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Modelling of growth and agglomeration processes leading to various non-crystalline materials

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Abstract

A statistical method is presented, based on stochastic transition matrices, to describe the growth of non-crystalline materials. The method is applied to model the growth of a typical covalent network glass like amorphous $\text{Ge}_x\text{Se}_{1-x}$. As a result, an analytical relation between the glass transition temperature, concentration of Ge and bonding energies is found. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

The successive agglomeration of atoms or clusters is a simple process that leads to the growth of numerous materials with very different thermodynamical and structural properties, such as glasses [1], fullerenes [2] or quasicrystals [3]. Such diversity makes it difficult to understand how the growth process is related to the properties of the material. As an example, in the case of glass, there is still no consensus [1] about which thermodynamical and structural factors are important to determine the glass transition temperature (T_g), although there is much work on the subject [4,5].

The recently introduced *stochastic matrix method* (SMM) [6,7], 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 are divided into two parts, the *rim* and the interior. The entities that composes the rim (atoms or any other building blocks) are found in a certain number of geometrical situations (called *sites*) that offer possibilities for a new entity to stick on them. The new entity sticks on each of these sites depending on the physical parameters involved in the process (such as temperature and potential energy). In the SMM, the rim is considered as a vector in which each element is the probability of observing a certain kind of site. The growth is then described by the application of a matrix on a vector because the rim is changed after adding one entity to the cluster. This transformation of the rim depends on the sticking probabilities on each kind of site and thus the matrix has the probabilities of transformation of each kind of site into others as components.

As it will be shown, the SMM converges to a final configuration for the material independent of the initial conditions. It also predicts an oscillatory behavior for the first steps of growing and that the oscillations

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are damped in an exponential way as the solid grows. As all these properties are derived from the eigenvectors and eigenvalues of the stochastic matrix, 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 each material comes in the way the stochastic matrix is constructed. In this article, the ideas behind the SMM are elaborated for modelling a typical covalent network: $\text{Ge}_x\text{Se}_{1-x}$ glass. This glass was chosen because it is one of the simplest covalent network glasses for which there is a lot of experimental data [8–10], although most of the relationships between glass transition temperature and structural or physical properties are empirical [5] (an important exception is the constraint theory introduced by Phillips [11]). Among these empirical relationships, the Gibbs–Di Marzio law is particularly well adapted for predicting T_g [12]. This law is obtained from equilibrium principles. It assumes that the glass is formed by a network of chains (made of Se atoms) and a cross-linking agent (Ge). In the original Gibbs–Di Marzio law, T_g is related to the cross-linking density [12]. Later on, a modified version was used by Sreeram and co-workers [8] to relate T_g to the network average coordination number, $\langle r \rangle$. This law can be expressed as

$$T_g = \frac{T_{g0}}{1 - \beta(\langle r \rangle - 2)}, \quad (1)$$

where T_{g0} is the limiting T_g when the concentration of cross-linking agents goes to zero. β is a constant that depends on the system. Usually, it varies from 0.55 to 0.75 depending on the system [8].

As will be shown, the SMM also produces a similar relationship between T_g and the concentration of cross-linking agents. For vitreous $\text{Ge}_x\text{Se}_{1-x}$, this relationship contains the energy differences between creating Se–Se, Ge–Se and Ge–Ge bonds. In the present work, these energies are fixed using some experimental data.

2. The stochastic matrix method

Glass usually grows from a surrounding medium (such as a liquid or solution) which contains the basic entities to form the glass. In the case of vitreous $\text{Ge}_x\text{Se}_{1-x}$, these entities are atoms of Ge and Se with concentration c_B and $c_A \equiv 1 - c_B$, respectively (observe that in principle c_B is not equal to the concentration in the glass (x), although at the end one will demand that $c_B = x$). With only two types of atoms that form covalent bonds, there are three elementary processes of single bond creation, as shown in Fig. 1. Each process involves a characteristic energy for creating a bond between two atoms; each of these energies will be denoted by E_1 , E_2 and E_3 for Se–Se, Se–Ge, Ge–Ge bonds, respectively.

During the cooling process which forms the glass, clusters of different sizes appear; these clusters are the seeds from which the material grows. When a new atom (Ge or Se) comes close to the cluster, it can be attached to one of the unsatisfied bonds 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, as shown in Fig. 2. Here it will be assumed that there are no two or three membered rings, i.e., the growth is dendritic. This assumption allows one to simplify the size of the stochastic matrix. It is only valid in the case of concentration $x \ll 1$.

Each kind of site has a certain frequency of occurrence (denoted by s, y, z, t) in the rim of the cluster. For example, a free bond that belongs to a Se has a frequency s in the rim, while a Ge atom with only one free

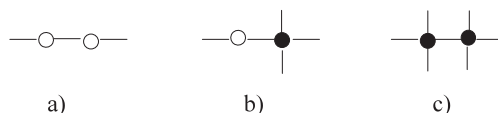


Fig. 1. The three agglomeration processes: (a) Se–Se, (b) Se–Ge, and (c) Ge–Ge.

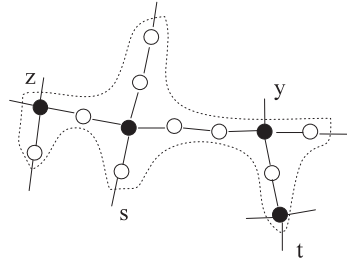


Fig. 2. A typical cluster with four kinds of site in the rim.

bond has a frequency t . Thus, the *distribution of each kind of valency* at any stage of the growing process can be represented by the vector (s, y, z, t) , with its trace normalized to one: $s + y + z + t = 1$.

The new Ge or Se atom has a certain probability to stick in each of the free bonds in the rim. Once this atom sticks, a new site on the rim is created and the rim changes. For example, if a Ge or Se atom is added at a site s , the transformation follows the next scheme,

$$s + \text{Se} \rightarrow s: P(s, s) \sim 2c_A e^{-E_1/KT}, \quad (2)$$

$$s + \text{Ge} \rightarrow t: P(s, t) \sim 4c_B e^{-E_2/KT}, \quad (3)$$

where the probabilities of each sticking process (represented by $P(s, s), P(s, t)$) are given by two factors, one is the purely statistical factor (the number of ways of joining the 4 (2) valencies of Ge (Se) in each kind of site), and the other is the Boltzmann factor which takes into account the corresponding energy barrier to form a bond. Similar expressions can be found when a Ge and Se atoms are added to each of the sites,

$$y + \text{Se} \rightarrow s: P(y, s) \sim 2c_A e^{-E_2/KT}, \quad (4)$$

$$y + \text{Ge} \rightarrow t: P(y, t) \sim 4c_B e^{-E_3/KT}, \quad (5)$$

$$z + \text{Se} \rightarrow s, y: P(z, s) = P(z, y) \sim 2c_A e^{-E_2/KT}, \quad (6)$$

$$z + \text{Ge} \rightarrow t, y: P(z, t) = P(z, y) \sim 4c_B e^{-E_3/KT}, \quad (7)$$

$$t + \text{Se} \rightarrow s, z: P(t, s) = P(t, z) \sim 2c_A e^{-E_2/KT}, \quad (8)$$

$$t + \text{Ge} \rightarrow t, z: P(t, t) = P(t, z) \sim 4c_B e^{-E_3/KT}. \quad (9)$$

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

The transformation of the rim is written as a matrix that acts on a vector because the total probability for an atom to stick in a certain site is the sticking probability of the process multiplied by the frequency of occurrence in the rim of that kind of site. The components of the matrix are the probabilities of transformation of each kind of site into others. Inserting all the contributions, the explicit matrix is written as

$$M = \begin{pmatrix} 2c_A e^{-E_1/kT} & 2c_A e^{-E_2/kT} & 2c_A e^{-E_2/kT} & 2c_A e^{-E_2/kT} \\ 0 & 0 & 2c_A e^{-E_2/kT} + 4c_B e^{-E_3/kT} & 0 \\ 0 & 0 & 0 & 2c_A e^{-E_2/kT} + 4c_B e^{-E_3/kT} \\ 4c_B e^{-E_2/kT} & 4c_B e^{-E_3/kT} & 4c_B e^{-E_3/kT} & 4c_B e^{-E_3/kT} \end{pmatrix}. \quad (10)$$

However, this matrix acts on a vector that represents the probabilities of finding each class of sites and, as stated previously, it is normalized. The vector obtained after applying the matrix must also be normalized since it represents a distribution of probabilities. In order to assure this, the sum of elements in each column of the matrix must be one. After normalizing each column of the matrix, one gets

$$M = \begin{pmatrix} \frac{c_A}{(c_A\zeta + 2c_B\mu)} & \frac{c_A\zeta}{(c_A\zeta + 2c_B\mu)} & \frac{c_A\zeta}{2(c_A\zeta + 2c_B\mu)} & \frac{c_A\zeta}{2(c_A\zeta + 2c_B\mu)} \\ 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ \frac{2c_B\zeta}{(c_A\zeta + 2c_B\mu)} & \frac{2c_B\mu}{(c_A\zeta + 2c_B\mu)} & \frac{2c_B\mu}{2(c_A\zeta + 2c_B\mu)} & \frac{2c_B\mu}{2(c_A\zeta + 2c_B\mu)} \end{pmatrix}, \quad (11)$$

where $\zeta = \exp((E_1 - E_2)/kT)$, and $\mu = \exp((E_1 - E_3)/kT)$.

The growth of clusters is modelled by a successive application of the matrix on an arbitrary initial vector (\mathbf{v}_0). After applying the matrix j times, the final configuration of the rim is given by

$$\mathbf{v}_j = a_1\lambda_1^j\mathbf{e}_1 + a_2\lambda_2^j\mathbf{e}_2 + a_3\lambda_3^j\mathbf{e}_3, \quad (12)$$

where \mathbf{e}_i are the eigenvectors of M corresponding to the eigenvalue λ_i , and a_i are the projections of \mathbf{v}_0 onto the eigenvectors.

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 real part always less than one. This means that only the eigenvectors with eigenvalue one remain after a successive application of the stochastic matrix. If we suppose that M has only one eigenvalue one (corresponding to $\lambda_1 = 1$), then, in the limit of big j , \mathbf{v}_j converges to

$$\mathbf{v}_j = \mathbf{e}_1, \quad (13)$$

since a_1 must be one due to conservation of probability. Thus, the rim attains a stable statistical regime after successive steps of growing; this regime is governed solely by the statistics of the eigenvector with eigenvalue one. Observe that before the growing process attains the stable regime, there are fluctuations in the first generations, due to eigenvalues different from one, which are in general complex numbers.

The explicit form of the eigenvector one is obtained by solving the system of equations given by

$$(M - 1)\mathbf{e}_1 = 0 \quad (14)$$

which for the present case yields the following vector,

$$\mathbf{e}_1 = \frac{1}{4B + 7A} (4B, A, 2A, 4A), \quad (15)$$

where A is

$$A = \frac{2c_B\zeta}{c_A + 2c_B\zeta} \quad (16)$$

and

$$B = \frac{c_A}{c_A\zeta + 2c_B\mu}. \quad (17)$$

Once the asymptotic regime is attained, the concentration of Se atoms in the rim is given by the statistics of the only eigenvector that remains. If $(s_\infty, y_\infty, z_\infty, t_\infty)$ is the eigenvector which corresponds to eigenvalue one, then the proportion of Se atoms in the stable regimen is

$$1 - x = \frac{s_\infty}{s_\infty + y_\infty + (z_\infty/2) + (t_\infty/3)}, \quad (18)$$

where the factors behind each component of the vector take into account that, for calculating the concentration, one must sum over the atoms that are in the rim instead of the number of free bonds. An important

point is that the SMM gives information about the evolution of the rim with each step. Thus, information about some structural property of the interior is obtained by summing over all the layers. In some sense, this is like differential geometry where the interior is the *integral* of the surface.

In this paper, the composition of the glass is the only structural parameter considered and so the composition in the rim must be the same as in the interior. Because of this fact, Eq. (18) can also be considered as the composition of the interior. In other systems, like vitreous B_2O_3 , obtaining some structural information about the interior from the rim can be more complicated, since, for example, the formation of rings requires at least two or three steps of agglomeration [7].

The concentration obtained from Eq. (18) is a function of the concentration in the liquid (c_B), but since the glass is growing at the expense of the surrounding medium, it is expected that $x = c_B$. This condition is equivalent to searching for the *fixed points* of the transformation. If one puts $c_B = x$ in the right-hand side of Eq. (18) three solutions are obtained, $x = 0, x = 1$ and the following equation for the concentration:

$$x = \frac{3 - 5\xi}{3 - 11\xi + 10\mu}. \quad (19)$$

The last equation gives the required relation between the glass transition temperature, concentration and difference of energies for forming the bonds.

3. Discussion

Eq. (19) can be compared directly with experimental data if $(E_1 - E_2)$ and $(E_1 - E_3)$ are known. Another approach is to fix these energies using the experimental value of T_g and dT_g/dx as x goes to zero.

The first energy difference, $E_1 - E_2$, is fixed by observing that in Eq. (19), x is zero when $\xi = 3/5$. An extrapolation from experiments on Ge_xSe_{1-x} glass [9,10] shows that in the limit $x \rightarrow 0$, the glass transition temperature is $T_{g0} = 316$ K. Thus, the energy difference between Se–Se and Ge–Se bonds is

$$E_1 - E_2 = kT_{g0} \ln(3/5) = -0.014 \text{ eV}. \quad (20)$$

The other energy is obtained by fixing the slope of the derivative dT_g/dx in the limit $x \rightarrow 0$. From Eq. (19), it can be shown that

$$\left. \frac{dT_g}{dx} \right|_{T_g=T_{g0}} = \frac{T_{g0}}{\ln(5/3)} \left(\frac{18 - 50e^{(E_2-E_3)/kT_{g0}}}{15} \right). \quad (21)$$

The experimental data taken from Ref. [9,10] show that dT_g/dx at T_{g0} is nearly $1,43T_{g0}$. By making Eq. (21) equal to this number, $E_1 - E_3 = -0.057$ eV, is obtained i.e., a bond between two Ge atoms needs more energy than other kinds of bonds, as also observed in experiments [9] and postulated by a model of a *chemically disordered network* [13].

In Fig. 3, a plot of Eq. (19) is shown and is compared with the experimental data. Observe that the agreement is good for smaller x as expected since the formation of rings was not considered here. Fig. 3 also shows a comparison with the Gibbs–Di Marzio law with $\beta = 0.72$ (calculated by a least-square fit from experimental data [8]) and $\langle r \rangle = 4x - 2(1 - x)$. As can be seen, for smaller x Eq. (19) is almost the same as the Gibbs–Di Marzio law.

As a matter of fact, using the following identity for ξ ,

$$\xi = e^{(E_2-E_3)/kT_g} = e^{T_{g0} \ln(3/5)/T} = \left(\frac{3}{5} \right)^{T_{g0}/T} \quad (22)$$

and the Taylor's expansion of $\log(1 - x)$ for x small, Eq. (19) can be written in a similar way to that for the Gibbs–Di Marzio law,

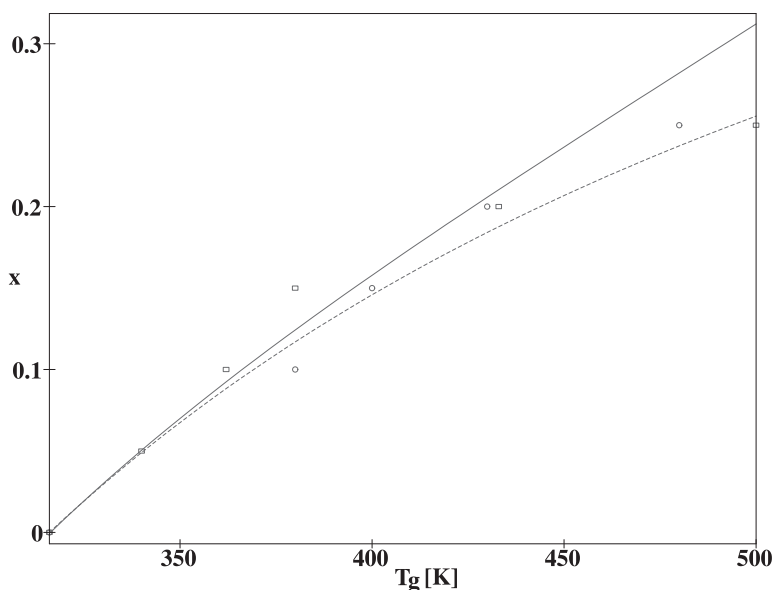


Fig. 3. Comparison between Eq. (19) (solid line) and experimental data [9,10], where x is the concentration of Ge. Squares (circles) are taken from Ref. [9] ([10]). The dashed line corresponds to the Gibbs–Di Marzio law.

$$T_g \approx \frac{T_{g0}}{1 - (2\beta_S x)}, \quad (23)$$

where

$$\beta_S = \frac{\left(\frac{12}{10} - \frac{\mu}{\zeta}\right)}{2 \ln(5/3)}. \quad (24)$$

An important point here is that β_S also depends on T_g . However, the number found for $E_1 - E_3$ means that μ/ζ is $\ll 1$, since μ can be written as $\zeta^{3.86}$ at any temperature and ζ is always less than one. If the term μ/ζ is neglected (this corresponds to not considering the effect of the less stable Ge–Ge bond), β_S is 1.18, which is larger than the β_S found in Ref. [8] ($\beta = 0.72$). A better approximation is obtained by taking μ/ζ as $(3/5)^{2.86}$, which is the first term in the expansion of T_g for

$$\mu/\zeta = (3/5)^{2.86 T_{g0}/T_g} \quad (25)$$

with this approximation, β_S is 0.72.

4. Conclusions

The stochastic matrix method for studying a covalent network glass has been presented. This method allows one to model agglomeration processes of glasses in a simple way. Using it, an analytical relationship between relevant physical parameters of the glass was found. For the a-Ge–Se system, the corresponding relation is similar to the Gibbs–Di Marzio law in the limit of small x . The method can be also applied to other systems such as vitreous B_2O_3 and quasicrystals [7].

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