



Deformation–activation model of viscous flow of glass-forming liquids



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ABSTRACT

We suggest a model, according to which the local low activation stretching of a valence bond network is a necessary condition for the realization of an elementary act of viscous flow of inorganic glasses and their melt-activated transition of the kinetic unit (bridge atom) into a deformed microregion. Exactly this kind of local configurational change of structure of a kinetic unit responsible for yield plays an important role in the temperature dependence of the viscosity of these systems, especially in the vicinity of vitrification of liquids. In the framework of this model the temperature dependence of free activation energy of viscous flow of glass melts in the wide temperature range is described and explained.

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1. Introduction

Viscosity is principally an important property determining the specifics of the glassy state of substances. A rapid increase of the viscosity of the melt with a temperature decrease slows down the crystallization process and enables the transition of the system to a glassy state. There are many works devoted to the description and treatment of the temperature dependence of the viscosity of glass-forming liquids, theoretical as well as experimental. However, this problem has not been fully solved (see e.g. [1]).

There have been suggested different types of atomic mechanisms of viscous flow of inorganic glasses [1–16]. Mueller [3,4] developed the idea that the elementary act of yielding of these systems is reduced to the switching of valence bonds, otherwise, to the interchange of the locations of bridge atoms like oxygen atoms in the Si–O–Si bridge. This concept has been further developed in Nemilov's valence-configurational theory [8,15,17,18].

Smyth, Finlayson and Remde [5] suggested the model of viscous flow of silicate glasses, where the possibility of breaking and switching of Si–O bonds is taken into account. If the bridge oxygen ion in the Si–O–Si bridge as the result of transverse thermal vibrations becomes close enough to the unsaturated silicon ion, then the switching of valence bridge bond Si–O–Si can occur, as is shown in the scheme of the bond switching mechanism according to Nemilov (Fig. 1) [18].

Among the known theoretical relations for coefficient of viscous flow of liquids, the Eyring equation is the most popular [19]

$$\eta = \eta_0 \exp\left(\frac{\Delta F_\eta}{RT}\right), \quad (1)$$

where ΔF_η is the free activation energy of yield, η_0 is the pre-exponential factor

$$\eta_0 = \frac{Nh}{V_\eta} \quad (2)$$

is the volume of particles, V_η the overcoming activation barrier, Planck's constant h , Avogadro's number N , and the gas constant R .

In glass-forming liquids the value $\Delta F_\eta(T)$ depends on the temperature, especially sharply in the vicinity of vitrification. Currently there is no generally accepted formula expressing the explicit form of function $\Delta F_\eta(T)$.

In the valence-configurational theory [8,15,17], the free activation energy of viscous flow $\Delta F_\eta(T)$ is expressed as the sum of the potential of bridge bond switching ΔF_η^0 and the potential of the configurational change of the structure around the location of valence bond switching $\Delta F_{\eta k}(T)$

$$\Delta F_\eta = \Delta F_\eta^0 + \Delta F_{\eta k}(T). \quad (3)$$

And the explicit form of the function $\Delta F_{\eta k}(T)$ is not disclosed. The idea of dividing ΔF_η into two components has been suggested before in the works [6,20]. Recently such an approach to the activation energy of yield has been successfully used by Ojovan et al. [1,14].

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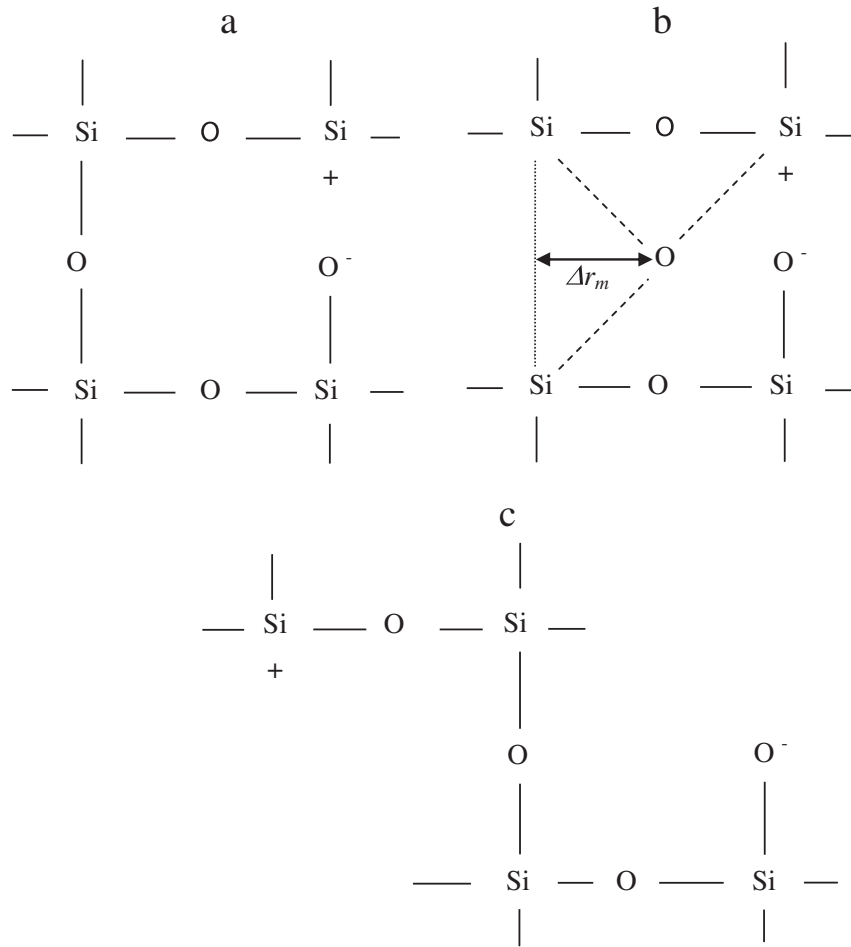


Fig. 1. Scheme of valence bond switching in silicate glasses according to Nemilov [8,18]. Δr_m – hopping of oxygen bridge atom leading to switching of bridge bond Si–O–Si.

In Nemilov's theory [15,17] it is supposed that the switching of the bridge bond and the configurational change of the structure around the location of bond switching occur simultaneously.

Mueller [4] considered that before the switching of valence bonds there is an "induction period of time of low activation network stretching with the change of angles between localized bonds". "Interaction of rotational vibrational oxygen bridges occurs after reaching the known stretching of the network", this interaction "leads to bond switching with the formation of a new bridge" (see Figs. 1 and 4 in [4]). However, this idea was not expressed quantitatively, in particular there was no estimate of "low activation energy" of stretching of valence bond networks.

In accordance with Muller's hypothesis, one can suggest that in Nemilov's scheme (Fig. 1), the displacement of oxygen bridge atoms in the Si–O–Si bridge is divided into two steps. The first step is some critical displacement of a given atom leading to local low activation stretching of the silicon–oxygen network (Fig. 1, transition a–b). The second step is related with the climbing of the bridge atom to the top of the barrier, which corresponds to the switching of valence bridge bond Si–O–Si (Fig. 1, transition b–c).

In our opinion Muller's idea about low activation deformation of a structure network as a precursor of switching of valence bridge bonds is worthy of further development.

The work by Mauro et al. [11] is of interest. It is based on the modification of the known Adam–Gibbs equation [6], expressing the relation between the liquid viscosity and configurational entropy $S_c(T)$,

$$\eta = \eta_0 \exp\left(\frac{B}{TS_c}\right). \quad (4)$$

It is supposed, that the value $S_c(T)$ is closely connected with the topological degrees of freedom of an atom $i(T)$ [21,22]. From the simple two level model the relation for the temperature dependence of the number of degrees of freedom of an atom $i(T)$ was suggested [11]

$$i = 3 \exp\left(-\frac{\Delta\epsilon_d}{kT}\right), \quad (5)$$

where $\Delta\epsilon_d$ is the energy of the formation of defects in the network of interatomic bonds (the energy difference between defective and normal states of a bond network). At high temperatures $T \rightarrow \infty$, according to relation (5), the number of degrees of freedom of an atom equals $i = 3$ (degrees of freedom of translational motion), and at the absolute zero temperature $T = 0$ K we have $i = 0$, since in this case there is no energy of thermal motion of atoms and the bonds network is defectless (completely "solid like").

Assuming in the Adam–Gibbs Eq. (4) that $S_c(T) \approx i(T)$ Mauro et al. [11] finally come to the temperature dependence of the viscosity of glass-forming liquids

$$\eta = \eta_0 \exp\left[\frac{K}{T} \exp\left(\frac{\Delta\epsilon_d}{kT}\right)\right], \quad (6)$$

where K is the parameter, related with the effective activation barrier B in the Adam–Gibbs Eq. (4).

Eq. (6) like the known Vogel–Fulcher–Tammann (VFT) [23–25] and Avramov–Milchev [10,26] equations has three fitting parameters, however in comparison with them better fits the temperature dependence of viscosity of glass-forming liquids, especially at low temperatures [11].

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