A Brillouin scattering study of glasses of various fictive temperatures

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The problem of the determination of configurational changes in glasses in the transformation range is first discussed. For want of a detailed description, a one parameter "fictive temperature" approximation is adopted to characterize glasses stabilized at various temperatures. The Brillouin scattering spectra show that hypersonic velocity and the elastic constant c_{11} undergo changes of about 3 and 6% respectively in the temperature range, whereas the variations of the attenuation are up to 50%.

1. Glass transition

1.1. Relaxation phenomena in the transformation range

When an undercooled liquid solidifies without crystallizing to form a glass, its physical proproperties, such as dilatation, specific heat, etc, undergo abrupt changes in a narrow temperature range for which the viscosity reaches about 10^{13} P. The viscosity itself decreases without any discontinuity as the temperature is lowered. The kinetics of the volume-temperature or enthalpy-temperature curves, which currently serve to define the transition temperature, T_g, are thus explained in terms of a viscous relaxation mechanism: the liquid continually adjusts its molecular configuration as the temperature is lowered; however, the rate of configurational changes decreases with temperature. When it becomes of the order of magnitude of the rate of change of external constraints (e.g. cooling rate in a dilatation experiment), the system no longer "follows" and a corresponding kink is observed at a temperature, T_g, in a property-temperature curve. When the cooling rate is increased the corresponding T_g point shifts to a higher temperature. The temperature interval comprised between the lowest and highest T_g

observable constitutes the transformation range of the glass. This separates the region of the supercooled liquid which is metastable with respect to the (equilibrium) crystalline phase from the region of the solid glass which is in a non-equilibrium state. This relaxational approach shows why the physical properties of glasses depend on the rate of cooling: the structure of glass corresponds to the molecular configuration of the liquid which was "frozen-in" at the corresponding temperature, T_g, and brought to the ambient temperature.

When a glass is annealed at a fixed temperature in the transformation range, it may further relax in order to adjust its present molecular configuration to the new configuration corresponding to the anneal temperature – this last process is called stabilization.

1.2. Characterization of configurational changes

It would be highly interesting to obtain detailed information about the structural modifications which accompany the configurational changes during the freezing-in and stabilization. Unfortunately, the radial distribution functions which can be obtained from X-ray or neutron

diffraction experiments are not sufficiently sensitive to render the small structural modifications – to observe significant changes it is necessary to considerably extend the temperature range.

High-temperature X-ray diffraction studies have shown [1] that for molten B_2O_3 it is necessary to reach the 1200 to 1600°C range before the structure starts to differ from that of the corresponding glass at 20°C. One is, therefore, restricted to a necessarily more global thermodynamic treatment without the detailed description of structural configuration.

A glass being essentially in a non-equilibrium condition, the usual thermodynamic variables are insufficient to define its state; theoretically additional configurational parameters have to be considered in order to define the configurational state of the supercooled liquid and those are set constant at their values corresponding for T_g when the glass is formed ("frozen-in"). The important problem of the number of these configurational parameters is still unsolved. From the thermodynamical considerations it is possible to show [2] that if one parameter is sufficient the following relation should hold:

$$\Delta\beta\,\Delta C_p/(\Delta\alpha)^2\,TV = 1 \qquad (1)$$

where $\Delta\beta$, $\Delta\alpha$ and ΔC_p are differences in compressibility, thermal expansion and specific heat as measured in slow and fast experiments, V and T volume and absolute temperature. This expression becomes an inequality

$$\Delta\beta\,\Delta C_p/(\Delta\alpha)^2\,TV \geqslant 1 \qquad (2)$$

where more than one parameter would be required. Complete data for glasses are still scarce but in most cases values significantly superior to 1 have so far been obtained [3]. It appears, therefore, that more than one parameter would be needed to characterize the configuration. This is equivalent to assuming the existence of a spectrum of retardation times for the compliance [4].

The simplified approach of Tool [5] and Ritland [6] consists in considering a single configurational parameter: the so-called "fictive temperature" $\bar{T}$ which is identified with the T_g at which the glass was formed. The state of a glass is thus defined by temperature in the usual sense, pressure and the "fictive temperature" which is used to label the configurational equilibrium frozen in at the particular temperature, T_g.

This description of the system using a single order parameter implies that all the glassy states of the system which may be brought into the same liquid state by instantaneous changes of temperature and pressure are to be considered as equivalent. This represents only a first approximation as this hypothesis is in fact equivalent to the introduction of a single retardation time for the compliance [4].
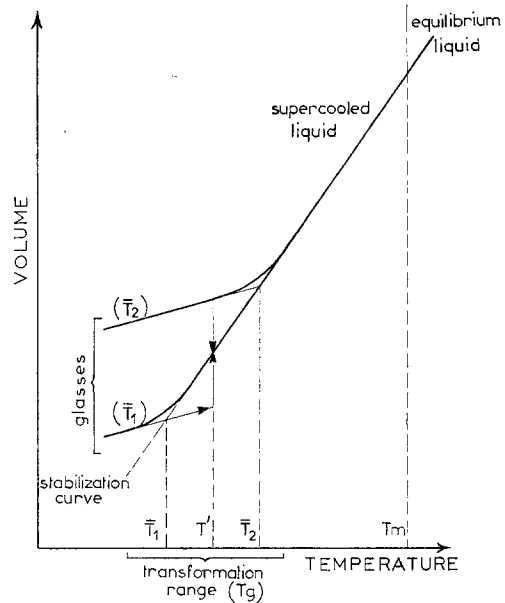

Figure 1 Schematic representation of glass-transition and stabilization phenomena. $\bar{T}_1$ and $\bar{T}_2$ are "fictive temperatures" of two glasses quenched with different speeds and $\bar{T}'$ an intermediate stabilization temperature.

During an isothermal anneal of the glass at a fixed temperature, T', its fictive temperature, $\bar{T}$, relaxes towards the anneal temperature, T', which will ultimately represent its new fictive, (configurational) temperature. When two glasses with fictive temperatures $\bar{T}_1$ and $\bar{T}_2$ are annealed at an intermediate temperature, T' (Fig. 1), they are seen to relax from both sides towards the state corresponding to the fictive temperature, T'; the stabilization curve which is an extrapolation into the transformation range of the curve of supercooled liquid, therefore represents a locus of points where the glass is in a metastable equilibrium state. This method of equilibrium stabilization thus provides a convenient way of obtaining specimens with a determined fictive
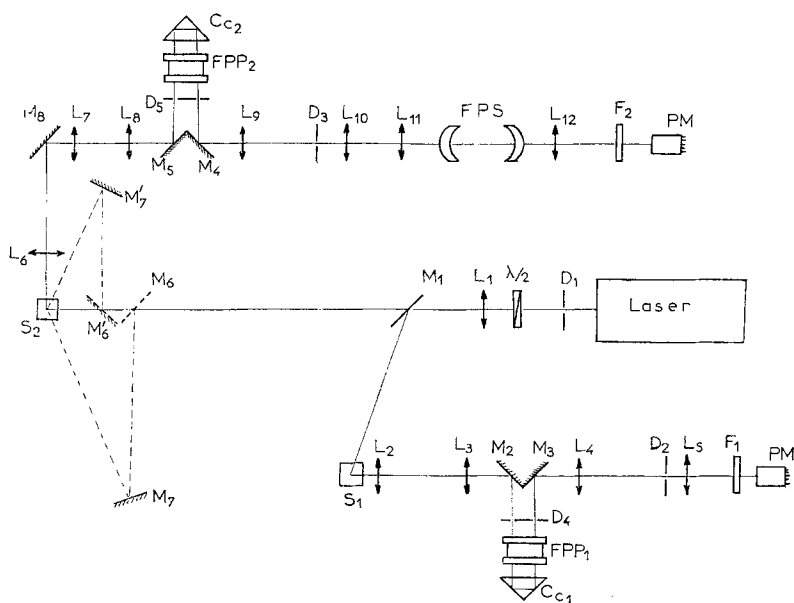
Figure 2 Schematic representation of the optical device. D, apertures; L, lenses; M, mirrors; F, interferential filters; PM, photomultipliers; S, samples; FPP and FPS, plane and spherical Fabry-Pérot interferometers; Cc, cornercubes (retroreflectors); λ/2, half-wave plate.

temperature, i.e. of a given configurational order and will be used in this study.

2. Brillouin scattering study
2.1. General

The acoustical properties of condensed media in the 1 to 100 GHz frequency range may be studied by Brillouin scattering. The elastic constants and the attenuation are measured with an accuracy of about 0.2 and 5% respectively even on samples of small size. The hypersonic wavelengths involved are of the order of 0.1 μm. Therefore, this technique is quite suitable to the study of the stabilization processes and the local order differences due to the thermal treatments.

The frequency shift, ν_B, of the Brillouin lines in an isotropic medium is given by

$$\nu_B/\nu_0 = 2n(V/c)\sin\theta/2, \qquad (3)$$

where ν_0 is the frequency of the monochromatic incident light, n the refractive index, V the phase velocity of the elastic wave responsible for the scattering, c the light velocity and θ the scattering angle (the angle between the incident and scattered beams). The propagation velocity of the hypersonic wave at the frequency, ν_B, may be deduced from the measurement of ν_B when n and θ are known [7].

The Brillouin lineshape is related to the time

decay of the acoustic waves in the medium. As far as this decay is proportional to $e^{-t/s}$ the profile is lorentzian; the measurement of the linewidth Γ gives s and the spatial attenuation coefficient α, according to the expression

$$\Gamma = 1/2\pi s = \alpha V/2\pi. \qquad (4)$$

2.2. Experimental method

An interferential spectrometer of high resolving power ($R = 10^7$) is necessary for studying the Brillouin spectra with sufficient accuracy. The Rayleigh component of the scattered spectrum is generally strong; the contrast of the spectrometer has, therefore, to be high to avoid overlapping. A sketch of the device is given in Fig. 2 (see [8] for a detailed description). The incident light is provided by an argon-ion laser with an output power of 500 mW for $\lambda_0 = 4880$ Å (Spectra Physics model 164). The apparatus is composed of two spectrometers: both may work at variable scattering angles.

The resolving unit of the first (lower part of the figure) is a double-passed plane Fabry-Pérot interferometer. The thickness varies from 2 to 20 mm, corresponding to a resolving power of 2×10^5 and 2×10^6 respectively. This device gives the preliminary frequency shift measurements which are necessary to adjust the second spectrometer and to interpret the final results.

The second device (upper part of the figure) is used for accurate frequency measurements and the study of the profiles. A double-passed plane Fabry-Pérot interferometer, the thickness of which is between 2 and 5 mm, is used as a monochromator. The frequency corresponding to the maximum transmission of this filter is matched with the frequency of the Brillouin line by air-pressure adjustment. The resolving unit is a confocal Fabry-Pérot interferometer (thickness 50 or 100 mm). Fast repetitive piezoelectric scannings are performed and the signal is accumulated in a multichannel analyser. A typical trace of the spectrum is reproduced in Fig. 3.
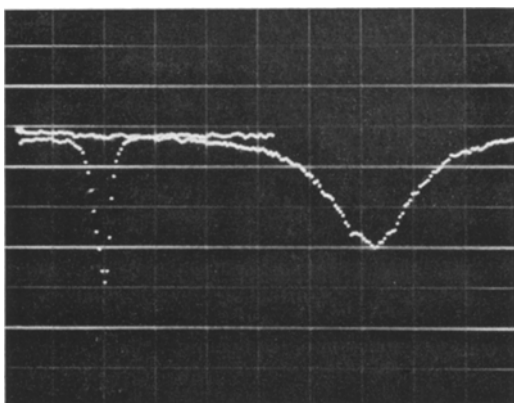

Figure 3 Typical trace of the spectrum analysed by the FPS. The narrow component is due to elastic laser light scattering, the broad component is the Brillouin line (the scale is approximately 100 MHz by cm).

2.3. Sample preparation

The glass studied was SOVIREL dense barium crown (B-90-60) whose composition is given in Table I. The size of the samples was $2 \times 2 \times 10$ mm^3 in order to ensure thermal homogeneity during heat-treatment. The stabilization procedure was that described above in which a series of quenched glasses and another series of glasses annealed near the lower limit of the transformation range were stabilized at various temperatures. The refractive index was used as a

TABLE I Glass composition (wt %)

SiO$_2$	B$_2$O$_3$	BaO	K$_2$O	Al$_2$O$_3$	PbO
38	14	42.8	0.8	4	0.4

parameter to check the progress of stabilization and for the quenched glasses was found to be $n_1 = 1.5840$ and the index of annealed glasses at 580°C was $n_2 = 1.5909$.
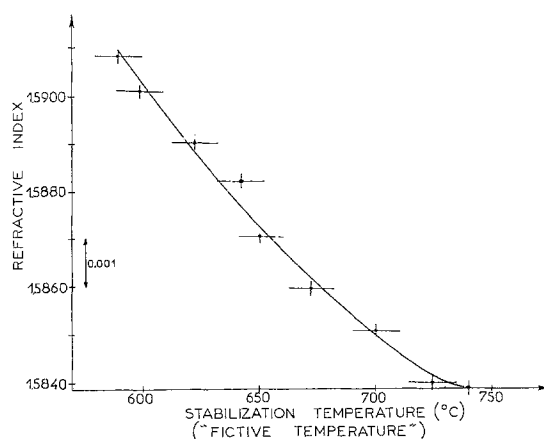

Figure 4 Limiting refractive index plotted as a function of the stabilization temperature.

Fig. 4 shows the common limiting refractive indices of both series of samples for various temperatures of stabilization. It can be seen that the refractive index varies by approximately 0.4% in the stabilization range.

2.4. Results and discussion

The variations of the hypersonic velocity and attenuation were first studied as a function of the stabilization temperature. Experiments were performed at room temperature (22°C) and at constant frequency (30 GHz). The results are given in Fig. 5. Starting from the values of longitudinal elastic wave velocity, V, the elastic constant, $c_{11} = \lambda + 2\mu$, was calculated from the relation $c_{11} = \rho V^2$; λ and μ are the Lamé coefficients and ρ the density. An average value of $\rho = 3.07$ was obtained from buoyancy measurements. The precision of the method being insufficient, however, to detect small differences of ρ in the transformation range, the relative variations of ρ with fictive temperatures were calculated from the values of the refractive index using Gladstone's relation $(n - 1)/\rho =$ constant. Fig. 6 shows the variation of c_{11} versus the stabilization temperature (fictive temperature). These results show an important variation of V and c_{11} of about 3 and 6%, respectively, in the transformation range. Furthermore, Fig. 5 shows that the hypersonic attenuation strongly depends on the stabilization temperature, the variation being of the order of 50%.
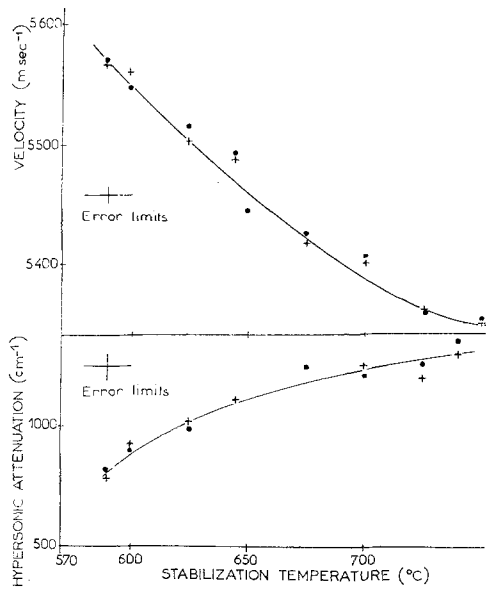
Figure 5 Velocity and attenuation of hypersonic waves ($\sim$ 30 GHz) at room temperature in stabilized glasses obtained from: ($\bullet$) annealed and ($+$) quenched specimens.
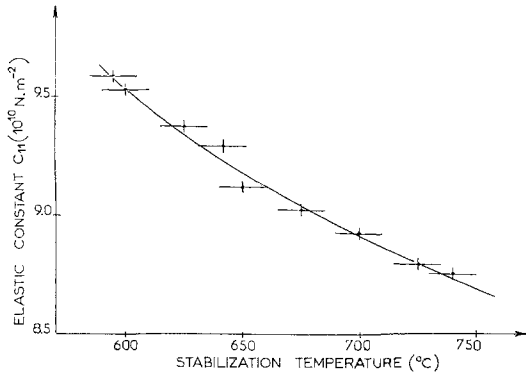

Figure 6 Elastic constant $c_{11} = \rho V^2$ at room temperature. The error limits indicated are relative uncertainties, the density variations being obtained from Gladstone's law.

This first set of experiments was followed by a study of the variation of the hypersonic velocity and attenuation as a function of frequency performed on four samples characterized by different stabilization temperatures. A method to interpret Brillouin spectra, allowing the measurement of the frequency shift and linewidth at various scattering angles, has recently been proposed [9] which makes it possible to measure the hypersonic velocity and attenuation in about a frequency decade (between 3 and 30 GHz in
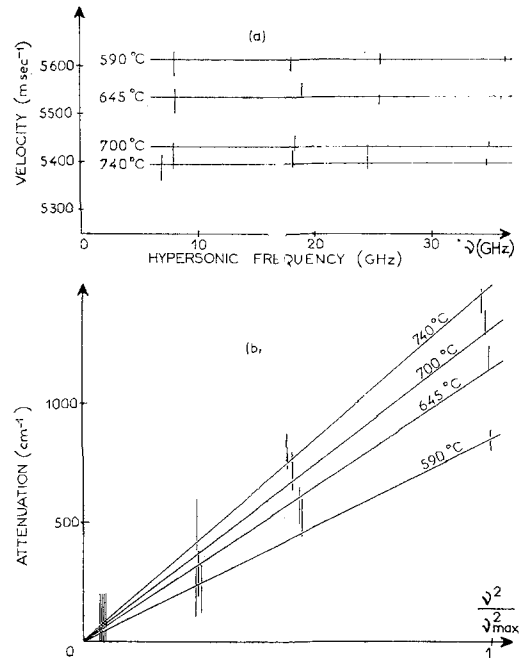

Figure 7 Velocity (a) and attenuation (b) of hypersonic waves at room temperature as a function of frequency for glasses of fictive temperatures indicated. In (b), $\nu_{max} = 36.38$ GHz.

this study). The results, plotted in Fig. 7, prove that the velocity remains constant in this frequency range.

The attenuation is derived from the linewidths which decrease with frequency. This makes the spectrum interpretations difficult and considerably limits the precision of the attenuation measurements at lower frequencies. Nevertheless, the results fit an ω^2-law with sufficient accuracy to eliminate the possibility of an attenuation independent of, or proportional to, the frequency. Assuming that the dispersion and the damping of elastic waves may be described by a relaxation process involving a single relaxation time, τ, the velocity and the attenuation are given by:

$$V = V_0 + (V_\infty - V_0)\, \omega^2\tau^2/(1 + \omega^2\tau^2), \quad (5)$$

$$\alpha = ((V_\infty - V_0)/V_0^2)\, \omega^2\tau/(1 + \omega^2\tau^2) \quad (6)$$

where V_0 and V_∞ are respectively the low and high frequency limits of the velocity and ω the angular frequency. A comparison between these relations and the experimental results shows that $\omega\tau$ is less than unity in the frequency range under study. Thus, the velocity measured may be considered as identical to V_0; the variation of V_0

is then known as a function of the stabilization temperature. The experiments give no information about V_∞. As for the relaxation time, they only prove that it is lower than 10^{-11} sec, and this is the order of magnitude of the thermal phonons' lifetime in a strongly anharmonic crystal.

3. Conclusion

In conclusion, it appears that the hypersonic velocity and attenuation strongly depend on the structural differences related to the different "fictive temperatures" of the samples. This point is interesting because the majority of physical properties are hardly – if at all – sensitive to these structural differences which are consequently very incompletely known. Hypersonic attenuation may, therefore, be advantageously used to follow the small structural changes arising during

stabilization. However, a detailed model of these structural modifications has yet to be elaborated.

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