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# Viscosity of undercooled melts

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A number of models describe the temperature dependence of viscosity $\eta$ of undercooled melts. According to the old-fashioned free volume approach, $\eta$ depends on the ratio of the occupied volume to the free volume. Gibbs *et al.* [1, 2] consider the molecular motion as a cooperative process involving a simultaneous rearrangement of a large number of particles. For that reason $\eta$ should depend on the configurational entropy. Scherer [3] has shown that the free volume model is not able to describe properly the isostructural viscosity of oxide glasses. On the other hand, the Adam–Gibbs equation represents well the viscosity of some glasses but it fails for others. It is well known that despite the differences in the mechanism of molecular transport, all undercooled melts show a remarkable similarity in the temperature dependence of their shear viscosity. For that reason a generalized model was suggested [4] describing the kinetics of molecular motion in undercooled melts. In the present paper we discuss some aspects of the physical background and values of the parameters involved in the model. Moreover, the number of the parameters is reduced and their dependence on the composition is considered taking into account existing experimental data [5].

The most popular representation of the dependence of the jump frequency $\nu$ on temperature $T$ and activation energy $E$ is formulated in terms of the active complex theory as:

$$\nu = \nu_0 \exp\left(-\frac{E}{RT}\right) \tag{1}$$

where $\nu_0 \approx 10^{(11\pm1)}\,\mathrm{s}^{-1}$ is the mean vibration frequency.

Every motion in undercooled melts is a cooperative process with a broad distribution of barrier heights, $E$. The disorder in amorphous media implies some probability distribution function, $W(E, \sigma)$, of the activation energy, $E$, for the jump of a building unit to a new position. The dispersity $\sigma$ of $W(E, \sigma)$ reflects the degree of disorder in the system and is related to the entropy, $S$. The $\sigma(S)$-dependence is described [4, 6] with sufficient accuracy through the dispersity $\sigma_r$ at a given reference state at which the entropy is $S_r$.

$$\sigma = \sigma_r \exp\left(\frac{2(S - S_r)}{ZR}\right) \tag{2}$$

Here $R$ is the ideal gas constant and $Z$ is the number of channels along which the building unit could escape from the given position. The entropy can be expressed through the heat capacity $C_p$. Adopting, as usual, $c_p \approx$ constant, it follows that

$$\sigma = \sigma_r \left(\frac{T}{T_r}\right)^{\alpha} \tag{3}$$

where

$$\alpha = \frac{2C_p}{ZR} \tag{4}$$

The mean jump frequency is defined as

$$\langle \nu \rangle = \int_0^{\infty} W(E, \sigma)\, \nu(E)\, \mathrm{d}E \tag{5}$$

Fig. 1 shows schematically the dependence of $W(E, \sigma)$ (dashed line) and of $\nu(E)$ (dotted line) on the activation energy $E$. Also given on the same figure is the product $P(E) = W(E, \sigma)\, \nu(E)$. It is clear that the maximum of $P(E)$ and correspondingly the value of the integral, depends on the position and on the shape of the first peak of $W(E, \sigma)$ because at higher energies the value of the jump frequency $\nu$ (and correspondingly the value of $P(E)$) drops very quickly. This is the reason why we can neglect so many details of the motion. In this way the problem is simplified considerably and the unknown explicit form of $W(E, \sigma)$ can be replaced by a Poissonian distribution between 0 and $E_{\max}$ (Fig. 1). In [4] it was shown that for $\sigma > RT$ the solution of Equation 5 is given with sufficient accuracy as

$$\langle \nu \rangle = \nu_0 \exp\left(-\frac{E_{\max}}{\sigma}\right) \tag{6}$$

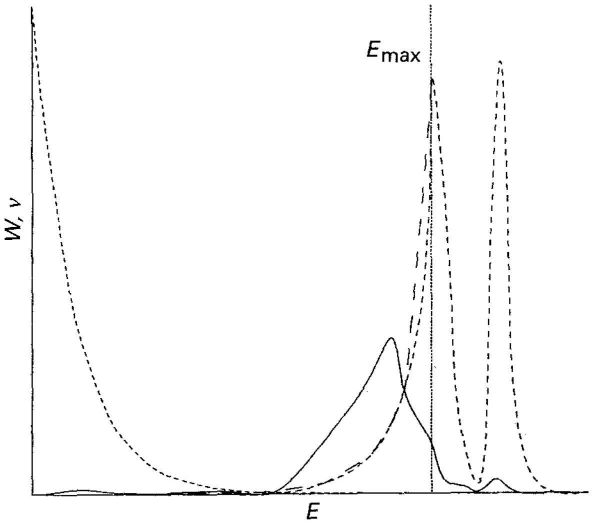

*Figure 1* The dependence of probability distribution function $W(E, \sigma)$ (----), of jump frequency $\nu(E)$ (·····) and of the product $P(E) = W(E, \sigma)\, \nu(E)$ (—) on the activation energy $E$. (-- W approximation).

The combination of Equations 3 and 6 leads to

$$\langle \nu \rangle = \nu_0 \exp\left[-\frac{E_{\max}}{\sigma_r}\left(\frac{T_r}{T}\right)^{\alpha}\right] \qquad (7)$$

In general the mean jump frequency and shear viscosity are reverse proportional $\langle \nu \rangle \eta = K$, where according to [4, 5] $K = 2.5 \times 10^9$ Pa for most glass-forming systems. So, the temperature dependence of viscosity is

$$\eta = \eta_0 \exp\left[\frac{E_{\max}}{\sigma_r}\left(\frac{T_r}{T}\right)^{\alpha}\right] \qquad (8)$$

where the pre-exponential constant $\eta_0$ is the lower possible value of the viscosity of the melt at high temperatures.

$$\eta_0 = \frac{K}{\nu_0} = 10^{-A}\ \mathrm{Pa\,s} \qquad (9)$$

with $A \approx 2 \pm 1$. From Equations 8 and 9 it follows that if we determine $T_r$ as a temperature at which the viscosity $\eta_r$ is a given constant than the $E/\sigma_r$ value can be assumed a constant for all substances because the parameter $A$ varies over narrow limits.

It is useful to choose for a reference state the temperature $T_g$ at which the viscosity is $\eta_g = 10^{12.5}$ Pa s. In this case

$$B \equiv \frac{E_{\max}}{\sigma_g} = 2.3\,(12.5 + A) \approx 33 \qquad (10)$$

Thus glass transition occurs usually at a temperature at which the degree of disorder scales for all substances is such that $E_{\max}/\sigma_g = 33$. The temperature dependence of $\eta$ can be expressed through $\eta_g$ as

$$\eta = \eta_g \exp\left\{B\left[\left(\frac{T_g}{T}\right)^{\alpha} - 1\right]\right\} \qquad (11)$$

or

$$\lg \eta \approx 12.5 + 14.5\left[\left(\frac{T_g}{T}\right)^{\alpha} - 1\right] \qquad (12)$$

There is an easy way to obtain the value of $\alpha$ from the experimental data. At a given temperature $T$ the slope $L(T)$ of the $\lg \eta$ against $1/T$ curve is

$$L(T) = \alpha\,(12.5 + A)\left(\frac{T_g}{T}\right)^{\alpha-1} T_g$$

$$\approx 14.5\alpha\left(\frac{T_g}{T}\right)^{\alpha-1} T_g \qquad (13)$$

It is readily seen [4] that the exponent, $\alpha$, can be determined by comparing the slopes at two temperatures $T_1$ and $T_2$:

$$\alpha = 1 + \frac{\ln\left[L(T_1)/L(T_2)\right]}{\ln\left[T_2/T_1\right]} \qquad (14)$$

Once the value of exponent $\alpha$ is known the determination of $A$ is trivial. The determination of $\alpha$ is possible even if experimental data are available in a narrow region around $T_g$ only. The slope $L(T_g)$ is given with 7% accuracy as

$$L(T_g) = \alpha\,(12.5 + A)\,T_g \approx (14.5 \pm 1)\,\alpha T_g \qquad (15)$$

The temperature dependence of viscosity of more than 40 substances is described successfully in terms of Equation 15. The theoretical curves are always in excellent agreement with the experimental data [5], as illustrated in Fig. 2. According to Equation 11, in coordinates $\lg \eta$ against $(10^3/T)^{\alpha}$, the experimental data lay on straight lines having intercepts $A \approx -2$ and slopes equal to $33(T_g/10^3)^{\alpha}$. The agreement of this prediction with existing experimental data [5] is illustrated in Fig. 3.

We find that the value of $\alpha$ increases simultaneously with the molar concentration $x$ of modifying oxides. For most silicates this is described by the equation:

$$\alpha = 1 + 6x \qquad (16)$$

The dependence of $\alpha$ on composition is given in Fig. 4 for a number of substances.

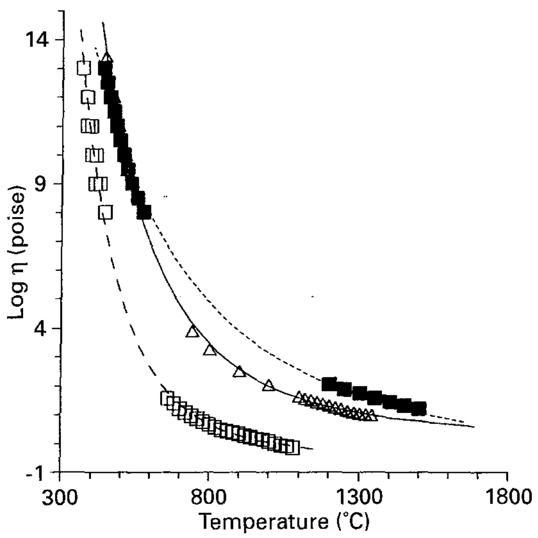

*Figure 2* Temperature dependence of viscosity of some silicate melts. The theoretical curves are shown as lines (-△- 40PbO-60SiO$_2$; -⊟- 60PbO-40SiO$_2$; -■- 30Li$_2$O-70SiO$_2$).

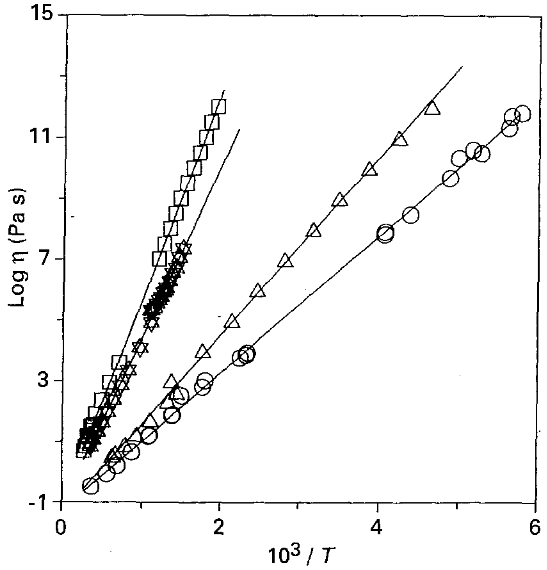

*Figure 3* The temperature dependence of viscosity of some typical glassforming melts. Note that in these coordinates the theory predicts straight lines (□ 20Na$_2$O-80SiO$_2$; ◇ Na$_2$O-2SiO$_2$; △ 13.5Na$_2$O-86.5B$_2$O$_3$; ○ Na$_2$O-2B$_2$O$_3$).

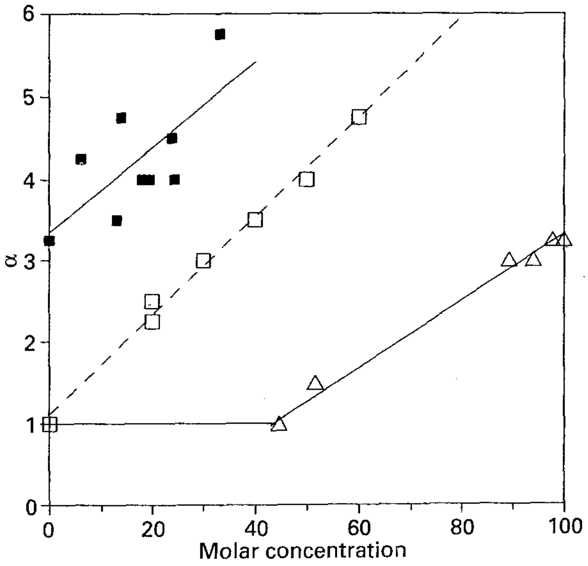

*Figure 4* The dependence of exponent $\alpha$ on composition (△ $B_2O_3 + SiO_2$; □ silicates; ■ borates).

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