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Abstract. In a recent paper the probability of forming a ring in vitreous B_2O_3 was evaluated using the stochastic matrix method, as a description of the growth process of a solid. In this work we generalize this method for the same substance introducing a probabilistic cut-off temperature and find a theoretical Vogel–Fulcher–Tamman-like equation for the average relaxation time (or viscosity) of the strong-glass-forming liquid. We take the average relaxation time to be inversely proportional to the probability of forming a ring, calculated for a large number of steps of growth. We also use the temperature derivative method to recognize the functional dependence of the relaxation time.

1. Introduction

Many liquids can be supercooled below their equilibrium melting points and solidified to the glassy state, provided that the cooling rate is fast enough to avoid crystallization. The most significant features on approaching glass transition are a rapid increase in the viscosity and a slowing down of the structural relaxation. It turns out that the relaxation patterns in different glass-forming liquids show several common features, such as the temperature dependence of the structural relaxation time τ usually well represented by the Vogel–Fulcher–Tamman (VFT) empirical equation

$$\tau = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right). \tag{1}$$

T_0 corresponds to the temperature at which τ is infinite, τ_0 is a reference relaxation time and D is a measure of the structural 'strength' of the system. The largest D ($D \approx 20$–100) values characterize liquids that are most resistant to temperature-induced changes. These liquids display a nearly Arrhenius behaviour and are referred to as 'strong' [1]. To this group belong covalent bonded network glass formers like SiO_2 ($D = 100$) [1] and B_2O_3 ($D = 35$) [2]. At the other extreme are the 'fragile' glasses, i.e. those systems with the smallest D values ($D \approx 3$–5), exhibiting the most rapid changes of τ in the supercooled region. In fragile systems

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dramatic changes of τ in the transition range imply that T_0 is close to T_g while for strong glasses T_0 is far below T_g ($T_g/T_0 \approx 2$ for B_2O_3), T_g being the glass transition temperature.

Another characteristic of the dynamics at the glass transition is the non-exponential time decay of the structural relaxation function $\phi(t)$. It is commonly expressed by the stretched exponential function

$$\phi(t) = A \exp[-(t/\tau_{KWW})^{\beta_{KWW}}]. \tag{2}$$

Experimental findings suggest that the smaller the stretching parameter β_{KWWW} is, the more fragile is the system [3–5]. However, there are recent indications of a more complicated time decay of the relaxation function than that stated by equation (2). Investigations of various fragile glass formers show a two-step behaviour, including a fast process, generally in the picosecond regime, which precedes the main so-called α-relaxation [6–12].

In the case of B_2O_3 the stretching parameter β_{KWW} obtained in this fit is found to increase slightly with temperature, from 0.6 close to T_g (526 K) to about 0.8 at the highest temperature of observation, which is also in agreement with previous measurements of the α-process [13–15]. As T_g is approached, the rapidly increasing time scale of the α-relaxation makes it difficult to detect $\phi(t)$ by photon correlation spectroscopy (PCS). Even though the spectra display only the initial part of the α-process and the final decay towards the base line is not observed, a stretched exponential fits the curves well in the limited range $10^{-2} < t < 10^2$ s and with a stretching parameter β_{KWW} similar to that found at higher temperatures. More interesting is that the short duration of the correlation function ($<10^{-2}$ s) deviates from the functional form of equation (2). This implies that some other relaxation process occurs over a considerably shorter time scale than the α-process [16]. The effect is so sharp that about half of the decay occurs in a time less than that which can be measured by PCS. Indeed the correlation function decays to about $\phi(t) = 0.5$ at very small times ($\sim 10^{-6}$ s). Therefore only the tail of the faster process can be observed, which mainly relaxes at times $<10^{-6}$ s. No temperature dependence of τ was noted for the faster process in the range 506–543 K where it was observed.

From a theoretical point of view, many efforts have been made towards elucidating the temperature dependence of τ and other properties of liquid glass formers. In a recent theoretical work, Barrio *et al* [17] used a statistical model in which the stochastic matrix method (SMM) was applied to find the fraction of boron atoms belonging to boroxol rings in a boron oxide (B_2O_3) glass. They evaluated the characteristic energies related to the formation of a single B–O–B unit in an oxygen bridge or in a boroxol ring and the probability of forming a ring. The model also gave a reasonable qualitative prediction for a characteristic exponent ruling the growth of microclusters.

In a recent article [18] we derived a theoretical Arrhenius equation for the average relaxation time (or viscosity) of the strong-glass-forming liquid B_2O_3 using the SMM. The main idea is to take the average relaxation time as inversely proportional to the probability of forming a ring, calculated for a large number of growth steps. To identify the type of equation that was obtained for the average relaxation time, we used the method of temperature derivatives [19, 20]. This method rests on the idea of investigating the structure of expressions $d^n \log x/dT^n$ and $d \log x/d(1/T)$ ($n = 1, 2$) to reduce the number of fit parameters and linearize both the VFT and Arrhenius equations.

The purpose of this work is to generalize the SMM by introducing an Arrhenius probabilistic cut temperature and to show that this generalization leads to a non-Arrhenius form for the relaxation time, as well as to a physical interpretation of significant parameters which is related to the topology of growth of boroxol rings. The paper is divided as follows. In section 2 we present the generalization of the SMM. In section 3 we use the results obtained

in section 2 to study the relaxation time for B_2O_3 and, finally, in section 4 we conclude with some remarks on the nature of these results.

2. Generalization of the SMM and theoretical framework for the VFT equation

Through the SMM it is possible to describe the growth process of a solid [17]. In this method such a process can be described by a matrix acting on a vector. The matrix components define the statistical weights of the transitions resulting in the corresponding transformation of sites. The vector components represent the probabilities of finding a given site on the rim of such a cluster. The matrix is used to transform this vector into a new one after adding one atom to the cluster. Transformation of the rim depends on the site to which the new atom sticks. Each sticking process has a certain probability of occurring, so that the matrix elements contain the probabilities of transforming each kind of site into others. The probability factors must include two contributions. (1) The statistical weight for each process, that is the number of ways leading to the same final result and (2) the Boltzmann factor taking into account the energy barrier necessary to form a certain kind of bond. The probability of sticking a new unit to the bulk is taken to be proportional to $\exp(-E_m/k_BT)$, where E_m is the energy cost of sticking a unit in the m form at temperature T and k_B is the Boltzmann constant. It is important to note that, according to this assumption, it is possible to stick a unit at every temperature T. Nevertheless, it would be much more physically meanngful if a temperature T' is introduced into the Boltzmann factor such that, for $T = T'$, the probability of sticking a unit in the bulk is equal to zero. This argument can be supported because at some temperature below T_g the glass system is unable to displace any unit for possible attachment to the bulk. Thus by introducing this probabilistic cut-off temperature we may generalize the SMM so that the probability of sticking a new unit at the rim is proportional to $\exp(-E_m/k_B(T - T'))$. Clearly if we set $T' = 0$ the results obtained in the previous calculation are recovered.

To identify T' as a physical property of the system we next calculate the relaxation time for the growth system using the SMM and the generalization described above. To do this we proceed as follows. We first take the average relaxation time to be inversely proportional to the probability of forming a ring. Next, we identify the form of the relaxation equation by appealing to the temperature derivative method. Finally we compare the resulting equation with that used to reproduce the experimental data. We therefore begin with the SMM according to which the probability for an average transition can be written as $P(\xi)$ where $\xi = \exp(\Delta E/k(T - T'))$ and ΔE is the difference between two E'_m at temperatures T and T' respectively. If

$$\tau \propto 1/P(\xi) \tag{3}$$

and we use the method of temperature derivatives to linearize equation (3) we get

$$\left(\frac{\mathrm{d}\ln\tau^{-1}}{\mathrm{d}T}\right)^{-1/2} = \left(\frac{\Delta E}{k_B}\right)^{-1/2}\left(\xi\frac{\mathrm{d}\ln P(\xi)}{\mathrm{d}\xi}\right)^{-1/2}(T - T'). \tag{4}$$

For typical activation energies the temperature dependence of $P(\xi)$ can be neglected and the second factor of equation (4) reduces to a constant so that integrating yields a VFT-like equation. Thus, T' can be identified as T_0 and if $T_0 = 0$ the Arrhenius equation is obtained. It is important to note that in this theoretical context, T_0 is interpreted not only as the temperature that yields an infinite relaxation time, but it also is the temperature at which the probability of sticking a unit into the bulk of the glass system is zero.

3. Non-Arrhenius equation for the α-relaxation time

3.1. B_2O_3 as an example

In this section we wish to derive the viscosity of B_2O_3 using the results obtained in the last section, as well as the probability of forming a ring of B_2O_3. To do this we proceed in exactly the same way as in the derivation of equation (4). We obtain the probability of forming a ring when passing from the jth layer to the $(j + 1)$th layer by simply given by counting the proportion of rings that were formed between step j and step $j + 1$. If we calculate this for a large number of steps of growth, P_B^j can be replaced by its limiting value. According to Barrio *et al* [17] for B_2O_3 this is given by

$$P_B^\infty = \frac{24\xi^2 + 16\xi}{84\xi^2 + 107\xi + 25}. \tag{5}$$

According to our second assumption, we can now identify the transition probability as the probability of forming a ring in B_2O_3. Furthermore, since the viscosity is proportional to the relaxation time (τ), and the α-relaxation time is inversely proportional to the average transition probability, then

$$\tau \propto \frac{1}{P_B^\infty} = \frac{84\xi^2 + 107\xi + 25}{24\xi^2 + 16\xi}. \tag{6}$$

Taking the derivatives $d^n \log x/dT^n$, $d \log x/d(1/T)$ ($n = 1, 2$) of equation (6) where $x = \tau$, we find that

$$\left(\frac{d\ln(P_B^\infty)}{dT}\right)^{-1/2} = (T - T_0) \left(\frac{E_2 - E_1}{k_B}\right)^{-1/2} L_{B_2O_3}^{-1/2} \tag{7}$$

$$\left(-\frac{d\ln(P_B^\infty)}{dT^{-1}}\right)^{-1/2} = \left(1 - \frac{T_0}{T}\right)\left(\frac{E_2 - E_1}{k_B}\right)^{-1/2} L_{B_2O_3}^{-1/2} \tag{8}$$

where

$$L_{B_2O_3} \equiv \left(\xi \frac{d\ln P(\xi)}{d\xi}\right) = \frac{48\xi^2 + 16\xi}{24\xi^2 + 16\xi} - \frac{168\xi^2 + 107\xi}{84\xi^2 + 107\xi + 25}. \tag{9}$$

Taking typical values for the activation energy as quoted in reference [18], we know that for $\tau \ll 1$ and $L_{B_2O_3} \approx 1$ the temperature dependence of $L_{B_2O_3}$ can also be neglected so that equations (7) and (8) can be written as:

$$\left(\frac{d\log(P_B^\infty)}{dT}\right)^{-1/2} = (T - T_0)\left(\frac{E_2 - E_1}{k_B}\right)^{-1/2} \tag{7a}$$

and

$$\left(-\frac{d\log(P_B^\infty)}{dT^{-1}}\right)^{-1/2} = \left(1 - \frac{T_0}{T}\right)\left(\frac{E_2 - E_1}{k_B}\right)^{-1/2}. \tag{8a}$$

From equation (6) we can also calculate $\Theta(x) \equiv [d\ln(x)/dT]/[d^2 \ln(x)/dT^2]$ and if $L_{B_2O_3}$ is a constant we obtain

$$\Theta(x) = -(T - T_0)/2. \tag{10}$$

If equations (7a), (8a) and (10) are integrated, a theoretical VFT-like equation is obtained, namely

$$\tau = \tau_0 \exp\left(\frac{E_2 - E_1}{k_B(T - T_0)}\right) = \tau_0 \exp\left(\frac{DT_0}{T - T_0}\right) \tag{11}$$

where the constant τ_0 is the pre-exponential factor and D is a constant equal to $[(E_2-E_1)/T_0 k_B]$ that can be determined by comparing it with the experimental VFT equation. Equation (11) is the main result of this paper. Comparing the experimental values obtained from the VFT equation with equation (11), values for E_2-E_1 can be calculated (see table 1).

Table 1. In the first and second columns experimental parameters used to fit the VFT equation are shown, taken from references [16] and [21]. In the third column the values obtained for E_2-E_1 from equation (11) are given.

Experimental data D	Experimental data T_0 (K)	Calculated by equation (11) E_2-E_1 (kcal mol^{-1})	Ref.
35	266	18.207	[16]
7.69	445	6.79	[21]

To reproduce the experimental data obtained using equation (11) for B_2O_3 we take $D \approx 35$, $T_0 \approx T_g/2$ [16] and $\tau(T_g) = 10^{13}$ Poise to calculate τ_0. With these values we can also calculate the activation energy at T_g, finding that $E_2-E_1 = 18.207$ kcal mol^{-1}.

3.2. Physical interpretation of the $L_{B_2O_3}$ function

In this section we discuss the physical interpretation of $L_{B_2O_3}$. This can be achieved by calculating the relaxation time using the fact that its value is proportional to the probability of assembling two rings linked by a bridge. To do this we proceed as follows. Starting with the SMM we calculate the probability of forming two rings in B_2O_3 linked by an oxygen bridge. With this probability we can calculate the relaxation time if the transition probability is associated with the form of this structure.

For B_2O_3, inspection of the possible configurations which may occur at the rim of the clusters resulting from the agglomeration of the boron–oxygen singlets $(B(O_{1/2})_3)$ shows that whenever a new singlet comes close to the rim, it can attach itself to one of the sites presenting free valence ions; it may encounter one of six situations. Barrio *et al* [17] denote these configurations by x, y, z, t, u and w, with x meaning an isolated singlet at the rim with only one free valence ion available, y corresponding to a singlet at the rim with two free valence ions available, z denoting two singlets in a chain with three valence ions, and finally t corresponding to three singlets in a chain. The termination u corresponds to a free bond of a boron atom trapped in a ring, while the w termination corresponds to two valence ions of two different boron atoms trapped in the same ring. Then the factors $P(x, x)$, $P(x, y)$, ... that define the statistical weights of the transitions resulting in the corresponding transformations of sites can be displayed as a 6×6 matrix, namely

$$\begin{bmatrix} 0 & 0 & 0 & P(t, x) & 0 & 0 \\ P(x, y) & 0 & P(z, y) & P(t, y) & P(u, y) & P(w, y) \\ 0 & P(y, z) & 0 & P(t, z) & 0 & 0 \\ 0 & 0 & P(z, t) & 0 & 0 & 0 \\ 0 & 0 & 0 & P(t, u) & 0 & P(w, u) \\ 0 & 0 & P(z, w) & P(t, w) & 0 & 0 \end{bmatrix}. \tag{12}$$

After normalization, the stochastic matrix that transforms the probability of finding one configuration at the rim of a cluster $(P_x, P_y, P_z, P_t, P_u, P_w)$ into a new set of probabilities $(P'_x, P'_y, P'_z, P'_t, P'_u, P'_w)$ after an entire new layer of atoms has grown, with one new atom at each

available site, is given by [17]

$$
\begin{bmatrix}
0 & 0 & 0 & \dfrac{1+4\xi}{5+12\xi} & 0 & 0 \\[2mm]
1 & 0 & \dfrac{1}{2+2\xi} & \dfrac{3+2\xi}{5+12\xi} & 1 & \dfrac{1}{2} \\[2mm]
0 & 1 & 0 & \dfrac{1}{5+12\xi} & 0 & 0 \\[2mm]
0 & 0 & \dfrac{1}{2+2\xi} & 0 & 0 & 0 \\[2mm]
0 & 0 & 0 & \dfrac{2\xi}{5+12\xi} & 0 & \dfrac{1}{2} \\[2mm]
0 & 0 & \dfrac{2}{2+2\xi} & \dfrac{4\xi}{5+12\xi} & 0 & 0
\end{bmatrix}.
\tag{13}
$$

Using the above matrix, the growth of a cluster is modelled by the successive application of the matrix to an arbitrary initial vector v_0. Thus, the evolution of the probabilities at the rim after j steps is given by $v_j = \mathbf{M}^j v_0$. If $\mathbf{M}$ has only one eigenvalue 1 in the limit of large j, v_j for B_2O_3 is given by

$$
v_j = \begin{pmatrix} P_x^\infty \\ P_y^\infty \\ P_z^\infty \\ P_t^\infty \\ P_u^\infty \\ P_w^\infty \end{pmatrix} = \frac{1}{84\xi + 107\xi + 25} \begin{pmatrix} 1+4\xi \\ 24\xi^2 + 34\xi + 9 \\ 24\xi^2 + 34\xi + 10 \\ 12\xi + 5 \\ 3\xi(4\xi + 3) \\ 2\xi(12\xi + 7) \end{pmatrix}.
\tag{14}
$$

As stated above the probability of forming a ring when passing from the jth layer to the $(j+1)$th layer is given by counting the number of rings that were formed between step j and the step $j+1$. This information is encoded in the matrix as the probability of the processes $z_j \to w_{j+1}$ and $t_j \to u_{j+1}$, w_{j+1}, $P_B^j(T) = P_{z_j}(M_{63}) + P_{t_j}(M_{54} + M_{64})$ where M_{ij} are the respective i j elements of the matrix $\mathbf{M}$, so,

$$
P_B^j = \frac{\xi(24\xi + 16)}{84\xi^2 + 107\xi + 25}.
\tag{15}
$$

To calculate the probability of forming two rings in B_2O_3 linked by an oxygen (y) bridge it is important to note that in equation (15) the two forms of rings, u and w, are present. To calculate this probability we need to count the probability of forming bridges before a ring is formed, and then the probability of forming a ring before the ring itself with the bridge is formed. The u rings are given by $P_{t_j} M_{54}$ and all of them, in the next step to stick a unit, give an oxygen bridge (y-site), see matrix (12). The w rings are given by $P_{z_j} M_{63} + P_{t_j} M_{64}$ and half of them give a bridge before a unit is attached (see matrix (12)). Therefore the probability of finding a ring with an oxygen bridge is given by $P_{t_j} M_{54} + 1/2(P_{z_j} M_{63} + P_{t_j} M_{64})$. Focusing our attention on matrix (12), we note that starting with y (the y before a ring) to add the next ring there is only one way—to go beyond $P(y,z)$ to $P(z,w)$. All the y give a z before sticking a unit and we then have a probability equal to one to have this transition. But the probability to form a ring before the z is given by M_{63}, so we have $P_{2B}^\infty = 1/2M_{63}[P_{t_j} M_{54} + 1/2(P_{z_j} M_{63} + P_{t_j} M_{64})]$, where the factor of one half is added because we have two rings linked together. Finally

$$
P_{2B}^\infty = \frac{12\xi^3 + 9\xi^2}{(2 + 2\xi)(84\xi^2 + 107\xi + 25)}.
\tag{16}
$$

If, as noted above, the glass transition for B_2O_3 corresponds to the temperature at which rapid breakdown of two boroxol rings linked by an oxygen bridge first occurs and if the

relaxation time is inversely proportional to the average transition probability, using the method described in section 3.1 we find that

$$\left(\frac{\mathrm{d}\ln(P_B^\infty)}{\mathrm{d}T}\right)^{-1/2} = (T - T_0)\left(\frac{E_2 - E_1}{k_B}\right)^{-1/2} L_{2B_2O_3}^{-1/2} \tag{17}$$

$$\left(-\frac{\mathrm{d}\ln(P_B^\infty)}{\mathrm{d}T^{-1}}\right)^{-1/2} = \left(1 - \frac{T_0}{T}\right)\left(\frac{E_2 - E_1}{k_B}\right)^{-1/2} L_{2B_2O_3}^{-1/2} \tag{18}$$

where

$$L_{2B_2O_3} \equiv \left(\xi\frac{\mathrm{d}\ln P(\xi)}{\mathrm{d}\xi}\right) = \frac{36\xi^2 + 18\xi}{12\xi^2 + 9\xi} - \frac{\xi}{1 + \xi} - \frac{168\xi^2 + 107\xi}{84\xi^2 + 107\xi + 25}.$$

Taking typical values for the activation energy for B_2O_3, $\xi \ll 1$ and $L_{2B_2O_3} \approx 2$. On the other hand, when we calculate the probability of a transition corresponding to the formation of a single ring, $L_{B_2O_3} \approx 1$ [18], so with the previous result we conclude that $L_{2B_2O_3}$ contains information on how many rings are involved in the glass transition. Equations (17) and (18) can be rewritten in the following form:

$$\left(\frac{\mathrm{d}\log(P_B^\infty)}{\mathrm{d}T}\right)^{-1/2} = (T - T_2)\left(2\frac{(E_2 - E_1)}{k_B}\right)^{-1/2} \tag{17a}$$

and

$$\left(-\frac{\mathrm{d}\log(P_B^\infty)}{\mathrm{d}T^{-1}}\right)^{-1/2} = \left(1 - \frac{T_0}{T}\right)\left(2\frac{(E_2 - E_1)}{k_B}\right)^{-1/2} \tag{18a}$$

which, when integrated, lead directly to VFT-like equations.

Having a physical interpretation of $L_{2B_2O_3}$, equation (11) can be generalized to n rings giving

$$\tau = \tau_0 \exp\left(n\frac{E_2 - E_1}{k_B(T - T_0)}\right). \tag{19}$$

The importance of equation (19) relies on the fact that comparing this equation with the experimental expression for the relaxation time (equation (1)), the minimum number of rings needed for the glass transition is obtained as

$$n = Dk_BT_0/(E_2 - E_1). \tag{20}$$

Experimentally, for B_2O_3, it is known that $D \approx 35$ and $T_0 \approx 1/2T_g \approx 262$ [16]. Snyder [22] estimated ΔE to be 6.0 kcal mol^{-1}, on the basis of *ab initio* quantum mechanical calculations. Inserting these values into equation (20) gives that the minimum number of rings linked by oxygen bridges needed for the B_2O_3 glass transition is of the order of three. An activation energy of 6.4 ± 0.4 kcal mol^{-1} was obtained experimentally for B_2O_3 [21]; this number agrees well with the experimental value of ΔE used here.

4. Concluding remarks

In this work we have obtained a theoretical VFT-like equation for the average relaxation time (or viscosity) of the strong-glass-forming liquid B_2O_3 using the generalized stochastic matrix method. To generalize the SMM we introduced a probabilistic cut-off temperature (T'). This temperature was introduced because we assume that below some temperature the growth process cannot take place. Starting from these assumptions a non-Arrhenius form for the relaxation time was obtained. Comparing the theoretical expression for the relaxation time with the experimental one, we find that this probabilistic cut-off temperature corresponds to

T_0, the temperature at which the viscosity is infinite according to the VFT equation. This theoretical framework allows for an interpretation of non-Arrhenius behaviour. In fact, if the system has a probabilistic cut-off temperature we can expect a non-Arrhenius relaxation time; if not, it exhibits an ARR behaviour.

To determine an expression for the relaxation time with the generalized SMM we took the transition probability as the probability of forming a ring calculated for a large number of steps of growth; this probability was obtained form the SMM. To identify an equation for the average relaxation time we used the method of temperature derivatives and an VFT-like equation was obtained (equation (11)). For this equation three parameters remain to be determined, τ_0, D and T_0, and a comparison with experiment provided us with these values.

A physical interpretation of $L_{2B_2O_3}$ was also discussed. This result, and the value for the activation energy, allowed us to predict the number of rings that are expected to be present in a glass transition. For B_2O_3 we found that the minimum number of rings linked by oxygen bridges is three if E_2-E_1 is taken from *ab initio* quantum mechanical calculations or from experimental data.

Moreover, the results of this paper may also be extended to other strong glass formers, if the glassy state can be associated with the probability of assembling ring structures. Most of the ideas and methods presented in this article can be applied to dendritic systems like As_xSe_{1-x}, Ge_xSe_{1-x}, $Ge_xSb_{15}Se_{85-x}$, etc, the results of which will be dealt with in forthcoming papers.

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