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HAL Id: jpa-00225481
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Submitted on 1 Jan 1985

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INTERNAL FRICTION AND RHEOLOGICAL BEHAVIOUR OF GLASSES NEAR Tg

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Abstract - The main experimental features about internal friction and rheological behavior of glasses near the glass transition temperature Tg are recalled. Some are now well established, others have been obtained recently. In order to interpretate all these new ideas have to be developed: hence, the concepts of “defect” on which local shear is obtained and of correlated atomic (molecular) movements, are applied to non-crystalline solids. New Eq. including the Kohlrausch law exp [- (t/T)^b] emerge naturally from such physical basis and are discussed by reference to experimental data.

I - INTRODUCTION

There have been numerous investigations on the homogeneous flow and anelastic-plastic deformation of vitreous solids. Most attention has been given to rheological behaviour of glasses near glass transition temperature Tg and several review articles have been published in this field /1,2,3/.

The main interest of internal friction studies done with glasses is connected to the informations thus obtained about atomic (molecular) mobility in this state of the matter, as internal friction is a very sensitive and effective tool to detect internal atomic rearrangements. Atomic movements are usually associated with lattice defects. Since vitreous solids could be considered as extremely defective solids it is expected that they may exhibit a considerable amount of internal friction especially when the temperature is increased approaching the glass transition temperature Tg. Actually it is generally admitted that long range atomic (molecular) movements are only possible at temperature equal or higher than Tg although more local movements could exist at lower temperature /4/.

In the work reported in this paper, attempts were made to bring some new contribution in the analysis of internal friction of glasses near Tg. In this aim the main experimental and theoretical features will be firstly recalled. In a second part, new results or results recently obtained will be presented in order to focus our attention on the peculiar points which must be taken into account to improve the theories previously proposed. A new approach about the interpretation of atomic (molecular) mobility in glasses will be discussed in the third part which will be followed by the interpretation of anelasticity and viscous glow of glasses in the glass temperature region. As a conclusion, the view thus presented will be tested with the available literature data.
II - INTERNAL FRICITION AND RHEOLOGICAL PROPERTIES OF GLASSES NEAR Tg : THE WELL ESTATISHED FEATURES

As numerous experimental results are reviewed in references /1,2,3/, only the main points will be summarised in the following.

a) The internal friction $\gamma_\text{G}$ increases and the modulus decreases as the temperature is increased. In the glass transition temperature region, $\gamma_\text{G}$ increases further in the case of oxides or metallic glasses but a maximum is observed in the case of macromolecular glasses due to the rubbery effect which is otherwise followed, at higher temperature, by the diffusion of entangled chains.

b) From the rheological point of view the former and the latter case correspond to a Maxwellian and a Burger's behaviour respectively.

c) Actually, there is a broad distribution of relaxation times and the theory of linear viscoelasticity gives relations describing the storage and loss modulus $G$ and compliance $J$:

$$G'(\omega) = G_{R} + \int_{-\infty}^{\infty} \frac{H(\tau) \omega^2 \tau^2}{1 + \omega^2 \tau^2} d\log\tau$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{H(\tau) \omega \tau}{1 + \omega^2 \tau^2} d\log\tau$$

$$J'(\omega) = J_{U} + \int_{-\infty}^{\infty} \frac{L(\tau) \tau}{1 + \omega^2 \tau^2} d\log\tau$$

$$J''(\omega) = \int_{-\infty}^{\infty} \frac{L(\tau) \tau}{1 + \omega^2 \tau^2} d\log\tau$$

with subscripts $R$ and $U$ corresponding to relaxed and unrelaxed values respectively; $H(\tau)$ is the relaxation time spectrum and $L(\tau)$ the retardation time spectrum. But these relations lead only to a phenomenological description of results and the physical basis of such a description is generally unclear.

d) In order to use more convenient relations having a simpler analytic form, other expressions have been proposed let us mention:

- the Davidson-Cole equation: $\gamma_\text{D}(i\omega) = 1/G_{U} \left\{ 1 + (i\omega T_{M})^{-1} + S(1 + i\omega T)^{-b} \right\}$ which has been shown to be nearly identical to Zener's parabolic model /3/.

- the B.E.L. equation /5/ $\gamma_\text{B}(i\omega) = 1/G_{U} \left\{ 1 + (i\omega T_{M})^{-1} + 2K(1 + i\omega T)^{-0.5} \right\}$. Although empirical in their origin, such equations fit generally fairly well with experimental data in the case of molecular glasses /5/ and oxide or metallic glasses /3/.

In some cases, authors have made attempts to give a physical basis to such equation. Thus, Phillips et al /6/, extending the work of Glarum /7/ found an expression equivalent to the B.E.L equation; the model proposed by Glarum involves the concept of a defect in the liquid structure, moving by a process of diffusion through the liquid: in the presence of such a defect, instantaneous reorientation of a molecule is possible; two characteristic times are introduced $T_{1}$ (molecular reorientation in the absence of defects) and $T_{D}$ (diffusion). Another approach has been put forward (8) in terms of thermomechanical activation (mean time $T_{1}$) of some sites leading to the formation of sheared microdomains (smd); such smd could be extended with the assistance of diffusional process, thus inducing the loss of the local memory of stress (mean time $T_{2}$); such a concept have lead to an expression very similar to the Davidson-Cole equation and applied to experimental results obtained with oxide glasses /3,8/.

In the case of macromolecular glasses, the situation is more complicated as the rubbery effect and diffusion of intangled chains must be taken into account /9/.

e) The relaxation time obtained by either expression preceding recalled is obviously temperature dependent; an Arrhenius law is observed at $T < T_{g}$ and a Tamann-Vogel-Fulcher (TVF) variation ($\tau \propto \exp(\text{cte}/(T-T_{0}))$) is generally verified at $T > T_{g}$ /10/.

It is well know, now /11/, that vitreous solids, metallic as well as non metallic, are in states which are configurationally frozen. Upon annealing, these solids may relax configurationally without crystallization. Thus two types of atomic transport behaviour may be distinguished. Indeed, the rate constant for atomic movement varies
roughly as the probability of some critical excitation of the configuration required for the movement, multiplied by the frequency of rearrangement of the system in its critical state. Thus at $T > T_g$ the former factor is temperature dependant since the material is in a metastable equilibrium leading to the TVF equation (equilibrium measurements). On the contrary, at $T < T_g$ only the latter factor depends on temperature leading to the Arrhenius law (iso-configurationnal measurements).

d) Vitreous solids are well known as structural relaxation sensitive materials. Thus internal friction of glasses is decreased during aging at temperature lower but not too different than $T_g$. During the same aging treatment, the storage modulus increases. This is a very general behaviour observed with oxide glasses /12/, metallic glasses /12/, selenium glass /14/, organic glasses /15/.

To state more clearly the interpretation of internal friction and other rheological properties of glassy solids near the glass transition temperature, other experimental informations are needed. As new results have recently been obtained, we suggest to emphasize these in the following part.

III - EXPERIMENTAL: NEW RESULTS OR PARTICULAR CHARACTERISTICS

3.1 - Frequency dependance

The temperature dependance of internal friction just mentioned above is connected to frequency dependance; then, internal friction and modulus measurements made by frequency scanning in isothermal conditions bring us very useful data. For instance the figure 1 shows results obtained in the case of an oxide glass /8/. It was observed that $\gamma$ varies as $\omega^{-\beta}$. Thus, $\beta$ was determined in a large temperature range between $T < T_g$ and $T > T_g$: it appears that $\beta$ increases with the temperature from 0.3 to 0.94. Furthermore, it seems, at least at lowest temperature, that $\beta$, which is the slope of the curves $\log \gamma - \log \rho$ ($P = 2\pi/\omega$ is the period of the cyclic stress applied on the material during internal friction measurements), increases with $P$.

The non-linear frequency dependance has to be compared to the non-exponential time dependance of strain (stress) observed during a creep (stress relaxation) test: the Kohlrausch's Eq. implying an exponential factor such as $\exp[-(t/\tau)^\beta]$ with $0 < \beta < 1$ is generally accepted to obtain a good fit between experimental data and calculated curves.

Such a behaviour is also observed when the dielectric response of materials is studied; this point has been reviewed by Jonscher /16/ who concluded to the existence of a remarkable "universality" of frequency and time responses suggesting the dominant role of many-body interactions.

3.2 - Relaxation time and activation energy

The results of figure 1 were analysed using different methods /8/ but all have lead to determine a characteristic time which was plotted against $1/T$: an apparent activation energy (4.3 eV) and a frequency factor ($10^{13}$ s$^{-1}$) were found but these values were considered to have no physical meaning. In order to distinguish equilibrium from iso-configurationnal measurements as explained in the preceding part, creep and recovery deformation measurements were made with an other oxide glass /17/. Assuming the rules of linear viscoelasticity, the experimental data were analysed as explained in the figure 2 and the slope $1/\eta$ of the curves $\eta_{visco}(t)$ are shown as a function of $1/T$ in the figure 3. Each point has been obtained after a thermal treatment of the material allowing us to separate results corresponding to the material in equilibrium or isoconfigurationnal states. In a first approximation, a characteristic time $\tau = \tau_0 \exp u/kT$ with $u = (2.8 + 0.1)$ eV and $\tau_0 = 5.10^{-15} + 1)$ for iso-configurationnal conditions.

$\tau \propto \exp A/T_0$ with $T_0 \sim 790$ K for metastable equilibrium state.

Such a result is in agreement with the general pattern about glass behaviour near $T_g$. Although, it can be noticed that even in iso-configurationnal state, the apparent activation energy and the frequency factor seem rather large by comparison to values expected from the assumptions of simple atomic (molecular) jump and "lattice" frequency ($10^{13}$ s). Such large values are also obtained as well with organic macromolecular glasses /18/ as with amorphous Se /19/.
Fig. 1 - Internal friction and storage modulus of an oxide glass /8/.

Is this large value of the apparent activation energy observed at lower temperature? The figure 4 concerning results obtained with the same material as for results of the figure 3, shows that this is not the case since the application of the time superposition principle, although not strictly verified, need a shift factor varying with the temperature with an apparent activation energy equal to (0.9 + 0.1)eV.

To conclude, let us recall that Berry /13/ nearly ten years ago, did mention similar features in the case of metallic glasses, implying a frequency factor $10^{25}$ s$^{-1}$, which was considered as an "apparently ridiculous result".

Fig. 2 - Compliance as obtained from a creep test; separation of components: $J_{\text{anel}}(t) = J_{\text{anel}}(t-t_1)$ and $J_{\text{viscop}}(t) = J_{\text{tot}}(t)-J_{\text{anel}}(t)$.

Fig. 3 - Oxide glass: Variation of the slope $dJ_{\text{viscop}}(t)/dt$ with temperature either in isoconfigurational condition (X) or in metastable equilibrium (●).

Fig. 4 - Oxide glass: Variation of $J_{\text{anel}}(t)$ with temperature.
3.3 - Aging effect

Many papers have been published on aging effect observed with glasses. A largely developed review of the situation concerning polymeric organic glasses can be found in Struik's book /20/ although some features may be argued. The main point put forward by Struik is that aging induces a shift of the whole spectrum of relaxation (retardation) times without deformation of this spectrum. Such a point of view is questionable as results obtained with glassy selenium rather support the idea of a modification of the form of the spectrum during aging. More recently, CHAI and MC CRUM /21/ have subjected the Struik model to an experimental verification. For isotactic polypropylene which was quenched from 353 K to 313 K, they found that the derivative \( \frac{d \log J}{d \log t} \) varied smoothly from -0.749 to -0.858 as the aging time varied from 180 s to 1.91 \( 10^5 \) s, thus implying a modification of the form of the retardation spectrum. Hence, at least for this material, it appears that the Struik model is not consistent with the experimental finding of CHAI and MC CRUM. This point may be connected to the fact that the ratio \( J_{viscosp} / J_{anel} \) is decreased after aging /22, 23/.

On another hand a reversible structural relaxation is sometimes mentioned from detailed study of the effect of annealing on the internal friction of metallic glasses: it was found /24, 25/ that the glass reaches, after an extended period of annealing an internal pseudo-equilibrium state, which is function of the annealing temperature. A change in the annealing temperature results in a reversible change from one such state to another.

To sum up, a successful full theory of atomic (molecular) mobility in glasses near \( T_g \) must be consistent with those characteristics of aging phenomena and this has to be included in whatever kind of model of internal friction.

IV - ANELASTICITY AND VISCOPLASTICITY OF GLASSES NEAR \( T_g \) - PHYSICAL BASIS FOR A THEORY

4.1 - General grounds

In a recent paper /22/, we proposed that the basic deformation mechanism is the nucleation of shear microdomains. The nucleation occurs under the effect of the applied stress and is thermally assisted. A general case of shear microdomains was illustrated as follow /22/: the shear is along a surface \( S \) and the cooperative atomic rearrangement occurs inside the volume of matter limited by a surface \( \Sigma \). The curve \( C_n \) defined by the intersection of \( \Sigma \) and \( S \), separates the area \( S_1 \) where shear has occurred from the non sheared part of \( S \). In mechanics of continuous media, the line \( C_n \) is a dislocation loop; in amorphous solids, dislocations, as far as this concept is valid, would be of the Somigliana type, as LI /26/ has pointed out. The nucleation rate has been calculated by several authors but results appear to be unrealistic as far as such nucleation occurs everywhere in the amorphous solid. Therefore, it was proposed /22/ that nucleation can occur only in those regions where resistance to shear is appreciably weaker than in the rest of the material. Such soft sites may be regarded as "defects". The thermomechanical activation of a defect (mean time \( \tau_1 \)) may lead to the formation of a s.m.d. When the stress is removed, the solid recovers its previous configuration thus corresponding to anelastic behaviour. In order to obtain plastic deformation the growth of the s.m.d. must be necessarily invoked, but the line \( C_n \) being a Somigliana dislocation, is a sessile defect. Nevertheless, such a growth can be obtained through diffusionnal mechanism: this growth covers a distance (mean time \( \tau_2 \)) at which the line \( C_n \)
losses its identity by combination with other similar lines formed from the neighbouring defects, and become ineffective. This leads to a viscoplastic behaviour. Following these hypothesis, a quantitative description of the non-elastic deformation of glassy solids was given /22/ in terms of the following Eq.: 

\[ J(t) = A \left\{ \frac{\zeta(t, \zeta)}{(\zeta + \zeta)} \left[ 1 - \exp\left(-\frac{t}{\tau}\right) \right] + 2 \frac{t}{\zeta + \zeta} \right\} \]  

with \( A = v_0 \frac{v_a}{2} \frac{\Delta V}{k\Gamma}; \) \( v_0 \) : number of defect (volume \( v_a \)) per unit volume; \( v_a \) : activation volume; \( \Delta V \) : local shear; \( f \) : schmid factor; \( 1/\tau = 1/\zeta + 1/\zeta 

By assuming a distribution of values of \( \zeta \) (depending on distribution of either activation energy or frequency factor of both) we, recently obtained from Eq. (1) approximated Eq. in order to describe rheological behaviour of glasses near \( T_g /3 \): 

\[ J(t) \approx \left\{ 1 + \frac{A}{(\zeta + \zeta)^2} \left[ 1 - \exp\left(-\frac{t}{\tau}\right) \right] + 2 \frac{At}{(\zeta + \zeta)} \right\} \]  

and 

\[ J'(i\omega) \approx \left\{ 1 + (i\omega \zeta)^{-1} + \delta (1 + i\omega \zeta)^{-b} \right\} \]  

with \( \zeta_M = (\zeta + \zeta)^2/2A_G \) and \( \delta = G_u \zeta (\zeta - \zeta)^2/(\zeta + \zeta)^2 \) These Eq. can thus be "explained" by a suitable choice of the weight distribution of \( \zeta \). However, this approach is microscopically arbitrary and does not explain the universality of Kohlrausch's law \( \exp\left[-(t/\zeta)^b\right] \). So, instead of the picture of parallel relaxation, in which each degree of freedom \( i \) relaxes independently with characteristic time \( \zeta \), Palmer et al. /27/ considered a series interpretation, involving a distribution having a microscopic source in the correlations between different degrees of freedom. In other words, a hierarchy of degrees of freedom, from fast to slow is involved: the fastest might correspond to single-atom motion; other atoms, or groups of atoms, might only be able to move appreciably when several of the fastest happen to be placed in just the right way, leaving "free volume" or weakening a bond.

Hence as Palmer et al. /27/ let us consider a discrete series of levels \( n = 0, 1, 2, \ldots \) with the degrees of freedom in level \( n \) represented by \( N_n \) Ising spins. Each spin in level \( n \) is only free to change if a condition on some spins in level \( n \) is satisfied, e.g. \( N_{n-1} \) spins in level \( n-1 \) attain a particular state of their \( 2^n n-1 \) possible ones. The average relaxation time \( \zeta_n \) will be related by:

\[ \zeta_n = (\zeta + \zeta)^2 \]  

giving

\[ \zeta_n = 1 \exp \left( \sum_{k} \frac{\ln 2}{\mu} \right) \]  

One of the possibilities discussed by Palmer et al was \( \ln 2 \). \( \mu_K = \mu_1 k^{-p} \) so that Eq. (4) becomes:

\[ \zeta_n = \zeta_1 \exp \left( \sum_{k} \frac{\mu_1}{k} \right) \]  

In order to have a clearer connection with the microstructure of the material, we propose to modify the approach of Palmer et al in the two following ways:

a) If \( t_0 \) be the mean time necessary for the system to go from levels \( k \) to \( k+1 \), the ratio \( k = t_k/t_0 \) may be introduced \( t_k \) the time after which the system is at level \( k \).

Eq. (5) can be replaced by:

\[ \zeta(t) = \zeta_1 \exp \left( \mu_1 \sum_{k} \frac{t_k}{t_0} \right) = \zeta_1 \exp \left( \mu_1 \int_0^t u^{-p} du \right) \]  

giving

\[ \zeta(t) = \zeta_1 \exp \left( \frac{\mu_1 (1-u^{1-p})/(p-1)}{t_0} \right) \]  

(6)

0 < \mu_1 < 1 may be regarded as a structural parameter characterizing the correlation between the different atomic movements in the glass which, as a solid, is a strongly interacting system. For \( \mu_1 = 0 \) the matter surrounding the atom moving first, is not sensitive to such a movement and \( \zeta(t) \) reduces to \( \zeta_1 \). For \( \mu_1 = 1 \), the primary movement induces numerous correlated atomic movements and \( \zeta(t) \) can reach the maximum value \( \zeta_{max} \). If experimental time \( t_{exp} \) is shorter than \( \zeta_{max} \), glassy systems clearly breaks ergodicity so that equilibrium distributions in configuration space are not usable. On the contrary, if \( t_{exp} > \zeta_{max} \), the system is ergodic, so that statistics equilibrium laws becomes correct and relaxation phenomena require pure exponential relations.

We furthermore expect such features to be relevant to glassy materials when \( \zeta_1 < \zeta_{max} < \infty \).

This is the case when \( p = 1 + \zeta \) (Eq. (1)) and Eq. (6) can be written

\[ \zeta_{max} = \zeta_1 \exp \left( \mu_1/\zeta \right) \]  

(7a)
Finally, \( Z_{\text{max.}} \) must increase when the temperature is decreased, more rapidly than \( Z_1 \); this is obtained with \( \xi = \xi_1 \ T / \bar{T}_1 \) giving with \( Z_1 = Z_1 \exp(u_1 / kT) \)
\[
Z_{\text{max.}} = Z_1 \exp((u_1 + m_1 \ K \ T_1 / \xi_1)/kT) \tag{7b}
\]

b) An equivalent description can be given on the basis of the formation of a s.m.d. from the activation of a defect (mean time \( Z_1 \)) as discussed above. But, instead of atomic diffusion assisted growth of s.m.d., let us assume a repeated nucleation at and behind the slip front of the Somigliana dislocation \( C_n \) /26,28/; such nucleated micro-loops might be structurally equivalent to the pseudo-spins considered by Palmer et al. /27/. In such conditions, the activation of the defect in order to form a s.m.d. need the time \( Z_1 \)
the preceding phenomenon followed by the nucleation of the micro-loops \( N^0 \) 1 need the time
\[
Z'_n = Z'_n \exp(\Delta u_n / kT)
\]
giving
\[
Z'_n = Z'_1 \exp(\sum_{i'=1}^{n-1} \Delta u_i / kT)
\]
Similarly to the preceding paragraph \( (\Delta u_1 = \Delta u_1 \times i^p_1 ; p_1 = 1 + \xi_1 ; \xi_1 \leq 1) \) one can calculate
\[
Z'_n = Z'_1 \exp(\Delta u_n / kT \times 1 - n^{-p_1})
\]
and, for \( n \to \infty \), \( Z_{\text{max.}} = Z_1 \exp((u_1 + \Delta u_1 / \xi) kT) \) which is equivalent to Eq. (7b)
with \( u_1 = p_1 \ K \ T_1 \). In fact the time \( Z_{\text{max.}} \) thus introduced might be similar to the time \( Z_2 /22/ \ as \( Z_{\text{max.}} \) corresponds to the formation of a s.m.d whose size has the same value above which the growth of the Smd is irreversible due to annihilation with neighboring dislocation loops like \( C_n \); besides, the micro-loops nucleated at the front of two Somigliana dislocations being annihilated must be of reverse character and this leads to a diffusion transfer of matter.

The present description may be compared to the work of Ngai and White /28/ who proposed an unified theory of low frequency dynamic response of condensed matter: the relaxation of a primary species (side group, chain segment and, more generally, a dipole...) is followed by an interaction with correlated states presenting low energy excitations. To underline this comparison, let us calculate \( \zeta(t) \) from Eq. (6) by developing it in series around \( \zeta = 0 \): at the first order (which corresponds to \( p=1 \)), we have:
\[
\zeta(t) = \zeta_1 (t/t_0)^{1/2}
\]
which can be identified to the result of Ngai and White:
\[
\zeta(t) = \zeta_1 (t/t_0)^n \tag{8}
\]
with \( \zeta_1 = \zeta_1 \exp(\xi \ t / t_0) ; \xi = 0.577 ; n < 1 \); \( t_0 = \hbar/\xi \) and \( \xi \) is the upper "cutoff" of the correlated state excitation. The expansion to the second order is more interesting:
\[
\zeta(t) = \zeta_1 (t/t_0)^{a} \tag{9}
\]
with
\[
a = p_1 (1 - \xi/2 \ log u)
\]
Finally, by taking into account of the condition \( \zeta(t) = \zeta_{\text{max.}} \) for \( t = \zeta_{\text{max.}} \) we obtain
\[
\zeta(t) = \zeta_{\text{max.}} t^{-a} \tag{8}
\]
As said above, the system is ergodic when \( t \gg \zeta_{\text{max.}} \): relaxation phenomena then require pure exponential relations implying the characteristic time \( \zeta_{\text{max.}} \).

to sum up, as far as \( \zeta(t) < \zeta_{\text{max.}} \), the elemental shear process resulting from hierarchically constrained atomic movements, is reversible (anelasticity); for higher temperature, or longer time, \( \zeta(t) = \zeta_{\text{max.}} \) and shear is irreversible (viscoplasticity).

4.2 - Calculation of mechanical response

A general representation of the stress relaxation modulus (or any other rheological properties) must contain the relaxation time \( \zeta(t) \) but also a \( h(\zeta) \) distribution having a microscopic source in the correlations between different degrees of freedom. Palmer et al. /27/ considered the weights \( h_n = h_0 \lambda^{-n} \); as pointed out by these authors themselves, there is many ways to choose the \( h(\zeta) \) distribution; but in all cases, the condition \( \int h(\zeta) \ z \ d\zeta = A \) (A being the same constant as in Eq. (1)) must be fulfilled; Thus, the following pattern can be proposed:

(i) In glassy solids, atomic movements induced by both the stress and thermal activation occur on special sites ("defects", the concentration of which is \( N_0 \) per
unit volume,
(ii) each movement need a delay between \( \tau_1 \) and \( \tau(t) \),
(iii) the number of possible values of this delay is dependant on the characteristics of the defects so that the constant \( A \) of the Eq. (1) must be replaced by the product \( A \exp(\alpha \tau) \), \( P(\tau) \) representing the fraction of the total number of defects, being activated with the time \( \tau \). We suggest to test the symmetric Gaussian relation \( P(\tau) = 1/B \exp\left\{ -(\log \tau/\tau_{\text{max}})^2 \right\} \). Such a relation would take into account:
- the probability to have a movement necessitating a given delay,
- the structural source of the characteristics of the movement,
- the coupling strength of the processus.

By considering Eq. (7), it appears that any variation of the structural factor \( \mu_1 \) induces a variation of both apparent activation energy and frequency factor; this suggest to use a factor \( B \) of the form \( B = B_0 + B_1/T \).

Thus, in order to try some quantitative description of the mechanical response of glassy solids, two extreme cases may be considered:

i) for low temperatures \( T < T_g \), the mechanical response is mainly sensitive to the distribution relation \( P(\tau) \). Using \( \frac{\text{Tg}}{\tau} = \Delta(\tau) \rightdiv \omega/(1 + \omega^2 \tau^2) \), the relaxation strength can be taken from Eq. (3), recalling than internal friction comes only from the anelastic behaviour in this temperature range: thus one has:
\[
\frac{\text{Tg}}{\tau} = 0.5 A G_0 P(\tau) \tag{10}
\]

ii) for high temperatures \( T > T_g \), all values of \( \tau_1 < \tau(t) < \tau_{\text{max}} \) may intervene and all the defects may be concerned. The mechanical response is, then, mainly sensitive to the form of the expression giving \( \tau(t) \). The calculation of the compliance in glassy materials was made earlier /22/ but the time \( \tau_1 \) must be replaced by \( \tau(t) \) and some steps of the calculation thus are modified: the most important modification is in integrating Eq. (6) (ref. 22) as the characteristic time is now time dependant. A good approximation can be found as follow: on one hand, the anelastic behaviour is ruled out by the Eq. \( dN(t)/dt = -N(t)/\tau(t) \), \( N(t) = N_0 \exp \left[ -1/\left( b(t/\tau_{\text{max}})^b \right) \right] \) with \( b = 1-a = 1-\mu_1 \rightdiv \mu_2 \).

The strain rate is then
\[
\dot{\varepsilon}_{\text{anel}} = \frac{1}{\tau_{\text{anel}}} \left[ \dot{N}(t)/\tau(t) \right] \left( f_0 \sigma v_g/kT \right)
\]
and similarly
\[
\dot{\varepsilon}_{\text{visco}} = \frac{1}{\tau_{\text{visco}}} \left[ \dot{N}(t)/\tau(t) \right] \left( f_0 \sigma v_a/kT \right)
\]

By admitting that \( \dot{N}_1 = \dot{N}_2 v_1/v_2 \) and \( v_a \) are not too different of \( \dot{\varepsilon}_2 \) and \( v_a \), respectively, we have the compliance

\[
\frac{1}{\tau(t)} = \frac{1}{G_0} + A \left\{ 1 - \exp \left[ -1/b(t/\tau_{\text{max}})^b \right] \right\} + A t/\tau_{\text{max}} \tag{12}
\]

with may be compared to Eq. (2). Similarly to Palmer et al /27/ and to Ngai /29/, we have obtained a Kohlrausch exponential is based upon physical basis. The same Eq. (3) can be used to calculate internal friction but we have now:
\[
\tau_{\text{M}} = \tau_{\text{max}}/A G_0 \quad \text{and} \quad \tau = b t/\tau_{\text{max}} \tag{13}
\]

V - COMPARISON WITH EXPERIMENTAL RESULTS AND DISCUSSION

We firstly emphasize that the results fo Fig. 1 now can be clearly understood: on one hand, as the temperature is increased, the value of \( b \) increases, approaching the unit when \( T \approx 1.2 T_g \); this appears to be induced by a decrease of the factor \( \mu_1 \) (see Eq. (9) and (11)) as the correlation between the preliminary and subsequent atomic movements becomes less and less efficient. On the other hand, Eq. (11) shows us that \( b \) might increase with the time and this could explain that \( b \) is higher when the period of measurement is larger. To conclude about the results of Fig. 1 we only mention that it is also possible to understand their presentation in the Cole-Cole diagram /8/ showing that (i) \( b \) is constant at \( T < T_g \) (ii) \( b \) increases with \( T \) at \( T > T_g \) and (iii) the form of the Cole-Cole diagram /3/ suggests \( \tau_1 = \tau_2 \) (Eq. (3)) and it happens that this is just the limit corresponding to \( b = 1 \) (see Eq. (12)).

A challenge more difficult is to explain at least semi-quantitatively in the scope of the present theory results observed with the same material in two different temperature range (fig. 3 and 4). Let us consider the results of Fig. 3: Eq. (12) indicates that the slope \( 1/\eta \) is equal to \( A/\tau_{\text{max}} \). In isoconfigurational conditions \( A \) is found to be closely independant of the temperature \( T \) and equal to \( 1.3+0.1 \times 10^{-10} \left( \tau_{\text{max}} \right)^{-1} \); hence \( \tau_{\text{max}} \) varies as a function of \( T \) with an apparent activation energy equal to \( (2.8 + 0.1) \text{eV} \) and a frequency factor equal to \( 10^{16} \text{ s}^{-1} \). On the other hand, in metastable conditions the slope is different and varies with \( T \) due to both \( A \) and \( \tau_{\text{max}} \) structure dependance.
Internal friction measurements (Fig. 4) does correspond to isoconfigurational conditions; so, it is worthwhile to verify if the preceding value of $A$ and $c_{\text{max}}$ (extrapolated towards the temperature range 473-673 K for the latter) can lead to calculated results in agreement with experiment: using Eq. (10) and the gaussian expression for $P(C)$, theoretical curves are calculated (dotted line: Fig. 4); Although the fit is very poor, the following features can be deduced: (i) the apparent activation energy is the same for both calculated and experimental curves ($0.9 \pm 0.1$ eV); (ii) $B$ is the lower, the temperature is high: the value $B \sim 0$ can be extrapolated for $T \approx 1.2 T_g$ meaning that all moving species behave in the same way without correlation effects; this is in agreement with the conclusion deduced from observing $b \neq 1$ in the same temperature range. (iii) the Fig. 5 shows the variation of $c_{\text{max}}$ obtained from both sets of results (Fig. 2 and 4); consequently, the curves $P(C)$ calculated for different temperatures are shown in the same Fig. 5.

![Graph 5](image)

Fig. 5 - Time relaxation spectra for 3 temperatures and variation of $c_{\text{max}}$ (isoconfigurational: • (creep test) and ○ (internal friction); metastable equilibrium: +) and of $B$ (x) with temperature.

Such curves although being not in agreement with the thermorheological simplicity assumption may be compared to relaxation spectra shown, by Chen /30/: in both cases, the whole spectrum lies either to the left of $t_{\text{exp}}$, so that the whole system undergoes frequent configurational transformation and is liquid-like, or, during cooling, the number of solid-like regions ($t > t_{\text{exp}}$) increases until they form an infinite cluster. In the latter case, the overall configuration is frozen-in at $T_g$ and the glass transition is then related to percolation process /31/. It may be emphasized however, that even at $T < T_g$, atomic (molecular) movements are possible in those defects for which $\tau(t) < t_{\text{exp}}$, thus leading to anelastic phenomena.

On another hand in metastable condition, the variation of $c_{\text{max}}$ with $T$ shown in Fig. 5 illustrates the decreasing correlation effect when the temperature is increased: for $T \approx 1.2 T_g$ each movement could correspond to the characteristic time $\tau_1$ which obeys to an Arrhenius law with an activation energy equal to that obtained from low temperature internal friction measurements (0.9 eV) thus justifying that $\beta$ relaxation times generally merge in $\alpha$ relaxation times at high temperature /2/. Furthermore, the viscosity is $\eta = c_{\text{max}}/A$ so that the variation of $A$ (i.e. the defect concentration, with the temperature results in a temperature dependance of viscosity (or diffusion) which obeys to the well known TVF Eq. /9/.

The aging experiments may be explained, too, in the light of the present theory: as an example the Fig. 6 shows experimental curves $J(t)$ obtained with the same oxide
glass as that giving results shown in Fig. 3 and 4. A good fit is obtained with curves calculated with Eq. (12) and, using the method summarized in Fig. 2 the parameters $A$, $\zeta_{\text{max}}$, $b$ are obtained successively. Thus, during aging, (i) $A$ decreases in agreement with the decreasing defect concentration /22/; (ii) $b$ decreases corresponding to an increase of $\zeta_1$ that is an increase of correlation phenomena; such a feature similar to that discussed in ref. /21, 32/, results in an increase of $\zeta_{\text{max}}$ and it can be verified through Eq. (7a) that both observed variation of $\zeta_{\text{max}}$ and $b$ are consistent. On another hand, reversible structural relaxation might be concerned with more local atomic rearrangements; hence $\zeta_{\text{max}}$ should not be sensitive to such aging treatment, contrarily to lower values of $\zeta(t)$; this can be described by considering that the constant $B$ of the gaussian distribution law decreases during a reversible structural relaxation.

![Figure 6](image-url)

Fig. 6 - Aging effect on the compliance (creep test and recovery of deformation made on the same material as for Fig. 3 and 4); experimental (full line) and calculated (dotted line) curves.

As a conclusion one may emphasize the main following points characterizing rheological properties of glasses near $T_g$: (a) atomic (molecular) movements in glasses occur in "defects" which are particular sites where entropy (disorder) is high and density is low; (b) the main and preliminary movement involve the excitation of correlated states: this corresponds to a hierarchy of degrees of freedom, from fast to slow; (c) when a stress is applied, the response of amorphous solids might be analysed in terms of (i) thermomechanical activation of defects leading to the formation of s.m.d. (main preliminary atomic movement) and (ii) subsequent extension of the Somigliana dislocation boarding the smd through hierarchically correlated atomic movements; (d) after the delay $\tau_{\text{max}}$, the extended loop is annihilated by combination with neighbouring loops; (e) the solid is mainly anelastic when $t_{\text{exp}} < \tau_{\text{max}}$ but viscous flow becomes important when $t_{\text{exp}}$ approaches $\tau_{\text{max}}$; (f) the value of $\tau_{\text{max}}$ is the higher the correlation effects are important, i.e. the temperature is low or the glass is structurally relaxed.

On the basis of such ideas a semiquantitative description of non-elastic deformation of glasses near $T_g$ has been proposed: Eq. (10), (12) and (13) are consistent with experimental features; in these Eq. the Kohlrausch factor $\exp\left[-(t/\tau)b\right]$ is introduced on physical arguments, the parameter $b$ caracterizing the effectiveness of correlation effects.
REFERENCES

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