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Abstract. Open network liquids like B_2O_3 show an Arrhenius variation of the viscosity (or structural relaxation time) between T_g and the high-temperature limit, and provide the 'strong' liquid extreme of the pattern. 'Fragile' liquids have quite non-Arrhenius relaxation properties and typically consist of molecules interacting through nondirectional, noncovalent interaction. This strong/fragile liquid pattern has been used as the basis for a classification of glass forming liquids to indicate the sensitivity of the liquid structure to temperature changes. In a recent paper Barrio *et al* evaluated the probability of forming a ring in vitreous B_2O_3 by the stochastic matrix method which is a description of the growth process of a solid. In this work we find a theoretical Arrhenius equation for the average relaxation time (or viscosity) of the strong glass forming liquid B_2O_3 using the stochastic matrix method proposed by these authors. To carry out our purpose we take the average relaxation time as inversely proportional to the average transition probability and the transition probability as the probability of forming a ring calculated for a large number of steps of growth. We also introduce the temperature derivative method to recognize the functional dependence for the viscosity.

1. Introduction

The transition from a liquid to a glass is characterized by an enormous increase of the viscosity and the related structural relaxation time. As the glass transition is approached from the liquid state the viscosity changes by some 15 orders of magnitude and the relaxation time rises from picoseconds to some hundreds of seconds at which the system appears solid for most experimental time scales [1].

The viscosity of B_2O_3, GeO_2, SiO_2 etc has been shown to exhibit an almost Arrhenius dependence while the viscosity and rotation times for *o*-terphenyl, glucose [2] etc are quite non-Arrhenius. On the basis of this property and others, supercooled liquids have been classified as strong or fragile [3]. *Strong* liquids (e.g., B_2O_3) show Arrhenius (ARR) relaxation processes and typically have a three-dimensional network structure of covalent bonds. *Fragile* liquids (e.g., *o*-terphenyl) have quite non-Arrhenius relaxation properties and typically consist of molecules interacting through nondirectional, noncovalent interaction (e.g., dispersion forces).

The Vogel–Fulcher–Tamann (VFT) equation was formulated several decades ago [4–6] to describe the behaviour of the viscosity and the relaxation time of a supercooled liquid as it approaches its glass temperature T_g, namely,

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

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where τ_0 is a reference relaxation time and B and T_0 are two independent parameters taken to be nonnegative. The VFT equation has turned out to be of practical importance for quantifying the deviation from ARR ($T_0 = 0$ in equation (1)) behaviour, yet no rigorous theoretical basis has been established to date [7].

In recent papers Stickel *et al* [7, 8] compare in detail the temperature dependence of f_{max} (the loss peak of dielectric data), σ_{dc} (dc conductivity) and η (viscosity) for a series of glass forming liquids. In order to reveal the fine details of the $\log(x)$ data ($x = f_{max}$ (Hz), $\sigma_{dc}\varepsilon_0^{-1}$ (s^{-1}), η^{-1} (Poise^{-1})) as a function of temperature, they employ the method of temperature derivatives. The method rests on focusing on the expressions $d^n \log x/dT^n$ and $d^n \log x/d(1/T)^n$ ($n = 1, 2$) which reduce the number of remaining fit parameters and linearize certain model functions. For instance, the VFT and ARR laws can be linearized by

$$[d \log x/dT]^{-1/2} = (T - T_0)B^{-1/2} \tag{2}$$

where $T_0 = 0$ for the ARR dependence. The analogous expression on a $1/T$ scale again linearizes the VFT case but transforms the ARR case into a constant,

$$[-d \log x/d(1/T)]^{-1/2} = (1 - T_0/T)B^{-1/2}. \tag{3}$$

They also define $\Theta(x)$ as the ratio of the first and second derivatives and for the VFT function,

$$\Theta(x) \equiv [d \log(x)/dT]/[d^2 \log(x)/dT^2] = -(T - T_0)/2 \tag{4}$$

which gives direct access to the Vogel temperature T_0. In the case of simple activated behaviour (ARR) it reduces to $\Theta(x) = -T/2$, namely, no fit parameters remain. Such a plot of $\Theta(x)$ against T is obviously extremely sensitive to qualitative changes in the temperature dependence of the $x(T)$ data, so that characteristic temperatures can be easily identified.

From the theoretical point of view, many efforts have been made in elucidating the temperature dependence of τ and other properties from the liquid glass formers. In a recent theoretical work Barrio *et al* [9] used a statistical model in which the stochastic matrix method is applied to find the fraction of boron atoms belonging to boroxol rings in a boron oxide (B$_2$O$_3$) 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 gives a reasonable qualitative prediction for a characteristic exponent ruling the growth of microclusters, which may in turn be related to the specific volume.

The purpose of this work is to find for the B$_2$O$_3$ a theoretical Arrhenius dependence for the viscosity using the results obtained from Barrio *et al*. In section 2 we summarize the main features of the stochastic matrix method. In section 3, we present our results and their comparison with experiment through the experimental ARR equation. Finally, in section 4 we give some remarks on the nature of these results.

2. The stochastic description of the growth process for the B$_2$O$_3$ glass

In their paper Barrio *et al* [9] evaluated the concentration of boroxol rings in vitreous B$_2$O$_3$ by the stochastic matrix method introduced by Kerner [10], which is a description of the growth process of a solid. At each particular stage of the evolution of the growth of a solid, they divided the growth into two parts: the rim (or the border), composed of all of the entities that offer a potential possibility for a new entity of stick and agglomerate, and the bulk (or the interior) that is, all of the units that have saturated all their bonds.

The process of growth at the rim can be described by a matrix acting on a vector. The matrix components are the probabilities of finding a given site at the rim of a cluster of a certain size. The vector components represent the probabilities of finding a given site on the rim of

a cluster. The matrix transforms this vector into a new one, because the rim is changed after adding one atom to the cluster. The transformation of the rim depends on the site on 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 should 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 of forming a certain kind of bond.

The authors apply these ideas to the B_2O_3 continuous network. The elementary unit, dictated by the bond chemistry, is a triangle $B(O_{1/2})_3$, which they call a 'singlet'. Two singlets can be connected only using one bond to form a 'doublet'. They assume that the energy cost to form this bonding is E_1. After a doublet is produced, two situations can occur if a new singlet is added: the newly arriving singlet forms a longer chain (a 'triplet') or it can close a ring, with a different energetic cost (E_2), since one has to deform the bridge angles on a ring. The agglomeration process occurs at a given temperature T, at which the individual bonds reach equilibrium. With this ideas in mind they can write the matrix (M) modelling the growth of clusters by a successive application on an arbitrary initial vector v_0. Thus the evolution of the probabilities on the rim after j steps is given by $v_j = M^j v_0$. They also derive an expression for the probability of forming a ring (P_B^j) before many steps, obtained by counting the proportion of ring that were formed during the process.

The final configuration depends only on the eigenvectors of the stochastic matrix. It is easy to prove that a matrix with all the columns normalized to one has at least one eigenvalue equal to one, while the others can be real, complex or imaginary, depending on the values of the parameters involved. Only eigenvectors with norm one remain after many successive applications of the stochastic matrix. If one assumes that M has only one such eigenvalue ($\lambda_1 = 1$), with eigenvector e_1, then, in the limit of large j, v_j converges to this eigenvector, independently of the initial conditions.

As a consequence, the evolution of the rim attains a stable statistical regime after successive steps of growth and this regime is governed solely by the statistics represented by the eigenvector with eigenvalue one. Barrio *et al* found for the (B_2O_3) that the eigenvector is

$$e_1 = \frac{1}{84\xi^2 + 107\xi + 25} \begin{pmatrix} 1 + 4\xi \\ 24\xi^2 + 34\xi + 9 \\ 24\xi^2 + 34\xi + 10 \\ 12\xi + 5 \\ 3\xi(4\xi + 3) \\ 2\xi(12\xi + 7) \end{pmatrix}.$$

In this model the only free parameter is ξ, the excess free energy used when closing a ring, and is written as $(E_1 - E_2) = kT \ln(\xi) = F$.

3. Results and comparison with experiment

In this paper we wish to show that, using the probability of forming a ring for B_2O_3 obtained from the stochastic method, we can derive the Arrhenius dependence for the viscosity. To do this we proceed as follows. First we identify the average transition probability with the average transition probability of forming a ring for B_2O_3 and, then, we apply the method of temperature derivative obtained the form of the relaxation time.

The probability of forming a ring when passing from the jth layer to the $(j + 1)$th one is simply given by counting the proportion of rings that were formed between the step j and the

step $j + 1$. If we calculate for a large number of steps of growth, P_B^j can be replaced by its limiting value and for B_2O_3 Barrio *et al* found that

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

Raman intensity data for molten B_2O_3 indicate [11] that BO_3 triangles in boroxol rings are favoured energetically over BO_3 triangles in a random network. The intensity data also suggests that the glass transition for B_2O_3 corresponds to the temperature at which rapid breakdown of boroxol rings first occurs. Therefore the transition probability is the probability of forming a ring for the B_2O_3. Indeed, since the viscosity is proportional to the relaxation time (τ), and the relaxation time is inversely proportional to the average transition probability, then

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

Taking the derivatives $\mathrm{d}^n \log x/\mathrm{d}T^n$, $\mathrm{d}^n \log x/\mathrm{d}(1/T)^n$ ($n = 1, 2$) of equation (6) ($x = f_{max}$ (Hz), $\sigma_{dc}\varepsilon_0^{-1}$ (s^{-1}), η^{-1} (Poise^{-1})), we find that

$$\left[\frac{\mathrm{d}\log(P_B^\infty)}{\mathrm{d}T}\right]^{-1/2} = T\left[\frac{(E_2 - E_1)}{k_B}\right]^{-1/2} L_{B_2O_3}^{-1/2} \tag{7}$$

$$\left[-\frac{\mathrm{d}\log(P_B^\infty)}{\mathrm{d}(1/T)}\right]^{-1/2} = \left[\frac{(E_2 - E_1)}{k_B}\right]^{-1/2} L_{B_2O_3}^{-1/2} \tag{8}$$

where

$$L_{B_2O_3} \equiv \frac{48\xi^2 + 16\xi}{24\xi^2 + 16\xi} - \frac{168\xi^2 + 107\xi}{84\xi^2 + 107\xi + 25}. \tag{9}$$

The values of and $L_{B_2O_3}$ for ξ different activation energies are given in table 1.

For boron trioxide, B_2O_3, Macedo and Litovitz [12] measured the longitudinal ultrasonic relaxation and found that above 800 °C the shear viscosity exhibits an Arrhenius temperature dependence and a single relaxation time for the shear relaxation process. The longitudinal relaxation is a mixture of shear and compressional processes [13]. They consider the shear relaxation time and the adiabatic constant volume compressional relaxation time to be approximately equal. Then, their common relaxation time data obey the Arrhenius temperature dependence: $\tau = 7.24 \times 10^{-12} \exp(8750K/T)$ s. Tauke *et al* [14] measured the ultrasonic shear and longitudinal relaxation in B_2O_3 and confirmed the earlier result. Above 800 °C they found that the shear relaxation spectrum is single and the relaxation time follows an Arrhenius law with the same slope as the measured shear viscosity, as one would expect from the relation $\eta = \tau G_\infty$. Most oxide glasses show a decreasing activation energy of viscous flow with increasing temperature, and indeed for B_2O_3 the activation energy varies from 83 to 12 kcal mol^{-1} between 26 and 1300 °C [15].

Taking the typical values for the activation energy as shown in table 1, $\xi \ll 1$ and $L_{B_2O_3} \approx 1$ so that equations (7) and (8) can be written in the following form:

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

and

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

Also we can calculate $\Theta(x)$, and if $L_{B_2O_3}$ is a constant, starting with equation (6) we obtain

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

Table 1. The values for $L_{B_2O_3}$ given by equation (9) and ξ for different temperatures and different activation energies. To obtain the values we take typical activation energies for the B_2O_3 (from $E_2 - E_1 = 12\,\text{kcal mol}^{-1}$ to $E_2 - E_1 = 83\,\text{kcal mol}^{-1}$). It is clear that the temperature dependence of $L_{B_2O_3}$ can be neglected. In fact the range of validity for equations (7a), (8a) and (11) should be inferred from the experimental data, not from equation (9) because for all the values of the activation energy, and for the respective range of temperatures its value is approximately equal to one.

T (K)	$\xi_1 = \exp\left(\frac{-15\,\text{kcal mol}^{-1}}{k_B T}\right)$	$L_{B_2O_3}$ (ξ_1)	$\xi_2 = \exp\left(\frac{-40\,\text{kcal mol}^{-1}}{k_B T}\right)$	$L_{B_2O_3}$ (ξ_2)	$\xi_3 = \exp\left(\frac{-80\,\text{kcal mol}^{-1}}{k_B T}\right)$	$L_{B_2O_3}$ (ξ_3)
100	3.3×10^{-34}	1	5.31×10^{-90}	1	2.82×10^{-179}	1
200	2.69×10^{-17}	1	6.51×10^{-45}	1	4.24×10^{-89}	1
300	9.78×10^{-12}	1	4.37×10^{-30}	1	1.91×10^{-59}	1
400	5.71×10^{-9}	0.99	1.04×10^{-22}	1	1.08×10^{-44}	1
500	2.28×10^{-7}	0.99	2.70×10^{-18}	1	7.31×10^{-36}	1
600	3.26×10^{-6}	0.99	2.34×10^{-15}	1	5.48×10^{-30}	1
700	1.99×10^{-5}	0.99	2.92×10^{-13}	1	8.54×10^{-26}	1
800	7.73×10^{-5}	0.99	1.08×10^{-11}	1	1.18×10^{-22}	1
900	2.22×10^{-4}	0.99	1.80×10^{-10}	1	3.27×10^{-20}	1
1000	5.15×10^{-4}	0.99	1.71×10^{-9}	1	2.93×10^{-18}	1
1100	1.02×10^{-3}	0.99	1.07×10^{-8}	0.99	1.15×10^{-16}	1
1200	1.82×10^{-3}	0.99	4.97×10^{-8}	0.99	2.47×10^{-15}	1
1300	2.966×10^{-3}	0.99	1.81×10^{-7}	0.99	3.30×10^{-14}	1
1400	4.49×10^{-3}	0.99	5351×10^{-7}	0.99	3.04×10^{-13}	1
1500	6.45×10^{-3}	0.99	1.44×10^{-6}	0.99	2.08×10^{-12}	1

If the equations (7a), (8a) and (10) are integrated the Arrhenius equations is obtained, namely

$$\eta = \eta_0 \exp\left(\frac{E_2 - E_1}{k_B T}\right) = \eta_0 \exp\left(\frac{B}{T}\right) \tag{11}$$

where the constant η_0 is the pre-exponential factor and B is a constant $((E_2 - E_1)/k_B)$ that can be determined comparing with the experimental data for the activation energy. The equation (11) is the main result of this paper. Notice should be made of the fact that although $\xi = \exp(-(E_2 - E_1)/k_B)$ is a small number, $\eta \sim \xi^{-1}$ is not. Further, the constant η_0 in (11) may be obtained from a plot of η against $1/T$. Therefore the two unknown parameters in this equation may be obtained from the experiment. Hence, starting with a simple model the stochastic matrix method and taking the relaxation time or the viscosity proportional to the probability of forming a ring, we obtain the Arrhenius equation for the viscosity with two unknown parameters, B and η_0.

4. Concluding remarks

In this work we obtain a theoretical Arrhenius equation for the average relaxation time (or viscosity) of the strong glass forming liquid B_2O_3 using the stochastic matrix method proposed by Barrio *et al* [9]. To do this we take the average relaxation time as inversely proportional to the average transition probability and the transition probability as the probability of forming a ring calculated for a large number of steps of growth. To identify the equation that we obtain for the average relaxation time we used the method of temperature derivation. The method rests on focusing on the expressions $d^n \log x / dT^n$ and $d^n \log x / d(1/T)^n$ ($n = 1, 2$) which reduce the number of fit parameters and linearize certain model functions. When an Arrhenius equation is found two parameters remain to be determined, η_0 and B. Comparison with the

experiment provides us with these values.

The relevance of the method proposed in this work is based on the method of temperature derivation to identify the form of the equation that describes the viscosity, namely the requirements imposed by equations (7), (8) and (10). Comparing with the experimental data obtained with the temperature derivative method, we can be sure about the range in which the function that describes the viscosity is valid. On the other hand this method can be applied to different theories. For example, if we start with the Adam–Gibbs [16] equation for the viscosity, namely, $\eta = \eta_0 \exp(K / T S_c(T))$ where K is a constant and $S_c(T)$ the configurational entropy, using the temperature derivative method one can obtain the value for $S_c(T)$ by direct comparison with the experimental values. On the other hand the constant K may be calculated by the methods already discussed in [17], so that this procedure may be used as an alternative way of computing the viscosity. The results so obtained may therefore serve as a basis to test whether the Arrhenius or VFT forms for the viscosity are the adequate ones for representing the experimental data. This comparison is based upon the fact that if $S_c(T) = $ constant one obtains the Arrhenius form for η whereas if $S_c(T) = $ constant T^{-1}, one obtains the VFT equation [18].

Moreover, the results of this paper may be also extended to study β relaxation in B_2O_3 and the α relaxation in other strong glass forming liquids if the glassy state may be associated with the probability of assembling ring structures. Also α and β relaxation processes in dendritic systems can be studied by this method where, by the way, a non-Arrhenius equation for the relaxation time is expected.

Acknowledgment

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