$	23,3±2,3	≥ 4,2±0,3	25,1±3,0
	24,4±0,4	—	22,6±3,0
$(R_C^{VV} - \frac{1}{3}R_C^{VH})/R_L^{VV}$	(T=295 K) 6,1±0,3	—	5,9±0,8
	(T=1400 K)		

whose refractive index is close to that of molten quartz, has a derivative $(\rho\partial\epsilon/\partial\rho)_T = 1.50$, which is considerably higher than possible values of molten quartz given by Eq. (8). Note that in glass (molten quartz) this value is even less: $-Y_0 = 1.01$ (Ref. 1).

This difference between the properties of molten quartz and those of the usual low-viscosity liquids seems to us natural. Slow relaxation parameters, which produce such a fundamental change in the state of the medium as the transition from a liquid to a glass, are manifested in all the properties including the density.

Another interesting question is related to the error of the parameters describing slow relaxation processes leading to the formation of a glass. If we assume that there is only one relaxation parameter, then the inequalities of Table I reduce to inequalities for the tensor relaxation parameter and we obtain

$$AT_g n^{(s)2} = (20 \pm 2) \cdot 10^{-8} \text{ cm}^{-1}. \quad (10)$$

The difference between this value and the experimental result of Eq. (6) is evidence of the correctness of this assumption. It is not possible to carry out a similar check in the case of scalar relaxation parameters because of the absence of independent data on the value of Y_{10} .

We conclude by considering once again the ratio of the spectral components. We may conclude from Table I that the temperature dependence of the Landau-Placzek ratio is

$$(R_c^{VV} - 4/3 R_c^{VH})/R_L^{VV} = C/T, \quad (11)$$

where in the first approximation the quantity C is independent of temperature. This dependence is reported for molten quartz in Ref. 10. Estimates based on Eqs. (7) and (6) allow us to determine the value of C and, therefore, the Landau-Placzek ratio at an arbitrary temperature. A comparison of the calculated temperature dependence with the experimental data¹⁰ obtained at two temperatures, listed in the last two rows of Table II, demonstrate that they are in full agreement.

CONCLUSIONS

It therefore follows that predictions of the modified relaxation theory are obeyed not only by the integral scattering coefficients,¹ but also by the total scattering coefficients as-

sociated with the specific spectral components. The correct temperature dependence of the Landau-Placzek ratio is obtained, confirming the main assumption in Ref. 1 of "freezing" of the slow subsystem of fluctuations. A combined analysis of the total and spectral scattering within the framework of the modified relaxation theory makes it possible to obtain new information on the investigated sample, molten quartz. Thus, without going into details of the spectrum of the melt but using simply an analysis of the total intensities of the spectral components at room temperature, we have been able to show that the process of formation of a glass involves more than one tensor relaxation parameter. Moreover, it is shown that molten quartz (in contrast to the usual liquids) should exhibit dispersion of the derivative $(\rho\partial\epsilon/\partial\rho)_T$.

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¹ An anomalous increase in the relaxation time on approach to the glass-transition temperature is the most striking feature of the liquid-glass transition, established quite reliably by experiments^{3,4} and utilized in recent theoretical models.^{5,6}

² The values of the scattering coefficients given in Ref. 1 must be reduced by an amount representing the Raman scattering contribution, which—according to Ref. 12—is 3% for R^{VV} and 7% for R^{VH} .

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