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GLASS TRANSITION AS A FUNCTION OF COOLING RATE

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Résumé. - On décrit une méthode permettant le calcul des relaxations de structure dans des verres refroidis très rapidement. L'obstacle majeur dans le modèle original a été l'hypothèse d'une loi d'Arrhenius pour la viscosité à l'équilibre. Ici on emploie l'équation de Macedo-Litovitz pour la viscosité à l'équilibre. On montre que la zone de transition vitreuse est déplacée vers les hautes températures et s'élargit quand on augmente la vitesse de refroidissement. Les verres à T_g élevé e.g. SiO_2 ont une zone de transition vitreuse plus large que les verres de T_g plus bas mais avec une énergie d'activation similaire.

Abstract. - The method is described for calculating structural relaxation in glasses cooled very rapidly. The major obstacle for the calculation was the assumption in the original model of Arrhenius behavior for the equilibrium viscosity. In this paper the Macedo-Litovitz' hybrid equation is used for the equilibrium viscosity. The glass transition region is shown to shift to higher temperatures and to broaden as the cooling rate increases. Glasses with higher T_g e.g. SiO_2 are shown to have broader glass transition region than glasses with lower T_g but similar activation energy.

Perpetual intensifying and shortening of the annealing cycles in glass manufacturing, the advent of fiber optics, metallic glasses and splat cooling technique raise the question how the glass transition occurs at cooling rates, q , 3, 5, 7 orders of magnitude higher than the one conventionally used in the laboratory. It is well known that the glass transition interval will shift to higher temperatures, or lower viscosities as the cooling rate increases. That formulates the problem.

In the structural relaxation model by Marayanaswamy [1] the viscosity is assumed to be related to the temperature by Arrhenius equation. According to Mazurin, Startsev and Potseluyeva [2] this is a good approximation for the viscosity below the glass transition temperature, T_g . For equilibrium viscosity it holds only for a narrow temperature interval. Fulcher-Vogel- Tamman or WLF equations give better results for the equilibrium viscosity but fail to predict Arrhenius dependence below T_g . Therefore we have chosen to work with the Macedo and Litovitz [3] hybrid equation, incorporating the elements of both free volume and activated flow theory.

The equation is:

$$\eta = \eta_0 \exp \left(\frac{\gamma v_c}{v_f} + \frac{Q}{T} \right) \quad (1)$$

where η = viscosity, η_0 , γ and Q are constants v_c = core or occupied volume of atoms (exclusive of interatomic volume), and v_f = free volume = $v - v_c$, where v = total volume.

In Eq. (1), v_f is inheritantly poorly defined. An important feature of v_f , i.e. freezing in the glass transition region during cooling has not been reflected in the mathematical formulation. We have derived and will publish the derivation elsewhere, the following equation for v_f/v_c in Eq. (1):

$$v_f/v_c \approx \int_{T_1}^{T_f} \alpha_s dT' \quad (2)$$

where $\alpha_s = \alpha_l - \alpha_g$ is the structural thermal expansion coefficient defined as the difference between the thermal expansion coefficients of liquid and glass. T_1 is the temperature at which the volume of the liquid equals the core volume ($v_f = 0$).

Eq. (2) clearly shows that v_f freezes when $T_f = \text{const.}$ The higher the limiting T_f , i.e. the higher the cooling rate, the larger is the free volume frozen in.

For some glasses α_s can be assumed to be constant and Eq. (1) becomes

$$\eta = \eta_0 \exp \left[\frac{\gamma}{\alpha_s (T_f - T_1)} + \frac{Q}{T} \right] \quad (3)$$

When $T_f = T$ the first term in the brackets is in form $B/(T - T_0)$ of Fulcher equation. When $T_f = \text{const.}$ this term is constant and the equation is Arrhenius.

For other glasses $\alpha_s = \alpha_0 + \alpha_1 T$ and Eq. (1) becomes

$$\eta = \eta_0 \exp \left[\frac{\gamma/\alpha_0}{(T_f - T_1) \left(1 + \frac{\alpha_1 (T_f + T_1)}{2\alpha_0} \right)} + \frac{Q}{T} \right] \quad (4)$$

Eq. (4) has been used for calculation of the glass transition in the MBS 710 glass cooled at a rate of 10^{-2} , 10^0 , 10^4 , 10^6 K/min. The input parameters included $\gamma/\alpha_0 = 2.65 \cdot 10^4$ K, $Q = 3.59 \cdot 10^4$ K, $\eta_0 = 3.69 \cdot 10^{53}$ Pa·s, $T_1 = 253.8$ K, $\alpha_1/\alpha_0 = -10.4 \cdot 10^{-4}$ K⁻¹. For the calculation of T_f we used the model developed by Narayanaswamy [1]. The results of the calculations are given in Fig. 1. The equilibrium viscosity of MBS 710 was carefully measured by Napolitano and coworkers [4]. The standard deviation of the fit of their data to Eq. (4) given above is .042 in terms of $\log \eta$. The quality of the fit is better than that to Fulcher equation for which the standard deviation is .06 [4]. When $T_f = \text{const.}$ Eq. (4) predicts Arrhenius behavior with $Q = 3.59 \cdot 10^4$ K experimentally found by Mazurin and coworkers [2]. The glass transition is not only shifted to higher temperatures but also becomes broader. It is shown better in Fig. 2. The lower and the upper temperatures of the glass transition region, i.e. the temperatures T_L and T_U , are defined in this work as the temperatures at which $\frac{dT_f}{dT} = .01$ and $.99$ respectively.

How can we rationalize the broadening of the glass transition as the cooling rate increases? The fundamental feature of glass transition is that the structural relaxation time, τ , increases much faster than the real time, t . At $T = T_U$, $\tau \ll t$ and the structure easily follows the change in the temperature. At $T = T_L$, $\tau \gg t$ and the structure is frozen. Our calculation shows that $\tau_L/\tau_U \approx 4 \cdot 10^5$ regardless of the cooling rate. The structural relaxation time has the same temperature dependence as the viscosity. Therefore Fig. 1 can be used to explain the observed broadening. At

Fig. 1. Viscosity of NBS 710 via hybrid equation; equilibrium viscosity and that for cooling and subsequent reheating with the rates given at the curves in K/min. Dashed line - Arrhenius approximation with the activation energy determined in the range of $10 \leq \log \eta \leq 13$.

Fig. 2. Broadening of the glass transition region with increase in cooling rate (given at the curve in K/min).

higher temperatures the temperature dependence of τ is shallower, therefore the liquid will travel a longer way on the temperature scale to accumulate the 5 orders of increase in τ needed for the glassification.

That suggests however that the glasses which intrinsically have higher T_g will have broader glass transition interval than the glasses with the lower T_g but the same activation energy. This is shown to be true in Fig. 3. We compare here a soda-lime-silicate glass ($T_g = 530^\circ\text{C}$) and SiO_2 ($T_g = 1098^\circ\text{C}$). Equations and parameters used for calculations are given in ref. [5].

Fig. 3. Glass transition during cooling and reheating at a rate 3 K/min in SiO_2 (1) and soda-lime-silicate glass (2). $T_u = 1253^\circ\text{C}$ for SiO_2 and 588°C for soda-lime-silicate glass.

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