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Abstract

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VITRIFICATION OF FLUCTUATIONS AND LIGHT SCATTERING

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The features of molecular light scattering in glasses are revealed by comparing glass with a liquid at a temperature exceeding the glass-transition temperature T_g. Light scattering in silicate glasses is hardly molecular in the true sense of the word; the indicated comparison is difficult here because of the high values of T_g. In the work of T. S. Velichkina ([1]), light scattering by the triacetin and β-chloroethyl ester of benzenesulfonic acid was investigated over a broad temperature interval above and below T_g. The scattering intensities for the glasses proved to be somewhat lower than for the liquids at $T > T_g$ (by 20 and 30%), but 100 and 130% higher than those calculated for the glasses, regarded as liquids, by Einstein' s formula with the Cabannes correction ([2]). The experimental intensities are an order of magnitude greater than the theoretical ones for isotropic solids ([3]). For fused quartz the intensity is 8 times greater than that calculated by Einstein' s formula. However, if in this formula one substitutes not the experimental T, but $T_g = 2100^{\circ}$K, one obtains a value smaller than the experimental one by only 20% ([4]).

Contrary to the Landau-Placzek formula ([5]), the central component of the Rayleigh line of viscous liquids and glasses is very intense and narrow. The displaced components in glasses are practically absent ([6–8]). This is also observed in substances with small anisotropy of the molecules, and the central component is polarized ([9]).

The explanation of these facts should be sought on the basis of kinetic considerations. Despite the external similarity of vitrification to a second-order phase transition, vitrification is not such a transition, and in this case one cannot apply the corresponding theory of light scattering ([10]). Vitrification of a liquid is a kinetic process ([11]). Consideration of a relaxation process characterized by the time τ gives the condition for vitrification

$$\left(\frac{d\tau}{dT}\right)_{T=T_g} = \frac{1}{q}, \tag{1}$$

where $q = -|\, dT/dt \,|$ is the cooling rate ([12]).

The features of light scattering in glasses are explained by the vitrification of fluctuations of structural entropy. In a liquid consisting of isotropic molecules, light scattering is determined by fluctuations of the specific volume, which may be represented in the form

$$\Delta v = \Delta v' + \Delta v'',$$

where

$$\Delta v' = \left(\frac{\partial v}{\partial p}\right)_S \Delta p, \quad \Delta v'' = \left(\frac{\partial v}{\partial S}\right)_p \Delta S = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p \Delta S. \tag{2}$$

The displaced components of the Rayleigh line are due to the fluctuations $\Delta v'$, and the undisplaced component to $\Delta v''$. The fluctuations Δp propagate as sound waves. Light scattering by them occurs only at sufficiently

large sound frequencies ω, satisfying the Mandelstam-Brillouin condition ([2]). Obviously, in a liquid being cooled only those infrasonic waves can freeze for which $\omega \sim |q|/T_g$. The fluctuations $\Delta v'$ do not freeze.

Entropy fluctuations ΔS may be represented as

$$\Delta S = \Delta S_1 + \Delta S_2 \tag{3}$$

and, correspondingly,

$$\Delta v'' = \frac{T}{c_p}\left(\frac{\partial v}{\partial T}\right)_p (\Delta S_1 + \Delta S_2) = \Delta v_1 + \Delta v_2. \tag{4}$$

Here ΔS_1 are fluctuations associated with translational and rotational degrees of freedom, while ΔS_2 are those associated with vibrational degrees of freedom. The relaxation time of ΔS_1 is τ, the time of structural relaxation of the liquid, which increases sharply as the temperature is lowered. For ΔS_2 the relaxation time τ' is the time of thermal-conductivity relaxation ([13])

$$\tau' \sim l^2/\chi, \tag{5}$$

where χ is the coefficient of thermal conductivity; l is the linear size of the fluctuation. Since τ' depends practically little on temperature, Δv_2 does not freeze, just as $\Delta v'$ does not. In the glass we have the equilibrium values

$$\overline{(\Delta v')^2} = -kT\left[\left(\frac{\partial v}{\partial p}\right)_S\right]_T; \tag{6}$$

$$\overline{(\Delta v_2)^2} = \frac{kT^2 (c_{p2})_T}{(c_p^2)_T} \left[\left(\frac{\partial v}{\partial T} \right)_p^2 \right]_T ; \tag{7}$$

c_{p2} is the heat capacity belonging to the vibrational degrees of freedom. Fluctuations Δv_1, associated with the structural entropy, owing to the strong dependence of τ on T, vitrify at a certain temperature T_g. We therefore obtain

$$\overline{(\Delta v_1)^2} = \frac{kT_g^2 (c_{p1})_{T_g}}{(c_p^2)_{T_g}} \left[\left(\frac{\partial v}{\partial T} \right)_p^2 \right]_{T_g} ; \tag{8}$$

c_{p1} is the structural heat capacity. The ratio of the intensities of the central and shifted components is equal to

$$\frac{J_\mathrm{c}}{J_\mathrm{sh}} = \frac{\overline{(\Delta v_1)^2} + \overline{(\Delta v_2)^2}}{\overline{(\Delta v')^2}} =$$

$$= \left(\frac{c_p - c_v}{c_v} \right)_{T_g} \frac{(\partial v/\partial p)_{T_g} (c_v/c_p)_{T_g} T_g (c_{p1})_{T_g}}{(\partial v/\partial p)_T (c_v/c_p)_T \, T \, (c_p)_{T_g}} + \left(\frac{c_p - c_v}{c_v} \right)_T \frac{(c_{p2})_T}{(c_p)_T}. \tag{9}$$

At $T = T_g$ this formula goes over into the Landau-Placzek formula, since $c_p = c_{p1} + c_{p2}$.

For T_g noticeably greater than T, the intensity of the central component must considerably exceed the intensity of the shifted lines, which agrees with experiment. The central line must be narrow, since the rate of scattering of ΔS_1 is very small. It is obvious that the theory of the widths of the components of the Rayleigh line by V. L. Ginzburg ([14]) must be supplemented by taking into account the mechanism of scattering by ΔS_1.

Let us find the glass-transition temperature T_g of the fluctuations Δv_1. We have the kinetic equation ([15])

$$\frac{d\Delta v_1}{dt} = -\frac{1}{\tau} \Delta v_1 + A(t); \tag{10}$$

$A(t)$ is a quantity determined only statistically.

We solve this equation, taking into account the change in temperature at the rate $q = -|q|$. The solution has the form

$$\Delta v_1 = \Delta v_1^0 \exp \left[-\int_0^t \frac{dt'}{\tau} \right] + \exp \left[-\int_0^t \frac{dt'}{\tau} \right] \int_0^t \exp \left[\int_0^{t'} \frac{dt''}{\tau} \right] A(t') \, dt'; \tag{11}$$

Δv_1^0 is the initial value of Δv_1. We shall use the method described by Chandrasekhar (16) as applied to the stationary case ($\tau = \text{const}$). As $t \to \infty$, the fluctuation distribution tends to a Gaussian:

$$\lim_{t\to\infty} W(\Delta v_1) = \frac{1}{(T/c_p)(\partial v/\partial T)_p(2\pi k c_{p1})^{1/2}} \exp\left[-\frac{c_p^2(\Delta v_1)^2}{2kT^2 c_{p1}(\partial v/\partial T)_p^2}\right]. \quad (12)$$

In order that (12) hold, it is necessary that, when the integral on the right-hand side of (11) is divided into small intervals,

$$\exp\left[-\int_0^t \frac{dt'}{\tau}\right]\int_0^t \exp\left[\int_0^{t'} \frac{dt''}{\tau}\right] A(t')\,dt' \cong \sum_{j=0}^{n} \exp\left[-\int_{j\Delta t}^{t} \frac{dt'}{\tau}\right]\int_{j\Delta t}^{(j+1)\Delta t} A(t')\,dt' \quad (13)$$

the probability of finding different values of

$$B(\Delta t) = \int_t^{t+\Delta t} A(t')\,dt' \quad (14)$$

also obey a Gaussian distribution:

$$w(B) = \frac{1}{(4\pi b\Delta t)^{1/2}} \exp(-B^2/4b\Delta t), \quad (15)$$

where

$$b = \frac{kT^2(\partial v/\partial T)_p^2 c_{p1}}{c_p^2 \tau(t)}. \quad (16)$$

On cooling, $\overline{B^2} = 2b\Delta t$, and hence $\overline{A^2}$ rapidly decreases. Expression (13) is not rigorous in the nonstationary case considered by us, since in the vitrification interval the factor $\exp\left(-\int_{t'}^{t} dt''/\tau\right)$ may change more rapidly than $A(t')$. The proposed theory is valid only as a zeroth approximation, the more accurate the narrower the vitrification interval. The peculiarities of the process in this interval are not taken into account by the present theory.

If (15) holds, then for the quantity

$$R(t) = \int_0^t \exp\left[-\int_\xi^t \frac{dt'}{\tau}\right] A(\xi)\,d\xi \equiv \int_0^t \psi(\xi)A(\xi)\,d\xi \quad (17)$$

the distribution is valid

$$W(R) = (\pi D(t))^{-1/2} \exp(-R^2/D(t)), \tag{18}$$

where

$$D(t) = 4k \int_0^t \frac{c_{p1}}{c_p^2} \left(\frac{\partial v}{\partial T}\right)_p^2 T^2 \frac{1}{\tau(\xi)} \psi^2(\xi)\, d\xi. \tag{19}$$

We divide the integral $D(t)$ into parts from $t = 0$ (start of cooling, $T = T_0$) to $t = t_1$ (end of cooling, $T = T$) and from t_1 to t (constant temperature T). In the second integral $\tau = \tau(T) = \text{const}$. The first integral can be represented in the form

$$4k \int_0^t \frac{c_{p1}}{c_p^2} \left(\frac{\partial v}{\partial T}\right)_p^2 T^2 \frac{1}{\tau(\xi)} \psi^2(\xi)\, d\xi =$$

$$= 4k \exp\left[-2\frac{t-t_1}{\tau(T)}\right] \int_T^{T_0} \frac{c_{p1}}{c_p^2} \left(\frac{\partial v}{\partial T}\right)_p^2 T'^2 \frac{1}{|q|\tau(T')} \exp\left[-2\int_T^{T'} \frac{dT''}{|q|\tau}\right] dT'. \tag{20}$$

The quantities $c_{p1}, c_p, (\partial v/\partial T)_p^2, T^2$ depend on temperature much more weakly than τ and ψ^2. The function

$$f(T') = \frac{1}{|q|\tau(T')} \exp\left[-2\int_T^{T'} \frac{dT''}{|q|\tau}\right] \tag{21}$$

has a maximum at the temperature $T' = T_g$, for which

$$(d\tau/dT')_{T'=T_g} = -2/|q|. \tag{22}$$

Taking, at this temperature, $\dfrac{c_{p1}}{c_p^2}\left(\dfrac{\partial v}{\partial T}\right)_p^2 T^2$ outside the integral sign and integrating, we obtain

$$D(t) \simeq 4k \left[\left\{\frac{c_{p1}}{c_p^2}\left(\frac{\partial v}{\partial T}\right)_p^2\right\}_{T_g} \frac{T_g^2}{2} \exp\left\{-\frac{2}{\tau(T)}(t-t_1)\right\}(1-\exp[-2\Delta\varphi(T_1,T_0)]) + \left\{\frac{c_{p1}}{c_p^2}\left(\frac{\partial v}{\partial T}\right)_p^2\right\}_T \frac{T^2}{2}\left(1-\right.\right. \tag{23}$$

where

$$\Delta\varphi(T_1, T_0) = \int_T^{T_0} \frac{dT''}{|q|\tau(T'')} \to \infty, \tag{24}$$

since τ is very small at $T_0 > T_g$ and $\tau \to \infty$ at $T < T_g$ (cf. (12)). The final distribution (for $t - t_1 \ll \tau(T) \to \infty$)

$$W(\Delta v_1) = (\pi D)^{-1/2} \exp[-(\Delta v_1)^2/D], \tag{25}$$

where

$$D = \frac{2kT_g^2 (c_{p1})_{T_g}}{(c_p^2)_{T_g}} \left[\left(\frac{\partial v}{\partial T}\right)_p^2\right]_{T_g}, \tag{26}$$

and we obtain (8).

Since, according to (23), $\overline{(\Delta v_1)^2}$ relaxes with the time $\tau/2$, for $\overline{(\Delta v_1)^2}$ the vitrification condition (22) coincides with (1).

We see that the increased intensity of light scattering in glasses is explained by the freezing of fluctuations of the structural entropy. If the liquid consists of anisotropic molecules, then, in addition, orientational fluctuations are frozen, which in this way make their contribution to the intensity of the central component for glasses. In inhomogeneous liquids, concentration fluctuations freeze, since the rate of their dissipation, determined by diffusion, depends strongly on temperature. Obviously, this theory is applicable also to viscous liquids. The fluctuations Δv_1 may partially vitrify earlier than the entire liquid.

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