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The role of entropy on viscosity of silicates

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A R T I C L E I N F O

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The article compares different approaches describing shear viscosity of glassforming melts. It is demonstrated that they all could be derived from the original assumption of the Avramov and Milchev (*AM*) model that, due to the disorder, activation energy barriers of different heights appear. This leads to dependence of shear viscosity on the variance σ of the probability distribution function that the barrier of height E is present. All models are the result of the premise that (with different degrees of reliability) σ depends on temperature and/or on entropy. An approach is developed capable to describe, although with limited accuracy, the composition dependence of glass transition temperature.

1. Introduction

Shear viscosity provides an important link between thermodynamics and the kinetic properties of matter. Accurate knowledge of the dependence of shear viscosity, $\eta(T,x)$ on temperature, T, and composition, x, is of crucial importance to understand the fundamentals of materials science and the technology behind glasses. Although there are numerous definitions of the glass transition, here I follow the convention that T_g is the temperature at which the equilibrium value of shear viscosity is 10^{13} [poise] (resp. 10^{12} [Pa.s]). With this definition the temperature dependence of shear viscosity of all glassforming substances can be expressed in terms of one dimensionless parameter $\frac{T_g}{T}$ that varies in quite the narrow range of $1.05 > \frac{T_g}{T} > 0.55$.

Shear viscosity is not a pure thermodynamic variable because it has time in its dimensions. So, it cannot be determined by pure thermodynamic methods and needs a model description. The aim of the present paper is to compare the origin of derivation of the most widespread viscosity models and to demonstrate the similarities in their final forms. The second task of this article is to adapt the Avramov and Milchev (AM) model [1–4] to prognosticate the dependence of η on composition, x. The first attempt was already performed in [5] where the composition dependence of the glass transition temperature was expressed in a rather empirical way. We introduced in [5] the lubricant parameter $L_i = x_i k_i$, accounting for the special contribution of each element by the coefficient k_i whose values vary between 0 and 1. The reason is that one simple parameter like x is not sufficient to describe properly the dependence of the glass transition temperature on composition. Essentially, lubricant parameter is a sort of affinity accounting for the specific contribution of each element to shear viscosity. In the case of Al_2O_3 and Fe_2O_3 the definitions of $k_{Al_2O_3}$ and of $k_{Fe_2O_3}$ are more complex and the corresponding expression can be found in [5].

2. Equations of shear viscosity

Glasses consist of a continuous network of relatively “rigid” oxygen bridges connecting the network forming (*NF*) components (for instance Si, B, P etc.). The *NF* components occupy the nodes of the network. Viscous flow is a course the *NF* are changing their positions. These events, extremely rare at high viscosities, are controlled by the heights of activation energy barriers, related to the “rigid” bridges. The Avramov–Milchev (AM) model assumes [1–4] that disorder in the amorphous state results in the appearance of barriers of different heights. Therefore the average frequency to jump to a new position depends on product of the probability p(E) that barrier of height E will appear and the frequency $\nu(E)$ of jumping over it, i.e. $\langle\nu\rangle = \sum \nu(E)p(E)$. The probability p(E) can be described by E_c, the maximum value of the distribution function and by its variance σ. This is illustrated in Fig. 1 where the thick solid line represents the probability p(E) of the appearance of activation energy barrier of height E; the dashed line represents the exponential decay of the jump frequency $\nu(E)$. The product $\nu(E)p(E)$ is presented by the dotted line. Note that the maximum depends on the low energy tail of the p(E) curve, not on the shape near the maximum of this curve.

In [1–4] it was shown that, if p(E) is a sequence of independent events the average jump frequency is approximately equal to

$$\langle\nu\rangle = \nu_\infty \exp\left(-\frac{E_c}{\sigma}\right) \qquad (1)$$

under the condition that $RT < \sigma < E_c$. Here $\nu_\infty = \nu_o \frac{RT}{\sigma}$ depends on vibration frequency, ν_o, of the *NF* units. Since viscosity is related to the reciprocal

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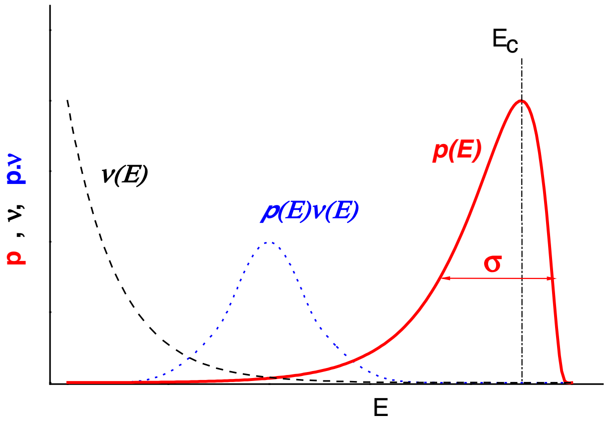

Fig. 1. Dependence of the jump frequency $\nu(E)$ on the height E of activation energy (dashed line). The thick solid line is the dependence of the probability p(E) that activation energy barrier of height E will appear. The product $\nu(E)p(E)$ is presented by the dotted line. Note that the maximum depends on the low energy tail of the p(E) curve, not on the shape near the maximum of this curve.

of the average jump frequency the shear viscosity is expressed in the form

$$\log\eta = \log\eta_\infty + \frac{E_c}{2.3\sigma}. \tag{2}$$

In the following it is assumed that the parameter $\log\eta_\infty$ is a constant because it depends on temperature in a much less important way as compared to the $\frac{E_c}{2.3\sigma}$ term.

Eq. (2) could serve as the origin for derivation of most of the known viscosity equations. Indeed, it is sufficient to assume that σ is proportional to temperature increase above the Kauzmann temperature, $\sigma \sim (T-T_o)$, and VFT

$$\log\eta = \log\eta_\infty + \frac{B}{T-T_o};\quad B = \frac{E_c}{2.3\sigma_g}\left(T_g - T_o\right) \tag{3}$$

equation follows straightforward.

If one assumes that σ is proportional to the product of configuration entropy ΔS and temperature, i.e. $\sigma \sim T\Delta S$, then the expression of Adam–Gibbs

$$\log\eta = \log\eta_\infty + \frac{C}{T\Delta S} \tag{4}$$

is obtained.

The AM model is based on Eq. (2), with an accurate solution of the dependence of the variance σ on entropy S according to expression of statistical thermodynamics.

$$\sigma = \sigma_g \ \exp\left[\frac{2\left[S-S_g\right]}{ZR}\right] \tag{5}$$

Here R is the ideal gas constant and σ_g is the variance at a reference state with entropy S_g. From the view point of mathematics the parameter Z/2 is the degeneracy of the system. Actually, Z is the coordination number because Z/2 accounts for the number of escape channels and each escape channel can be used in two directions. It is seen that, unlike most of the recent approaches (see [6–9] and literature cited there), σ depends on the total entropy. Combining Eqs. (2) and (5) the shear viscosity is obtained

$$\log\eta = \log\eta_\infty + (13 - \log\eta_\infty)\exp\left[-\frac{2\left[S-S_g\right]}{ZR}\right]. \tag{6}$$

If heat capacity is assumed constant then $S-S_g \approx C_p \ln\frac{T}{T_g}$ and the AM equation follows

$$\log\eta = \log\eta_\infty + (13 - \log\eta_\infty)\left(\frac{T_g}{T}\right)^{\alpha}. \tag{7}$$

Here $\alpha = \frac{2C_p}{ZR}$ is the dimensionless "fragility". It was already shown [5,10] that α is related to the Angell fragility, m, according to $\alpha = \frac{m}{\log\left(\frac{\eta_g}{\eta_\infty}\right)} \approx \frac{m}{13}$.

I failed to find a reasonable assumption for σ that will lead to the Mauro–Yue–Ellison–Gupta–Allan (MYEGA) [6–9] equation. However, if one assumes for the heat capacity a more sophisticated temperature function, for instance, from Eq. (6) an expression appears

$$\log\eta = \log\eta_\infty + \left(\log\frac{\eta_g}{\eta_\infty}\right)\exp\left[-\frac{4c}{ZRT_g}\right]\ \left(\frac{T_g}{T}\right)^{\alpha}\exp\left(\frac{4c}{ZRT}\right) \tag{8}$$

that is quite similar in form to the MYEGA equation.

$$\log\eta = \log\eta_o + \left[\left(\log\frac{\eta_g}{\eta_o}\right)\exp[-(\alpha-1)]\right]\ \left(\frac{T_g}{T}\right)\ \exp\left[(\alpha-1)\frac{T_g}{T}\right] \tag{9}$$

3. Composition dependence of glass transition temperature T_g

As discovered by the Phoenicians, T_g can be dramatically changed by adding few impurities. The dependence of viscosity of silicate melts on chemical composition was briefly discussed in [5,10], although the expression for the glass transition temperature derived there was rather empirical. Here we will find the composition dependence of T_g within the framework of the AM model. In Ref. [5] we introduced the "lubricant" coefficient L, so that in the following the composition dependence of the glass transition temperature will be expressed as $T_g(L)$. The reason to use L is that the molar fraction, x, of the network modifiers, *NM*, is not sufficient to describe properly the T_g dependence on composition. The particular nature of *NM* determines to what extent the otherwise "rigid", oxygen bridges between network formers, *NF*, are modified to the "lubricated" state. Therefore, the specific role of each *NM* component is accounted for by a particular, "lubricant", coefficient $0 \le k_i \le 1$. It reflects to what extent this component plays a role of *NM*. It reflects the ability of the *NM* to modify the "rigid" oxygen bridge to a "floppy" one. Although the "lubricant" effect is similar to Dietzel's field strength, the two concepts are not absolutely identical. At the present state of art we introduce a rather empirical variable "lubricated fraction", $L_i = x_i k_i$. Thus, the lithium oxide is almost perfect modifier, so that $k_{Li_2O} = 1$. On the other hand MgO is not that effective. Therefore we assume that $k_{MgO} = 0.1$ so that only 10% of Mg plays a role of *NM*.

In analogy with the molar fraction, *x*, the "lubricant coefficient", *L*, can be defined as:

$$L = \sum L_i. \tag{10}$$

We discuss here a homologous series of silicates with no phase separation. The determination of the composition dependence of $T_g(L)$ is based on the assumption that at the glass transition temperature the entropy $S_g(L)$ is independent on composition. This hypothesis is based on Eq. (6). Indeed, the condition that the left hand side of this equation is 13 [dPa.s] (i.e. the glass transition point) requires that in the right hand side the condition

$$S - S_g = 0 \tag{11}$$

is fulfilled. Let S_g be the entropy $S_g(L_r)$ at the glass transition temperature $T_{g,r}$ of a reference composition L_r. For convenience, in the following we choose for the reference composition $0.1Li_2O.0.9SiO_2$ so that