A theoretical framework for the Vogel-Fulcher-Tammann equation for covalent network glasses derived by the stochastic matrix method

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Abstract. A strong/fragile-liquid pattern has been used as the basis for a classification of glass-forming liquids indicating the sensitivity of the liquid structure to temperature changes. Also, variations in 'fragility' have been observed in the ternary system Ge–As–Se depending on the average coordination number. In recent papers, using a statistical method based on stochastic transition matrices, an equation for the viscosity of the strong glass-forming liquid B_2O_3 was obtained. In this work we find a theoretical equation for the viscosity for three different types of covalent network glass. To achieve this end, the average relaxation time is taken as inversely proportional to the average transition probability. To find an expression for the transition probability, previous results obtained by the stochastic matrix method were used. The temperature derivative method for finding the functional dependence for the relaxation time was also used; we arrived at a theoretical expression that predicts a variation in 'fragility' for the covalent network glasses that depends on the concentration (or coordination number).

Nomenclature

η viscosity
D measure of the structural 'strength'
T_0 temperature at which τ is infinite
η_0 reference viscosity
$\langle r \rangle$ coordination number
k_B Boltzmann constant
T' cut-off temperature
m valence
a atoms with $m = 2$
b atoms with $m' = 3$
c atoms with $m'' = 4$
E_1 energy cost of sticking a to a
E_2 energy cost of sticking a to b
E_3 energy cost of sticking b to b
E_4 energy cost of sticking a to c
E_5 energy cost of sticking c to c
E_6 energy cost of sticking b to c

$$\xi \qquad \exp\left(\frac{E_1 - E_2}{k_B(T - T_0)}\right)$$

$$\mu \qquad \exp\left(\frac{E_1 - E_3}{k_B(T - T_0)}\right)$$

$$\chi \qquad \exp\left(\frac{E_1 - E_4}{k_B(T - T_0)}\right)$$

$$\delta \qquad \exp\left(\frac{E_1 - E_5}{k_B(T - T_0)}\right)$$

u	atom of valence 2 at the rim with one valence free
$(P_u$	probability of finding it at the rim)
v	atom of valence 3 at the rim with two valences free
$(P_v$	probability of finding it at the rim)
w	atom of valence 3 at the rim with one valence free
$(P_w$	probability of finding it at the rim)
y	atom of valence 4 at the rim with one valence free
$(P_y$	probability of finding it at the rim)
t	atom of valence 4 at the rim with two valences free
$(P_t$	probability of finding it at the rim)
z	atom of valence 4 at the rim with three valences free
$(P_z$	probability of finding it at the rim)

1. Introduction

The structure and the structural changes occurring at the glass transition have been extensively investigated by numerous techniques for many glass-forming systems [1–3]. Around the glass transition temperature, T_g, the specific heat and viscosity exhibit different temperature dependences, which are not yet satisfactorily understood from the mesoscopic and/or microscopic point of view. In particular, for chalcogenide glasses, a lot of attention has been devoted to understanding chemical and physical properties [4], since such glasses exhibit electric and infrared transmission properties that make them useful in several technological applications [5]. The most significant features on approaching the glass transition are a rapid increase in the viscosity and a slowing down of the structural relaxation. It turns out that the relaxation patterns for different glass-forming liquids show several common features, such as a temperature dependence of the viscosity η which is usually well represented by the Vogel–Fulcher–Tammann (VFT) empirical equation

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right). \tag{1.1}$$

T_0 corresponds to the temperature at which η is infinite, η_0 is a reference viscosity and D is a measure of the structural 'strength' of the system. The largest values of D ($D \approx 20$–100) characterize those liquids which are most resistant to temperature-induced changes. These liquids display a nearly Arrhenius behaviour and are referred to as 'strong' [6]. Covalently bonded network glass formers like SiO_2 ($D = 100$) [1] and B_2O_3 ($D = 35$) [7] belong to this group. At the other extreme are the 'fragile' glasses: the systems with the smallest D-values ($D \approx 3$–5) exhibit the most rapid changes of η in the supercooled region. For the fragile systems the dramatic changes of η in the transition range imply that T_0 is close to T_g, while for strong ones T_0 is far below ($T_g/T_0 \approx 2$ for B_2O_3), T_g being the glass transition temperature.

Systems like $Ge_xAs_ySe_{1-x-y}$ cover almost the whole spectrum from strong to fragile behaviour [8] and this depends on the composition. In fact, the minimum fragility observed in this system occurs not at the highest value of the coordination number ($\langle r \rangle$) but rather at $\langle r \rangle = 2.4$, the rigidity–percolation threshold. At higher values of $\langle r \rangle$, specific chemical effects such as the occurrence of double Se bridges begin to require consideration; these are fragile structural elements [9].

In recent theoretical work, Barrio *et al* [10–12] used a statistical model in which the stochastic matrix method (SMM) is applied to find the fraction of boron atoms belonging to boroxol rings in a boron oxide (B_2O_3) glass. The SMM treats the problem of agglomeration in a generalized way. In this method, it is supposed that the material grows when the atoms agglomerate to form clusters. Each of these clusters is divided into two parts, the rim and the bulk. The rim is composed of all of the entities that have the potential to receive new entities that stick and agglomerate, and the bulk is all of the units that have saturated all their bonds. The entities that compose the rim (atoms or any other building blocks) are found in a certain number of geometric positions (called sites). In the SMM, the rim is considered as a vector, in which each element is the probability of observing a certain kind of site, so the growth is described by the application of a matrix to a vector, because the rim changes after adding one entity to the cluster. This transformation of the rim depends on the probabilities of sticking each kind of site onto others.

As has been shown [11], the SMM converges to a final configuration for the material, no matter what the initial conditions are. It also predicts an oscillatory behaviour for the first steps of the growth. These oscillations are damped in an exponential way as the solid grows. All these properties are derived from the eigenvectors and eigenvalues of the stochastic matrix and, thus, some of the convergence difficulties often found in numerical simulations are avoided. Many different agglomeration processes can be described by the SMM. The difference between the materials appears in the manner of constructing the stochastic matrix.

Each sticking process has a certain probability of occurring, so 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 in 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 remark that according to this assumption, it is possible to stick a unit at every temperature T. In a recent paper [15] we showed that this would have a clear physical meaning if a temperature T' is introduced in 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 to stick it in the bulk. Thus by introducing this probabilistic cut-off temperature we generalize the SMM, and finally find 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 our previous discussion 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 as inversely proportional to the transition probability [12]. 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 of an average transition can be written as $P(\xi'')$ where

$$\xi'' = \exp(\Delta E/k_B(T - T'))$$

and ΔE is the difference between two E'_m. If

$$\tau \propto \frac{1}{P(\xi')} \tag{1.2}$$

then using the method of the temperature derivative [13, 14] to linearize equation (1.2) we obtain that

$$\left[\frac{\mathrm{d}\ln\tau^{-1}}{\mathrm{d}T}\right]^{-1/2} = \left[\frac{\Delta E}{k_B}\right]^{-1/2} \left[\xi'\frac{\mathrm{d}\ln P(\xi')}{\mathrm{d}\xi'}\right]^{-1/2} (T - T'). \tag{1.3}$$

For typical activation energies the temperature dependence of $P(\xi')$ is negligible and the second factor of equation (1.3) is reduced to a constant, so on integrating it we obtain a VFT-like equation. Comparing equation (1.3) with equation (1.1), T' can be identified as T_0 and if $T_0 = 0$ the ARR equation is obtained. It is important to remark that in this theoretical context, T_0 is interpreted not only as the temperature that yields an infinite relaxation time, but also as the temperature at which the probability of sticking a unit into the bulk of the glass system is zero. Equation (1.3) is not predicted starting from first principles; it is obtained as a consequence of introducing a cut-off temperature.

In the SMM the consecutive agglomeration and growth of clusters is represented by successive application of the matrix to the initial vector v_0. After applying the matrix N times, the final configuration of the surface is

$$v_N = \sum_{j=1}^{N} a_j (\lambda_j)^N e_j$$

where e_j are the eigenvectors of the matrix corresponding to the eigenvalue λ_j and a_j are the projections of v_0 onto the eigenvectors of the 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 all other (in general, complex) eigenvalues have their norm always less than one. This condition means that only the eigenvectors with eigenvalue one remain after many successive applications of the stochastic matrix. If we suppose that the matrix has a single eigenvalue, 1 (corresponding to $\lambda = 1$), then, in the limit of large N, v_N converges to e_1 since a_1 must be one due to conservation of probability [15].

The purpose of this work is to find for typical covalent network glasses a theoretical dependence of the viscosity on the temperature using the transition probability obtained by the SMM. We only consider materials that may be conceived of as showing the simplest case of purely dendritic growth—i.e. for which only one bond can be created between two closest neighbours, excluding the possibility of forming rings. There are three covalent networks studied in this work: those with valences two and four; those with valences two and three; and the system with valences two, three and four. In section 2, we summarize the main features of the SMM for covalent networks. In section 3, we present our results and their comparison to experimental values through the experimental VFT equation. Finally, in section 4 we make some remarks on the nature of these results.

2. The SMM description for covalent networks

2.1. The SMM description for covalent network systems formed from atoms of valences two and three

Consider two star-like elementary blocks, symbolizing two types of atom, with valences m and m'. Many network glasses correspond fairly well to this definition, e.g. $As_x S_{1-x}$ glass,

$Ge_x Se_{1-x}$ glass. In our example we shall choose the lowest possible values $m = 2$ and $m' = 3$; the corresponding atoms will be denoted symbolically by a and b. Glass-forming systems of this type are indeed known, e.g. $As_x Se_{1-x}$. If we consider the simplest case of purely dendritic growth, only three types of site, denoted by u, v, w, can be found on the rim [16]. u is an atom of valence 2 at the rim with one free valence, v and w are atoms of valence 3 at the rim with two and one free valence respectively. Let the concentration of the b-atoms in the surrounding medium be c_b and that of the a-atoms be $1 - c_b$. It is easy to establish that there are six possible transitions contributing to the probability factors. The Boltzmann factors due the corresponding energy barriers are defined as follows: $\exp(-E_1/k(T - T_0))$ for a–a; $\exp(-E_2/k(T - T_0))$ for a–b; and $\exp(-E_3/k(T - T_0))$ for b–b. Inserting in the stochastic matrix all the contributions defining statistical weights of transitions resulting in the corresponding transformation of sites, the matrix can be displayed as a 3×3 matrix that satisfies the normalization condition. The eigenvalue-1 eigenvector shows the asymptotic distribution (P_u, P_v, P_w) to which the average statistic tends, and that the Ps satisfy the normalization condition $P_u + P_v + P_w = 1$. P_u, P_v and P_w are the probabilities of finding one of the three configurations on the rim of the cluster. After normalization, we get the stochastic matrix M_{ik} $(i, k = u, v, w)$ transforming the probabilities of finding one of the three configurations on the rim of a cluster (P_u, P_v, P_w) into a new set of probabilities (P'_u, P'_v, P'_w) after the characteristic time τ during which an entire new layer of atoms has grown, with one new atom at each available site, namely [16]

$$M1 = \begin{pmatrix} \dfrac{2(1 - c_b)}{2(1 - c_b) + 3c_b\xi} & \dfrac{(1 - c_b)\xi}{2(1 - c_b)\xi + 3c_b\mu} & \dfrac{2(1 - c_b)\xi}{2(1 - c_b)\xi + 3c_b\mu} \\ \dfrac{3c_b\xi}{2(1 - c_b) + 3c_b\xi} & \dfrac{3c_b\mu}{4(1 - c_b)\xi + 6c_b\mu} & \dfrac{3c_b\mu}{2(1 - c_b)\xi + 3c_b\mu} \\ 0 & 1/2 & 0 \end{pmatrix} \tag{2.1}$$

where

$$\xi = \exp\left(\frac{E_1 - E_2}{k_B(T - T_0)}\right) \qquad \mu = \exp\left(\frac{E_1 - E_3}{k_B(T - T_0)}\right).$$

A matrix of this type, with all the columns normalized to one, has at least one eigenvalue equal to one, while other eigenvalues can be real, complex or imaginary depending on the values of the parameters involved. The eigenvalue-1 eigenvector shows the asymptotic distribution $(P_u, P_v, P_w)_\infty$ to which the average statistics tends. This is also the statistics for the bulk if the number of steps is very large; for smaller clusters, one should take an average over the sums of many layers. The eigenvector $(P_u, P_v, P_w)_\infty$ is then

$$\begin{pmatrix} P_u \\ P_v \\ P_w \end{pmatrix}_\infty = \begin{pmatrix} \dfrac{4(1 - c_b)[2(1 - c_b) + 3c_b\xi]}{4(1 - c_b)[2(1 - c_b) + 3c_b\xi] + 9c_b[2(1 - c_b) + 3c_b\mu]} \\ \dfrac{6(1 - c_b)[2(1 - c_b)\xi + 3c_b\mu]}{4(1 - c_b)[2(1 - c_b) + 3c_b\xi] + 9c_b[2(1 - c_b) + 3c_b\mu]} \\ \dfrac{3c_b[2(1 - c_b)\xi + 3c_b\mu]}{4(1 - c_b)[2(1 - c_b) + 3c_b\xi] + 9c_b[2(1 - c_b) + 3c_b\mu]} \end{pmatrix} \tag{2.2}$$

where the homogeneous character of all rational expressions entering the definitions of the transition probabilities and the normalized eigenvector enables us to reduce the number of essential parameters to two ratios only, namely ξ and μ.

2.2. The SMM description for covalent network systems formed from atoms of valences two and four

In the case of vitreous Ge_xSe_{1-x}, when a new atom (Ge or Se) comes close to the cluster, it can be attached to one of the free valences that are in the rim. Since the coordination of Ge is four and that of Se is two, the new atom may encounter four kinds of site. The atoms with $m = 2$ will be denoted symbolically by a and the atoms with $m'' = 4$ by c. We take c and a to have concentrations c_c and $c_a \equiv 1 - c_c$. With only two types of atom that form covalent bonds, there are three elementary processes of single-bond creation. Each process involves a characteristic energy for creating the bond between two atoms: E_1, E_4 and E_5 will denote these energies for a–a, a–c, c–c bonds.

During the cooling process, by which the glass forms, clusters of different sizes appear, constituting the seeds from which the material grows. The growth is dendritic; there are no rings. This assumption allows us to reduce the size of the stochastic matrix, and it is only valid in the case of low concentration $x \ll 1$.

Each kind of site has a certain frequency of occurrence (denoted by u, y, z, t) in the rim of the cluster. For example, a free valence has a frequency t. u has the same meaning as in the preceding section and y, z, t are an atom of valence 4 at the rim with 1, 2 and 3 free valencies, respectively. Thus, the distribution of each kind of valency at any stage of growth can be represented by the vector (u, y, z, t), with its trace normalized to one: $u + y + z + t = 1$.

The new Ge or Se atom has a certain probability of sticking to each of the free valencies in the rim. Once this atom sticks, a new site on the rim is created and the rim changes. The probabilities of each sticking process (represented by $P(u, u)$, $P(u, t)$) are given by two factors; one is the purely statistical factor and other is the Boltzmann factor which takes into account the corresponding energy barriers to forming a bond.

Observe that for creating some kinds of site there are two possible paths with different probabilities (for example, for creating one z-site there are two possibilities: stick a Se on a t-site or a Ge on a t-site). In these cases, the total probability of creating a site is the sum of the probabilities of each of the paths.

The transformation of the rim is written as a matrix that acts on a vector, because the total probability of an atom sticking at a certain site is the sticking probability of the process multiplied by the frequency on the rim of that kind of site. The components of the matrix are the probabilities of transforming each kind of site into others. The vector obtained after applying the matrix must also be normalized, since it represents a probability distribution. In order to ensure that this is achieved, the sum of elements in each column of the matrix must be checked to be one. The normalized matrix is written as [17]

$$M2 = \begin{pmatrix} \dfrac{c_a}{c_a\chi + 2c_c\delta} & \dfrac{c_a\chi}{c_a\chi + 2c_c\delta} & \dfrac{c_a\chi}{c_a\chi + 2c_c\delta} & \dfrac{c_a\chi}{c_a\chi + 2c_c\delta} \\ 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ \dfrac{2c_c\chi}{c_a\chi + 2c_c\delta} & \dfrac{2c_c\delta}{c_a\chi + 2c_c\delta} & \dfrac{2c_c\delta}{c_a\chi + 2c_c\delta} & \dfrac{2c_c\delta}{c_a\chi + 2c_c\delta} \end{pmatrix}. \tag{2.3}$$

Only the eigenvector with eigenvalue one remains after successive applications of the stochastic matrix. The explicit form of the eigenvector one yields [17]

$$\begin{pmatrix} P_u \\ P_y \\ P_z \\ P_t \end{pmatrix}_\infty = \frac{1}{4B + 7A} \begin{pmatrix} 4B \\ A \\ 2A \\ 4A \end{pmatrix} \tag{2.4}$$

where A and B are given by

$$A = \frac{2c_c\chi}{c_a + 2c_c\chi} \tag{2.5}$$

$$B = \frac{c_a}{c_a\chi + 2c_c\delta} \tag{2.6}$$

and $\chi = \exp((E_1 - E_4)/k_B T)$ and $\delta = \exp((E_1 - E_5)/k_B T)$.

An important point to be remembered is that the SMM gives information about the evolution of the rim in each step. Thus, the information about some structural property of the bulk is obtained by summing over all the layers.

2.3. The SMM description for covalent network systems formed from atoms of valences two, three and four

Ternary systems like $Ge_x As_y Se_{1-x-y}$ and $Ge_x Sb_y Se_{1-x-y}$ have been extensively studied [5, 8, 18] not only in view of their applications, but also for testing the Phillips constraint theory [19], since the bonding numbers (valencies) of Ge, As, Sb and Se (4, 3 and 2 respectively) allow the realization of the rigidity threshold (attained with the average coordination number, $\langle r \rangle = 2x + y + z$, which is 2.4) for many different chemical compounds.

To construct the stochastic matrix for a ternary system, the basic entities can represent either single atoms or certain clusters that were already present in the liquid melt before the formation of the glass [19, 20]. For example for $Ge_x As_y Se_{1-x-y}$ one can assume that it contains three types of basic entity: clusters of two As atoms joined by one Se atom, and Ge and Se atoms, which will be labelled as b-, c- and a-units, their respective concentrations being c_b, c_c and c_a. These concentrations of basic entities are related to those of the atomic species by the following equations:

$$c_c = \frac{x}{1-y} \qquad c_b = \frac{y}{2(1-y)} \qquad c_a = 1 - c_b - c_c. \tag{2.7}$$

For the $Ge_x Sb_y Se_{1-x-y}$ compound the same relations hold, except that c_b represents the concentration of two b-atoms joined by an atom.

With these three basic entities forming covalent bonds among themselves, there are five elementary processes of single-bond creation. Each process involves its characteristic energy of activation for creating the bond between two units; these energies will be denoted by E_1, E_2, E_4, E_3 E_6 and E_5 for a–a, a–b, a–c, b–b, b–c and c–c bonds, respectively.

During the cooling process already occurring in the melt, and when a new basic entity comes close to a cluster, it can stick to one of the free valencies available on the surface. Since the valencies of a-, b- and c-units are 2, 3 and 4 respectively, the new entity may encounter seven types of configuration. If the growth is dendritic, it allows us to decrease the size of the stochastic matrix, but this is the case only in the chalcogen-rich region ($\langle r \rangle < 2.4$).

The different configurations that appear in the surface of a cluster are called sites. These configurations are u, v, w, y, z and t with the same meaning as in the preceding sections and o represents two free valences of two atoms of valence 3 linked by an atom of valence 2. Using all of this notation, the state of the surface is specified by the vector $v = (u, v, o, w, y, z, t)$ whose components are the relative frequencies of each kind of site; therefore its trace is normalized to one: $u + v + o + w + y + z + t = 1$. The main task of the SMM is to determine the evolution of this vector as the clusters continue to grow.

The probability of the sticking process is a product of two factors, one of which is purely statistical; the other one is the Boltzmann factor which takes into account the corresponding activation energy barrier necessary to form that bond. Similar expressions can be formed

when c, b–a–b and a are added to each of the sites. However, in the $Ge_xAs_ySe_{1-x-y}$ and $Ge_xSb_ySe_{1-x-y}$ systems, the Ge–Ge, Ge–As and Ge–Sb bonds are almost never observed, and thus the probability of these kinds of bond forming is close to zero. This fact allows us to reduce the number of possible transformations of sites.

The transformation of the surface of an average cluster is encoded in the matrix that acts on the vector v, because the total probability of an entity sticking to a certain site is equal to the probability of the sticking process multiplied by the frequency of occurrence of the corresponding type of site at the surface. The components of the matrix are the probabilities of transforming each kind of site into another, namely [20]

$$M3 = \begin{pmatrix} C & 1/2 & 1/2 & 1 & 1 & 1/2 & 1/2 \\ D & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/2 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ E & 0 & 0 & 0 & 0 & 0 & 1/2 \end{pmatrix}. \tag{2.8}$$

The surface attains a stable statistical regime after many successive steps of agglomeration, with the statistics given by the eigenvalue-1 eigenvector. The explicit form of this eigenvector 1 is [20]

$$\begin{pmatrix} P_u \\ P_v \\ P_o \\ P_w \\ P_y \\ P_z \\ P_t \end{pmatrix}_\infty = \frac{1}{13 - 7C} \begin{pmatrix} 4 \\ 4D \\ 2D \\ D \\ E \\ 2E \\ 4E \end{pmatrix}. \tag{2.9}$$

The entries C, D and E are defined as

$$C \equiv \frac{2c_a}{2c_c + 4(c_b\xi + c_c\chi)} \tag{2.10}$$

$$D \equiv \frac{2c_b\xi}{2c_a + 4(c_b\xi + c_c\chi)} \tag{2.11}$$

and $E = 1 - C - D$, where $\xi = \exp((E_1 - E_2)/k_BT)$ and $\chi = \exp((E_1 - E_4)/k_BT)$.

3. Results and comparison with the experiment

In this paper we would like to show that, using the probability of forming a preferential link obtained from the stochastic matrix method, we can derive the VFT dependence for the viscosity in dendritic systems. To do this we proceed as follows. First we identify the average transition probability with the average transition probability of forming some kind of preferential link, the link that gives the largest probability of occurring in the glass transition. In fact only the weakest bonds are broken or rearranged initially in the glass transition region [21]. Then following the Adam–Gibbs theory we take the relaxation time (or viscosity) as inversely proportional to the transition probability. Finally we apply the method of the temperature derivative to obtain the form of the relaxation time (or the viscosity). In section 3.1 we study the covalent network system formed from atoms of valences two and three, that for valences two and four in section 3.2 and, finally, that for valencies two, three and four in section 3.3.

3.1. Covalent network systems formed from atoms of valences two and three

To illustrate the method, without loss of generality, we take as an example a covalent network system formed from atoms of valences two and three: the $As_x Se_{1-x}$ system. The main property derived from the experimental relation between the composition and the transition temperature is: if the Se content increases, the transition temperature decreases [14, 22] and, adding the fact that x-ray and neutron scattering measurements as well as studies of the infrared and Raman spectra have shown that the short-range order in the glass-forming system $As_x Se_{1-x}$ is given by chain-like connected Se atoms and the structural units $AsSe_{3/2}$ in the given range of composition [18], we consider the transition probability to be directly proportional to form Se–Se bonds. Further, we are also assuming that the Se chains determine T_g [17, 20, 21, 23].

The probability of forming the weakest bond when passing from the jth layer to the $(j+1)$th one is simply given by counting the proportion of Se (a-atoms) formed between the step j and the step $j + 1$ linked by another Se. If for a large number of steps of growth we calculate the probability of forming the weakest bond, we find that it is given by $P^{\infty}_{Se-Se} = P^{\infty}_u M1_{11}$, where P^{∞}_u and $M1_{11}$ are defined by inserting equations (2.1) and (2.2) in P_{Se-Se}, we have that

$$P^{\infty}_{Se-Se} = \frac{8(1-x)^2}{4(1-x)[2(1-x)+3x\xi]+9x[2(1-x)+3x\mu]}. \tag{3.1}$$

Further, since the viscosity is inversely proportional to the average transition probability,

$$\eta \propto \frac{1}{P^{\infty}_{Se-Se}} = \frac{4(1-x)[2(1-x)+3x\xi]+9x[2(1-x)+3x\mu]}{8(1-x)^2}. \tag{3.2}$$

Taking the derivative $d \ln \eta^{-1}/dT$ of equation (3.2) we find that

$$\left[\frac{d \ln (P^{\infty}_{Se-Se})^{-1}}{dT}\right]^{-1/2}$$

$$= (T-T_0)\left[\frac{3x}{k_B}\frac{4(1-x)(E_2-E_1)\xi+9(E_3-E_1)\mu}{4(1-x)[2(1-x)+3x\xi]+9x[2(1-x)+3x\mu]}\right]^{-1/2}. \tag{3.3}$$

Equation (3.3) is one of the main results of this paper and is a complicated equation that depends on the activation energies and predicts theoretically that the viscosity should be a function of the concentration. Experimentally it is observed that energy differences involved in equation (3.3) are nearly zero or at most ~10 kcal mol^{-1} [20]. This result gives us four situations: $|E_2-E_1| \gg |E_3-E_1|$, $|E_2-E_1| \ll |E_3-E_1|$, $|E_2-E_1| \approx |E_3-E_1| \ll 1$ and $|E_2-E_1| \approx |E_3-E_1| \gg 1$. We analyse each case individually.

3.1.1. $|E_2-E_1| \gg |E_3-E_1|$ (case I).

With this approximation, $\xi \to 0$ and $\mu \to 1$, and equation (3.3) can be written as

$$\left[\frac{d \ln \eta^{-1}}{dT}\right]^{-1/2} = (T-T_0)\left[\frac{(E_3-E_1)}{k_B}\frac{27x^2}{8(1-x)^2+9x(x+2)}\right]^{-1/2}. \tag{3.4}$$

If equation (3.4) is integrated, a theoretical VFT-like equation is obtained, namely

$$\eta = \eta_0 \exp\left[\frac{(E_3-E_1)}{k_B(T-T_0)}\frac{27x^2}{8(1-x)^2+9x(x+2)}\right] = \exp\left[\frac{D^*(x)T_0}{T-T_0}\right] \tag{3.5}$$

where the constant η_0 is the pre-exponential factor and may be obtained from a plot of η against $1/T$. In this equation, $D^*(x)$ is not a constant but depends on the concentration:

$$D^*(x) = \frac{27x^2}{8(1-x)^2+9x(x+2)}D \tag{3.6}$$

where D is a number to be fixed by experiment at a known concentration and whose value is obtained from the experimental VFT equation (see figure 1). $E_3 - E_1$ can be determined by comparing equation (3.5) with the experimental VFT equation at a known concentration. Also, it is important to remark that the energy dependence in equation (3.5) has the lowest energy difference involved in the growth of these systems, as has been pointed out in the experiment [20]. Equation (3.6) predicts that for these systems, fragility (inversely proportional to D) decreases when the concentration x increases.
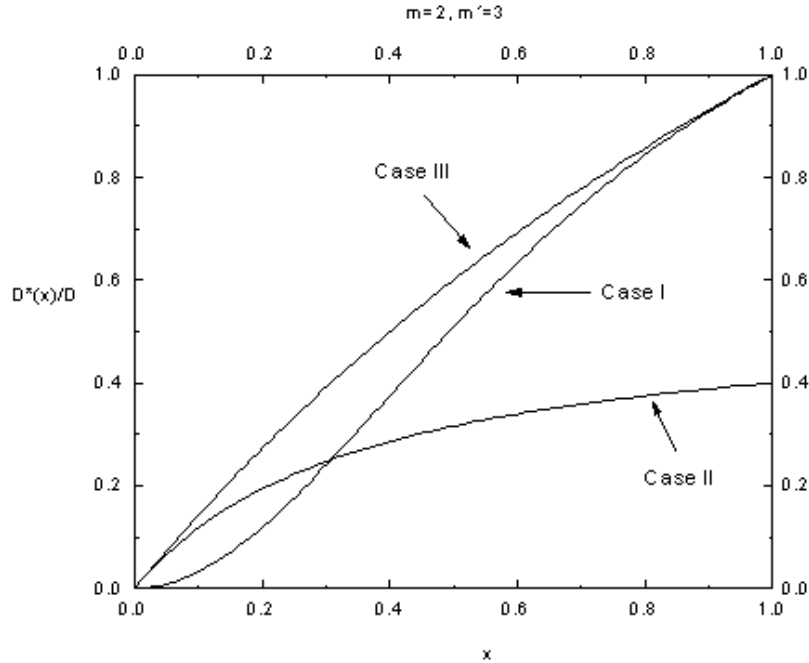

Figure 1. The changes of $D^*(x)/D$ against the concentration from equations (3.6), (3.9) and (3.12).

3.1.2. $|E_2 - E_1| \gg |E_3 - E_1|$ (case II). A typical material with these characteristics of its activation energies is $As_x Se_{1-x}$, and in this approximation one has $\xi \to 1$ and $\mu \to 0$, so equation (3.3) can be written as

$$\left[\frac{\mathrm{d}\ln\eta^{-1}}{\mathrm{d}T}\right]^{-1/2} = (T - T_0)\left[\frac{(E_3 - E_1)}{k_B}\frac{12x}{22x + 8}\right]^{-1/2}. \tag{3.7}$$

If equation (3.7) is integrated, a theoretical VFT-like equation is obtained:

$$\eta = \eta_0 \exp\left[\frac{(E_3 - E_1)}{k_B(T - T_0)}\frac{12x}{22x + 8}\right] = \exp\left[\frac{D^*(x)T_0}{T - T_0}\right] \tag{3.8}$$

and as in the last subsection this equation depends on the concentration and $E_3 - E_1$ can be determined by comparing it with the experimental VFT equation:

$$D^*(x) = \frac{12x}{22x + 8}D. \tag{3.9}$$

Experimentally, for $x = 0.4$ ($As_2 Se_3$), $D = 33$ [24] and inserting this value in equation (3.8) it is possible to predict that $D = 46.2$ for $x = 1$ (As); see figure 1. Inserting $D = 33$ and

$T_0 = 236$ K [23] in equation (3.8) one obtains that $E_3 - E_1 = 55$ kcal mol^{-1}. Experimentally, for Se ($x = 0$), $D = 10$ [8], equation (3.9) predicts $D = 10$ if $x \approx 0.07$. This is not the experimental value, but it predicts that it is almost zero. Also equation (3.9) predicts that the largest value for D occurs at $x = 1$.

3.1.3. $|E_2 - E_1| \approx |E_3 - E_1| \ll 1$ (case III). With this approximation for the energies, $\xi \to 1$ and $\mu \to 1$, and equation (3.3) can be written as

$$\left[\frac{\mathrm{d}\ln \eta^{-1}}{\mathrm{d}T}\right]^{-1/2} = (T - T_0)\left[\frac{(E_3 - E_1)}{k_B}\frac{3x}{x+2}\right]^{-1/2}. \tag{3.10}$$

If equation (3.10) is integrated, a theoretical VFT-like equation is obtained, namely

$$\eta = \eta_0 \exp\left[\frac{(E_3 - E_1)}{k_B(T - T_0)}\frac{3x}{x+2}\right] = \exp\left[\frac{D^*(x)T_0}{T - T_0}\right] \tag{3.11}$$

and

$$D^*(x) = \frac{3x}{x+2}D. \tag{3.12}$$

As in the preceding subsections, the energy dependence in equation (3.11) is given by the lowest difference energy ($E_3 - E_1$); see figure 1 (case III). Equation (3.12) predicts that if x increases, the fragility decreases, and as in equations (3.6) and (3.9), the largest value for D occurs when $x = 1$. Also in figure 1 one can appreciate that cases I and III are more fragile than case II.

3.1.4. $|E_2 - E_1| \approx |E_3 - E_1| \gg 1$ (case IV). With this approximation for the energies, $\xi \to 0$ and $\mu \to 0$, and equation (3.3) is equal to zero and predicts that the viscosity is independent of the temperature; it is well known that this is not a physical solution for vitreous systems. In fact, the model predicts that it is not possible to form an amorphous system with $|E_2 - E_1| \approx |E_3 - E_1| \gg 1$ that has a viscosity that depends either as an Arrhenius or a VFT form.

3.2. Covalent network systems formed from atoms of valences two and four

To obtain the viscosity equation for the system formed from atoms with valencies two and four, we take the Ge_xSe_{1-x} system as an example of a covalent network system formed from atoms of valences two and four. The main property derived from the experimental relation between the composition and the transition temperature is that if the Se content increases, the transition temperature decreases [21, 25], and for Ge_xSe_{1-x}, as for As_xSe_{1-x}, Feltz [21] has shown that the short-range order in the glass-forming system is provided by chain-like connected Se atoms; so we consider the transition probability as directly proportional to that of forming Se–Se bonds; we are assuming that Se chains determine T_g as for the As_xSe_{1-x} system [17, 20, 21, 26].

The probability of forming the weakest bond when passing from the jth layer to the $(j+1)$th one is given by counting the proportion of Se atoms (a-atoms) that are formed between the step j and the step $j + 1$ linked by another Se. For a large number of steps of growth the probability is given by $P_{Se-Se}^\infty = P_u^\infty M2_{11}$, where P_u^∞ and $M2_{11}$ are given by equations (2.3) and (2.4) respectively, and inserting these values we have that

$$P_{Se-Se}^\infty = \frac{4B^2}{4B + 7A} \tag{3.13}$$

where A and B have the same meaning as in section 2.2. If the viscosity is assumed to be inversely proportional to the average transition probability,

$$\eta \propto \frac{1}{P_{\text{Se}-\text{Se}}^{\infty}} = \frac{4B + 7A}{4B^2}.\tag{3.14}$$

Taking the derivative $\mathrm{d}\ln\eta^{-1}/\mathrm{d}T$ of equation (3.14),

$$\left[\frac{\mathrm{d}\ln(P_{\text{Se}-\text{Se}}^{\infty})^{-1}}{\mathrm{d}T}\right]^{-1/2}$$

$$= (T - T_0)\left[\frac{(E_4 - E_1)}{k_B}\left(\frac{7Ac_a/(c_a + 2c_c\chi) - 4B^2\chi}{4B + 7A} + 8B\chi\right)\right.$$

$$\left. + \frac{(E_5 - E_1)}{k_B}8\frac{c_c}{c_a}\delta\left(2B - \frac{1}{4B + 7A}\right)\right]^{-1/2}.\tag{3.15}$$

Equation (3.15) is one of the main results of this paper. As can be seen, it exhibits a dependence on the activation energies and predicts theoretically that the viscosity is a function of the concentration. To study equation (3.15), we take the same four situations as in the preceding subsection and the results for the viscosity are enumerated in table 1.

Table 1. Approximations obtained for equation (3.15) (see the text).

Approximation	Viscosity	Equation number
$\lvert E_2 - E_1\rvert \gg \lvert E_3 - E_1\rvert$	$\eta = \eta_0\exp\left(\dfrac{(E_5 - E_1)}{k_B(T - T_0)}4\dfrac{x^2 - 4x + 2}{(x - 1)^2}\right)$	(T1.1) (case I)
	$= \exp\left(\dfrac{D^*(x)T_0}{T - T_0}\right)$	
$\chi \to 0, \delta \to 1$	$D^*(x) = 4\dfrac{x^2 - 4x + 2}{(x - 1)^2}D$	(T1.2)
$\lvert E_2 - E_1\rvert \ll \lvert E_3 - E_1\rvert$	$\eta = \eta_0\exp\left(\dfrac{(E_3 - E_1)}{k_B(T - T_0)}7\dfrac{9x^2 + 13x + 2}{(x + 1)(9x + 2)}\right)$	(T1.3) (case II)
	$= \exp\left(\dfrac{D^*(x)T_0}{T - T_0}\right)$	
$\xi \to 1, \mu \to 0$	$D^*(x) = 7\dfrac{9x^2 + 13x + 2}{(x + 1)(9x + 2)}D$	(T1.4)
$\lvert E_4 - E_1\rvert \approx \lvert E_5 - E_1\rvert$	$\eta = \eta_0\exp\left(\dfrac{(E_4 - E_1)}{k_B(T - T_0)}\dfrac{1}{2}\dfrac{41x^5 + 93x^4 - 44x^3 - 42x^2 - 9x - 7}{x(x - 1)(x + 1)(6x^2 + 1)}\right)$	(T1.5) (case III)
	$= \eta_0\exp\left(\dfrac{D^*(x)T_0}{T - T_0}\right)$	
$\chi \to 1, \delta \to 1$	$D^*(x) = \dfrac{1}{2}\dfrac{41c^5 + 93x^4 - 44x^3 - 42x^2 - 9x - 7}{x(x - 1)(x + 1)(6x^2 + 1)}D$	(T1.6)

The energy dependence in equation (T1.1) is given by the lowest difference energy $(E_3 - E_1)$ as shown experimentally [20]. Equation (T1.4) predicts that if x increases the D-value decreases, and the largest fragility is obtained when $x \approx 0.6$.

Equation (T1.4) predicts that no changes should be observed in the fragility as a function of the concentration for $\text{Ge}_x\text{Se}_{1-x}$; see figure 2 (case II). Experimentally, Saiter *et al* [27]

found that the variation of the average coordination number has a big range over which D is constant, and this is in accordance with our theoretical prediction.
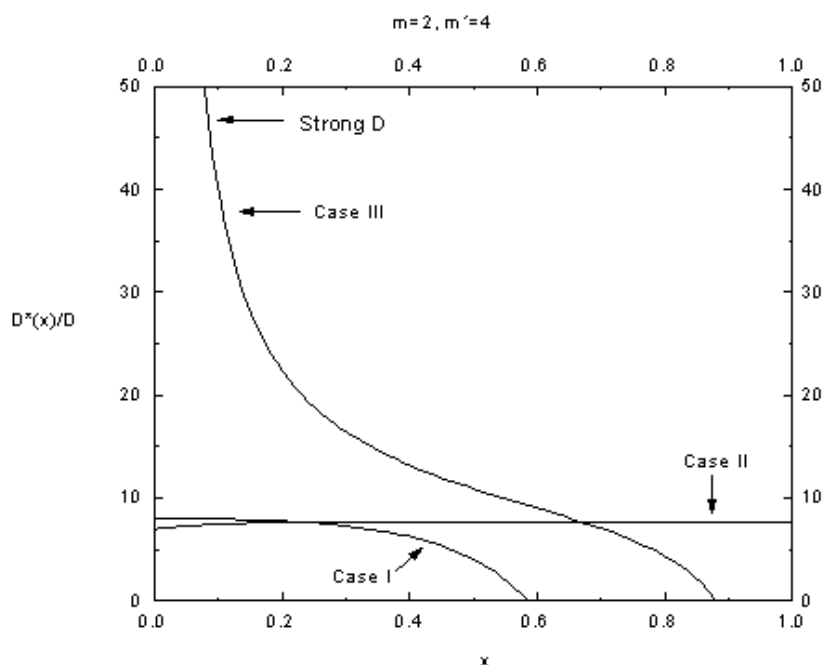

Figure 2. The changes of $D^*(x)/D$ versus the concentration from equations (T1.2), (T1.4) and (T1.6).

From equation (T1.6) an important prediction arises from the model (see figure 2), for larger concentrations. For larger fragility and for the lowest concentration, a strong system is obtained; in fact this predicts a transition from fragility to strength as the concentration decreases and if $x \to 0$, $D \to \infty$ an Arrhenius behaviour is obtained.

If $\chi \to 0$ and $\delta \to 0$, equation (3.15) is equal to zero and predicts that the viscosity is independent of the temperature; it is well known that this is not a physical solution for vitreous systems.

3.3. Covalent network systems formed form atoms of valences two, three and four

To illustrate the method, we take as an example of a covalent network system formed from atoms of valences two, three and four the $Ge_x As_y Se_{1-x-y}$ system. The main property is that as the Se concentration increases, the transition temperature decreases [14, 28], so we consider the transition probability as directly proportional to that of forming Se–Se bonds; also we are assuming that Se chains determine T_g [29, 17, 20].

The probability of forming the weakest bond when passing from the jth layer to the $(j+1)$th one is simply given by counting the proportion of Se chains that were formed between step j and step $j + 1$ linked by another Se. If we calculate for a large number of steps of growth, the probability is given by $P_{Se-Se}^{\infty} = P_u^{\infty} M3_{11}$, where P_q^{∞} and $M3_{11}$ are given by equations (2.8) and (2.9) respectively, and inserting these values to obtain the probability of forming a Se–Se

bond, we have

$$P_{\text{Se-Se}}^{\infty} = \frac{4C}{13 - 7C} \tag{3.16}$$

where C has the same meaning as in section 2.3. If we take the viscosity as inversely proportional to this probability, then

$$\eta \propto \frac{1}{P_{\text{Se-Se}}^{\infty}} = \frac{13 - 7C}{4C}. \tag{3.17}$$

Taking the derivative $\mathrm{d} \ln \eta^{-1}/\mathrm{d}T$ of equation (3.17), we obtain

$$\left[\frac{\mathrm{d} \ln(P_{\text{Se-Se}}^{\infty})^{-1}}{\mathrm{d}T} \right] = \frac{2}{k_B T} \left[c_d (E_2 - E_1) \xi + c_c (E_4 - E_1) \chi \right] \left[\frac{7C^2}{13 - C} \right]. \tag{3.18}$$

This last equation is also one of the main results of this paper, showing the dependence on the activation energies and predicting theoretically that the viscosity should be a function of the concentration. To study equation (3.18), we follow the same procedure as that described in the preceding sections, and the results for the viscosity are given in table 2.

Table 2. Approximations obtained for equation (3.18) (see the text).

Approximation	Viscosity	Equation number
$\lvert E_2 - E_1 \rvert \gg \lvert E_3 - E_1 \rvert$	$\eta = \eta_0 \exp\left(\dfrac{(E_4 - E_1)}{k(T - T_0)} \dfrac{1}{2} \dfrac{y(2x + 3y - 2)(82x + 19y - 82)}{(12x + 5y - 12)(1 - y)(2x + y - 2)} \right)$	(T2.1) (case I)
	$= \eta_0 \exp\left(\dfrac{D^*(x, y)T_0}{T - T_0} \right)$	
$\xi \to 0,\ \chi \to 1$	$D^*(x, y) = \dfrac{1}{2} \dfrac{y(2x + 3y - 2)(82x + 19y - 82)}{(12x + 5y - 12)(1 - y)(2x + y - 2)} D$	(T2.2)
$\lvert E_2 - E_1 \rvert \ll \lvert E_3 - E_1 \rvert$	$\eta = \eta_0 \exp\left(\dfrac{(E_2 - E_1)}{k(T - T_0)} \dfrac{1}{2} \dfrac{x(2x + 3y - 2)(126x - 123y + 82)}{(7x - 9y + 6)(y - 1)(2x - 3y + 2)} \right)$	(T2.3) (case II)
	$= \eta_0 \exp\left(\dfrac{D^*(x, y)T_0}{T - T_0} \right)$	
$\xi \to 1,\ \chi \to 0$	$D^*(x, y) = \dfrac{1}{2} \dfrac{x(2x + 3y - 2)(126x - 123y + 82)}{(7x - 9y + 6)(y - 1)(2x - 3y + 2)} D$	(T2.4)
$\lvert E_4 - E_1 \rvert \approx \lvert E_5 - E_1 \rvert$	$\eta = \eta_0 \exp\left(\dfrac{(E_2 - E_1)}{k_B(T - T_0)} \dfrac{1}{4} \dfrac{(2x + y)(2x + 3y - 2)(334x - 123y + 82)}{(20x - 9y + 6)(y - 1)(6x - 3y + 2)} \right)$	(T2.5) (case III)
	$= \eta_0 \exp\left(\dfrac{D^*(x, y)T_0}{T - T_0} \right)$	
$\xi \to 1,\ \chi \to 1$	$D^*(x, y) = \dfrac{1}{4} \dfrac{(2x + y)(2x + 3y - 2)(334x - 123y + 82)}{(20x - 9y + 6)(y - 1)(6x - 3y + 2)} D$	(T2.6)

Equation (T2.4) predicts for $x = y$ that the minimum fragility obtained occurs not at the highest value of the coordination number $\langle r \rangle$ but rather at $\langle r \rangle \approx 2.6$, see figure 3. Experimentally it is observed that the minimum fragility occurs at $\langle r \rangle = 2.4$ [8], the rigidity–percolation threshold. Tatsumisago *et al* [8] also found that the same low fragility is obtained for other ternary compositions with $\langle r \rangle = 2.4$. The agreement is in my opinion rather satisfactory.

The maximum value of equation (T2.6) is obtained at $y = 1$; this means that if Ge is absent from the system, we obtain the strongest glass.

If $\zeta \to 0$ and $\sigma \to 0$, equation (3.18) is equal to zero and predicts that the viscosity is independent of the temperature, which is not a physical solution for vitreous systems.
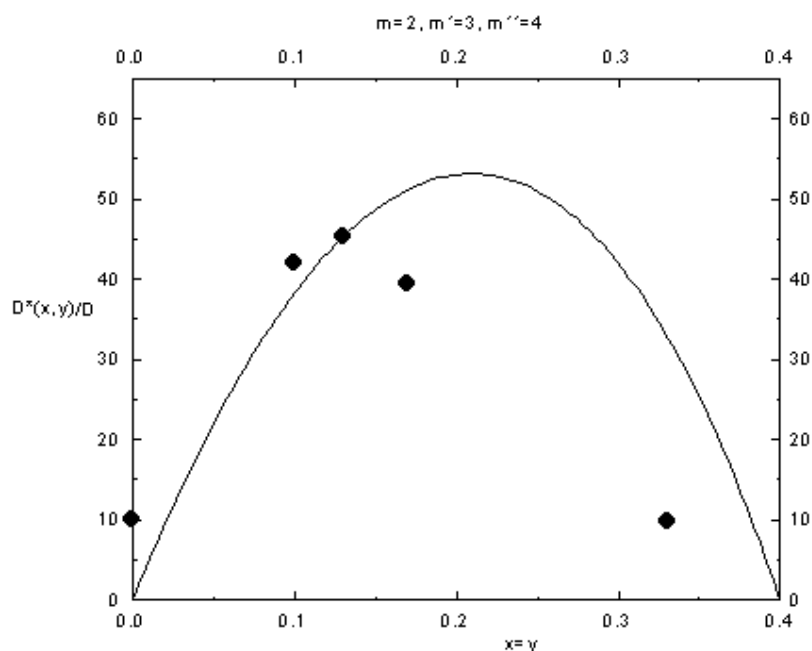
Figure 3. The changes of $D^*(x = y)/D$ against the concentration from equation (T2.4), compared with the experimental values for $Ge_x As_x Se_{1-x-y}$ (experimental data taken from reference [30]).

4. Concluding remarks

In this work we have obtained a theoretical VFT-like equation for the viscosity (average relaxation time) of covalent network glasses using the generalized SMM. To determine an expression for the viscosity using the generalized SMM, we took the transition probability as the probability of forming the weakest bond between the atoms that form the covalent network glass calculated for a large number of steps of growth; this probability was obtained by the SMM. To identify an equation for the viscosity, we used the method of the temperature derivative and a VFT-like equation was obtained (equation (3.3)), whose main property is that it predicts a dependence on concentration. For this equation three parameters remain to be determined, η_0, D and T_0, and a comparison with experimental data provides us with these values. Also, to compare equation (3.3) with experimental values it is necessary to make some approximations to reproduce the main properties for some covalent network glass. These approximations are made using the experimental values for the activation energies.

In section 3.1.2 we study the viscosity of the $As_x Se_{1-x}$ system and as a main result we find that the minimum fragility (which is inversely proportional to $D^*(x)$) occurs at the highest value of the concentration (or $\langle r \rangle$). Also, using equation (T2.4) we predict that $D \approx 10$ is obtained at $x \approx 0.07$; it is well known to occur experimentally at $x = 0$ (Se).

In section 3.2.2 we study the viscosity for $Ge_x Se_{1-x}$; our methods predict that no significant changes occur with the variation of the concentration. This is understood, because experimentally it was shown by Saiter *et al* [27] that the variation of the apparent activation energy for the equilibrium relaxation time versus the average coordination number has a big range over which the activation energies are constant: below 2.1 to almost 2.3. Also, when the

differences of activation energies are of the same order, the model predicts a transition from fragile to strong liquid for this glass-forming system.

In section 3.3 we study the viscosity for $Ge_x As_y Se_{1-x-y}$ and as a main result we find that the minimum fragility predicted by equation (T1.4) occurs not at the highest value of $\langle r \rangle$ but rather at $\langle r \rangle = 2.6$. Experimentally it is observed that the minimum fragility occurs at $\langle r \rangle = 2.4$, the rigidity–percolation threshold. And evidently at higher values of $\langle r \rangle$, specific chemical effects such as the occurrence of double Se bridges begin to require consideration. The credibility of this idea arises from the fact that Tatsumisago *et al* [8] have found that the same low fragility is obtained for other ternary compositions with $\langle r \rangle = 2.4$.

Moreover, the results obtained by combining the SMM and the derivative methods to find viscosity expressions are used to study the α- and β-relaxation in B_2O_3 (see references [11, 12]), a system formed principally of rings, and in this article the α-relaxation in dendritic systems (without rings). This gives us an important perspective on studying the viscosity in strong glasses taking into account important physical parameters and the constitution: with rings or without rings. At this time all the physical parameters obtained by the SMM come from configurational contributions.

Acknowledgments

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