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Stochastic matrix description of the glass transition

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Abstract. We present a model of the glass transition viewed as the agglomeration and growth of clusters forming a covalent network. The creation of new layers of atoms on the rims of the clusters is treated in a probabilistic way as a linear transformation (encoded in what is called a *stochastic matrix*) of a vector whose components represent the probability distribution of various sites found on the rim. The asymptotic limit of the statistics of sites in the network is given by the matrix eigenvector with eigenvalue equal to one. The model reproduces the modified Gibbs–DiMarzio equation with a system parameter that is comparable to the one observed experimentally for many chalcogenide glasses. Some other features of the glass transition process, like the form of the specific heat, are also obtained.

Although the glass transition has considerable practical and technological importance, there is still no consensus as to which thermodynamical and structural factors determine the glass transition temperature (T_g) [1]. However, this problem must be intimately related to how the complex structures forming the glass network grow as one decreases the temperature of a liquid. For chalcogenide glasses, attention has been devoted to correlating T_g with other physical and chemical properties [2], since such glasses have electric and infrared transmission properties that make them useful in technological applications [3].

In a series of previous papers [4, 5], we have introduced a model of agglomeration and growth which gave useful predictions for covalent network glasses. The model was based on the computation of probabilities of creation of clusters by agglomeration of stable elementary entities. We were able to compute the probability of finding a cluster of a particular type among all the clusters composed of N elementary blocks, and evaluate their time development. The stationary points of the process were identified with the ordered or amorphous configurations representing the dominant tendency of the system's evolution, in terms of the initial probabilities $P_k^{(0)}$. The dependence of the solutions on the temperature (identified with T_g in the amorphous case) and the concentrations of various components enabled us to derive simple relations between these quantities [5]. Nevertheless, in that model one needed exact knowledge of all possible configurations at each stage of the growth process. This was difficult to obtain, since the number of configurations grows in an exponential way.

Here we propose a more powerful method that not only allows us to obtain the most probable configuration in a simple way, but also displays many general features of growth and agglomeration processes. In this new method, the growth of clusters is represented by the successive application of a *stochastic matrix* in a similar way to that of the *transfer matrix* method [6]. However, in our approach, the matrix describes not only the probabilities

of various site occupations in a fixed network (e.g. spins on a lattice), but also takes into account the probabilities of *creation* of new sites in a growing network. The elementary entities are supposed to assemble into clusters, with well-defined rules that can be inferred from their geometrical structure and physico-chemical characteristics. During growth through agglomeration, many complicated processes compete, but gradually larger clusters and parts of the network appear everywhere. Whatever their shape, each can be divided in two parts: the *rim* (or the *border*), composed of all the entities that offer the possibility for a new entity to agglomerate, and the *bulk*, consisting of all entities saturated.

The elementary entities composing the rim are found in a finite number of geometrical situations (more or less entangled with the bulk, and offering one or more possibilities for another entity to stick to). We shall call them *sites*, assuming that the probability of a simultaneous agglomeration of two or more building blocks at a single site is negligible.

While the temperature slowly decreases, the average size of clusters grows due to progressive agglomeration of new atoms that stick to the rim, thus transforming the probabilities of observing various sites on the rim of each cluster. Such a transformation can be encoded in an $n \times n$ matrix (n denoting the number of different sites that can be found on the rim).

We stress the fact that this is an idealized representation of the agglomeration process which in reality is by no means as orderly in time and in space; but we assume that the resulting statistical distribution of larger clusters may be evaluated recurrently as if they were built via one-by-one agglomeration steps. The model that we analyse here concerns the covalent network glasses, which are well described by ball-and-stick models. Nevertheless, it also captures the most important features of any growth process in two or three dimensions.

Consider two star-like elementary blocks, symbolizing two types of atom, with valencies m and m' . Many network glasses correspond fairly well to this definition, e.g. $\text{Ge}_x\text{S}_{1-x}$ glass, or $\text{Ge}_x\text{Se}_{1-x}$ 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 known as $\text{As}_x\text{Se}_{1-x}$, etc.

We shall consider the simplest case of purely *dendritic growth*, when only one bond can be created between two closest neighbours, excluding the possibility of two- or three-membered rings (this assumption is valid only in the low-chalcogenide region; the case in which the massive formation of rings is important like in B_2O_3 glass has been treated in a previous paper [7]). Only three types of site, denoted by u , v , w , can be found on the rim, as shown in figure 1.

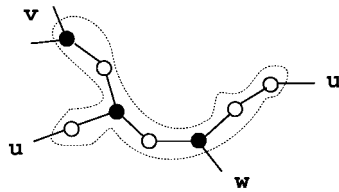


Figure 1. A cluster with the three types of site on the rim. Sites u correspond to A -atoms (white circles) with one free valency, while v and w are B -atoms (dark circles) with two and one free valencies respectively. The atoms in the bulk have all their valencies saturated.

At a time t_1 , one can observe N_u sites of type u , N_v of type v , and N_w of type w . Using these numbers, we can construct a vector that contains as entries the frequencies of each kind of site in the rim:

$$\mathbf{p} = \frac{1}{N_u + N_v + N_w} (N_u, N_v, N_w). \quad (1)$$

After a characteristic time τ , one of these dangling bonds is saturated by an atom A or B , with a certain probability that depends on the probability of making the bond between the atom in the rim and the one that is nearby. If the concentration of the B -atoms in the surrounding medium is c , and that of the A -atoms is $1 - c$, these bonding probability factors (which correspond to the transition factors that appear in the well-known Markovian processes) for each kind of site are:

(i) Bonding in a u -site:

$$\begin{aligned} u + A \Rightarrow u: & \quad P(u, u) \sim 2(1 - c)e^{-\epsilon}/Q_1 \\ u + B \Rightarrow v: & \quad P(u, v) \sim 3ce^{-\eta}/Q_1. \end{aligned}$$

(ii) Bonding in a v -site:

$$\begin{aligned} v + A \Rightarrow u + w: & \quad P(v, u) = P_1(v, w) \sim 4(1 - c)e^{-\eta}/Q_2 \\ v + B \Rightarrow v + w: & \quad P(v, v) = P_2(v, w) \sim 6ce^{-\alpha}/Q_2. \end{aligned}$$

(iii) Bonding in a w -site:

$$\begin{aligned} w + A \Rightarrow u: & \quad P(w, u) \sim 2(1 - c)e^{-\eta}/Q_3 \\ w + B \Rightarrow v: & \quad P(w, v) \sim 2(1 - c)e^{-\alpha}/Q_3. \end{aligned}$$

Here, Q_1 , Q_2 , and Q_3 are normalization factors. We have taken into account the statistical factors (2, 3, 4, and 6, according to the number of free bonds available for each transition), and the Boltzmann factors due to the corresponding energy barriers, defined as follows:

$$\begin{aligned} e^{-\epsilon} &= e^{-E_1/kT} & \text{for } A + A \\ e^{-\eta} &= e^{-E_2/kT} & \text{for } A + B \\ e^{-\alpha} &= e^{-E_3/kT} & \text{for } B + B. \end{aligned}$$

It is important to remark that some processes produce more than one kind of site in the next generation. For example, the process $v + B$ produces a site v and a site w in one step. As a result, there are two different paths of site creation for a w -site that we need to take into account, with probabilities $P_1(v, w)$ and $P_2(v, w)$.

After the saturation of one bond per unit time, the numbers of sites in the rim are given by N'_u sites of type u , N'_v of type v , and N'_w of type w , with frequencies

$$\mathbf{p}' = (p'_u, p'_v, p'_w).$$

These numbers depend on the sums of the probabilities of each process that leads to a certain kind of site. Each of these processes has a probability that is the product of the bonding probability multiplied by the frequency of the available bonds of each kind in the previous generation, i.e.,

$$N'_u = \frac{2(1 - c)e^{-\epsilon}}{Q_1} N_u + \frac{4(1 - c)e^{-\eta}}{Q_2} N_v + \frac{2(1 - c)e^{-\eta}}{Q_3} N_w \quad (2)$$

$$N'_v = \frac{3ce^{-\eta}}{Q_1} N_u + \frac{6ce^{-\alpha}}{Q_2} N_v + \frac{3ce^{-\alpha}}{Q_3} N_w \quad (3)$$

$$N'_w = \frac{4(1 - c)e^{-\eta} + 6ce^{-\alpha}}{Q_2} N_v. \quad (4)$$

Observe that in the last equations, the processes $v + A$ and $v + B$ each generate two sites instead of only one. Thus, new sites are created and we expect the normalization factor of the

vector (N'_u, N'_v, N'_w) to be different from that for (N_u, N_v, N_w) . In fact, using the vector \mathbf{p} we can write

$$\frac{N'_u}{N} = \frac{2(1-c)e^{-\epsilon}}{Q_1} p_u + \frac{4(1-c)e^{-\eta}}{Q_2} p_v + \frac{2(1-c)e^{-\eta}}{Q_3} p_w \quad (5)$$

$$\frac{N'_v}{N} = \frac{3ce^{-\eta}}{Q_1} p_u + \frac{6ce^{-\alpha}}{Q_2} p_v + \frac{3ce^{-\alpha}}{Q_3} p_w \quad (6)$$

$$\frac{N'_w}{N} = \frac{4(1-c)e^{-\eta} + 6ce^{-\alpha}}{Q_2} p_v \quad (7)$$

where $N = N_u + N_v + N_w$. Now we would like to define a new vector, normalized to one that contains the frequencies of $N'_u, N'_v,$ and N'_w . In order to do so, we need to normalize $(N'_u, N'_v, N'_w)/N$. But, from the last equations,

$$\frac{N'_u}{N} + \frac{N'_v}{N} + \frac{N'_w}{N} = \frac{2(1-c)e^{-\epsilon} + 3ce^{-\eta}}{Q_1} p_u + \frac{8(1-c)e^{-\eta} + 12ce^{-\alpha}}{Q_2} p_v + \frac{3ce^{-\alpha}}{Q_3} p_w. \quad (8)$$

If we set this sum to one, this is satisfied when

$$Q_1 = 2(1-c)e^{-\epsilon} + 3ce^{-\eta} \quad (9)$$

$$Q_2 = 8(1-c)e^{-\eta} + 12ce^{-\alpha} \quad (10)$$

$$Q_3 = 2(1-c)e^{-\eta} + 3ce^{-\alpha} \quad (11)$$

and thus the normalization of the new frequencies (p'_u, p'_v, p'_w) is assured. The equations of transformation of the rim can be written in a matrix form, if we define a 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 been grown, with *one new atom at each available site*:

$$\begin{pmatrix} \frac{2(1-c)e^{-\epsilon}}{2(1-c)e^{-\epsilon} + 3ce^{-\eta}} & \frac{(1-c)e^{-\eta}}{2(1-c)e^{-\eta} + 3ce^{-\alpha}} & \frac{2(1-c)e^{-\eta}}{2(1-c)e^{-\eta} + 3ce^{-\alpha}} \\ \frac{3ce^{-\eta}}{2(1-c)e^{-\epsilon} + 3ce^{-\eta}} & \frac{3ce^{-\alpha}}{4(1-c)e^{-\eta} + 6ce^{-\alpha}} & \frac{3ce^{-\alpha}}{2(1-c)e^{-\eta} + 3ce^{-\alpha}} \\ 0 & 1/2 & 0 \end{pmatrix}.$$

This matrix has all its columns normalized to one, and has at least one eigenvalue equal to 1, while other eigenvalues can be real, complex, or imaginary depending on the values of the parameters involved. Complex eigenvalues indicate the presence of an *oscillatory regime* of growth, usually damped by the eigenvalue's norm which is always less than 1. The eigenvalue-1 eigenvector shows the asymptotic distribution $(p_u, p_v, p_w)_\infty$ to which the average statistic tends. This is also the statistics in the bulks if they are very large; for smaller clusters, one should average over the sum of many layers. The eigenvector $(p_u, p_v, p_w)_\infty$ is then

$$\begin{pmatrix} p_u \\ p_v \\ p_w \end{pmatrix}_\infty = \begin{pmatrix} \frac{4(1-c)[2(1-c) + 3c\xi]}{4(1-c)[2(1-c) + 3c\xi] + 9c[2(1-c) + 3c\mu]} \\ \frac{6c[2(1-c)\xi + 3c\mu]}{4(1-c)[2(1-c) + 3c\xi] + 9c[2(1-c) + 3c\mu]} \\ \frac{3c[2(1-c)\xi + 3c\mu]}{4(1-c)[2(1-c) + 3c\xi] + 9c[2(1-c) + 3c\mu]} \end{pmatrix} \quad (12)$$

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

$$\xi = e^{\epsilon-\eta} = e^{(E_1-E_2)/kT} \quad \mu = e^{\epsilon-\alpha} = e^{(E_1-E_3)/kT}.$$

The statistical distribution of various sites on the rim of an average cluster enables us to evaluate the final concentration of the corresponding elementary building blocks in the resulting bulk matter, be it crystalline or amorphous in nature. This concentration need not be in principle the same as in the surrounding medium, especially if the agglomeration process takes place in a vapour or from a solution. But in the case of the glass transition, the concentration of the chemical modifier remains exactly the same as in the hot melt, because if the contrary were true, one would observe a segregation of chemical species, which is clearly not the case.

This circumstance enables us to introduce a constraint of self-consistency, which yields a very useful equation. Let us denote by x the asymptotic value of the concentration of the B -type atoms on the rim of typical cluster. Then the concentration of new B -atoms after a layer grows is given by $x = v_\infty$ (observe that in order to not count a B -atom twice, w -sites do not contribute to x , since this kind of site requires two steps of growth; we only count the first step which is always the formation of a v -site). For the A -atoms we have a similar condition, $1 - x = u_\infty$, which leads to

$$\frac{1-x}{x} = \frac{u_\infty}{v_\infty} = \frac{4(1-c)[2(1-c) + 3c\xi]}{6c[2(1-c)\xi + 3c\mu]}. \quad (13)$$

The requirement that the asymptotic value of the concentration x in the resulting bulk network be the same as in the surrounding hot liquid before the glass transition amounts to the equation $x = c$, which means that during the glass transition a stationary regime is established, i.e. where the mapping $c \rightarrow x(c, T)$ attains one of its *fixed points*. This condition has three solutions: $x = 0$ and $x = 1$, which must represent the fixed points of the agglomeration process (if $x = 0$, it will remain so whatever the rules of agglomeration, and similarly for $x = 1$); and a third fixed point is found:

$$x = \frac{3\xi - 2}{(6\xi - \frac{9}{2}\mu - 2)}. \quad (14)$$

This intermediate ($0 < x < 1$) solution represents a mixture of both A - and B -type atoms at the microscopic level; therefore it can be identified with an amorphous glassy state. It gives implicitly the dependence of the glass transition temperature on the concentration x .

In an efficient glass former the amorphous homogeneous configuration is easily obtained with arbitrarily low values of the *modifier concentration*; the corresponding glass transition temperature is denoted by $T_{0g} = T_g(x = 0)$. The comparison with the experimental value of T_{g0} enables us to fix the difference of the energies $E_1 - E_2$:

$$x = 0 \Rightarrow 3\xi - 2 = 0 \quad \text{or} \quad e^{(E_1-E_2)/(kT_{0g})} = (2/3) < 1. \quad (15a)$$

Therefore,

$$E_1 - E_2 = kT_{0g} \ln(2/3) < 0 \quad \text{i.e.} \quad E_2 > E_1. \quad (15b)$$

This is what should be intuitively expected from the glass-forming tendency: at the local level the system behaves randomly, in a 'frustrated' way, because while the purely statistical factor (3 versus 2) increases the probability of agglomeration of modifier atoms (of the B -type, with valence 3) versus the probability of pairing of the pure glass-former atoms (of the A -type, here with lower valence 2), the Boltzmann factors act in the opposite direction. For a covalent glass with atoms of valences 2 and 4, the model gives a similar result except that the factor $\ln(2/3)$

is changed to $\ln(2/4)$. For example, the average value of T_{0g} for $\text{As}_x\text{Se}_{1-x}$ is $T_{0g} = 316 \text{ K}$ [1], which gives an energy difference of: $E_1 - E_2 = -0.012 \text{ eV}$.

Recalling that $\xi = 2/3$ at $T_{0g} = 316 \text{ K}$, we can easily find the dependence of the glass transition temperature on the modifier concentration in the low-concentration limit:

$$\frac{dT}{dx} = \frac{T_{0g}(1 - \frac{9}{2}\mu)}{\ln(3/2)}. \quad (16)$$

The last equation also allows us to fix the value of $E_3 - E_1$, since once μ is fixed at T_{0g} from (16), then $E_3 - E_1 = KT_{0g} \ln \mu$. However, for $\text{As}_x\text{Se}_{1-x}$, the experimental value of dT/dx is $T_{0g}/0.43$ [8], while $\ln(3/2) = 0.41$. Thus, μ is nearly zero at T_{0g} , which means that the energy barrier $E_3 - E_1$ is large compared to $E_2 - E_1$, i.e., the activation energy for a bond between As atoms is higher than the others. This means that the probability of observing an As–As bond is nearly zero, as is also observed in experiments [9] and postulated by the model of a *chemically ordered network* [1].

Furthermore, when the Boltzmann factor corresponding to $E_3 - E_1$ may be neglected, the formula can be simplified even more, giving for small x

$$T = \frac{T_{0g}}{1 - \beta(\langle x \rangle - 2)} \quad (17)$$

where $\beta = 1/\ln(3/2) = 2.47$ and $\langle x \rangle$ is the *average coordination number*. This formula is the modified Gibbs–DiMarzio equation, which is a semi-empirical rule used for predicting the glass transition temperature [3]. In this law, β is fixed from experimental data; for $\text{As}_x\text{Se}_{1-x}$ and $\text{Ge}_x\text{Se}_{1-x}$, β takes the values 2.32 and 0.74 respectively (taken from references [3, 8]). These values are in agreement with those obtained with the stochastic matrix, since for $\text{Ge}_x\text{Se}_{1-x}$, the method presented here gives $\beta = (1/2) \ln(4/2) = 0.72$. Motivated by this agreement, we searched in the literature for the values of β for other chalcogenide glasses. The results are shown in table 1, where we show the experimental values of β for diverse compounds, classified according to the ratios between the coordination numbers of the atoms involved.

Table 1. The experimental values of β for diverse compounds.

Compound	β	Valence ratio	Reference
$\text{As}_x\text{Se}_{1-x}$	2.32	3/2	[8]
$\text{Ga}_x\text{Te}_{1-x}$	2.69	3/2	[10]
$\text{As}_x\text{S}_{1-x}$	2.32	3/2	[11]
$\text{Ge}_x\text{Se}_{1-x}$	0.74	4/2	[3]
$\text{Si}_x\text{Se}_{1-x}$	0.81	4/2	[12]
$\text{Ge}_x\text{Te}_{1-x}$	0.74	4/2	[13]
$\text{Si}_x\text{Te}_{1-x}$	0.70	4/2	[14]
$\text{Ge}_x\text{S}_{1-x}$	0.73	4/2	[15]

In general, as can be seen from table 1, the parameters obtained via the stochastic matrix are in good agreement with those observed in experiments, even for different kinds of chalcogenide glass.

Another characteristic behaviour of the glass transition that can be predicted by the model is the *inflexion points* occurring in several thermodynamical functions, like the specific heat C_p , defined as $(\partial U / \partial T)_{p=\text{constant}}$.

In order to evaluate $U(T)$ as a function of the parameters E_k , we shall assume that each covalent bridge can be considered as a harmonic oscillator whose instantaneous energy contains essentially *three* contributions: its kinetic energy, the potential energy, roughly equal to the kinetic part if the system is not too far from thermal equilibrium, and the third contribution,

which is the energy needed to create the bonds, which can also be interpreted as the *latent heat*. In the present model, all we need do is to count the relative density of three types of bridge, A – A type with the energy E_1 , A – B type with the energy E_2 , and B – B type with the energy E_3 . But this is very easy to compute if we recall how the creation of those bonds is described by the stochastic matrix: for example, the process leading to the creation of a new A – A bond corresponds to the matrix element $\{M_{uu}\}$ acting on the component p_x of the probability vector, giving the contribution $E_1 M_{uu} p_x$, and so on. New bonds of the A – B type are created each time a B -atom joins the site u , or when an A -atom joins one of the sites v or w , and the B – B bonds are created when a B -type atom joins a site v or w . Summing yields the following expression for $U_l(T)$:

$$U_l = E_1 M_{uu} p_u + E_2 [M_{vu} p_u + M_{uv} p_v + M_{uw} p_w] + E_3 [M_{vv} p_v + M_{vw} p_v + M_{vw} p_v w] \quad (18)$$

using the elements of the matrix M_{ik} defined above.

The resulting curve representing $c_p(T)$ is shown in figure 2, where the inflexion point corresponds to the glass transition temperature [1].

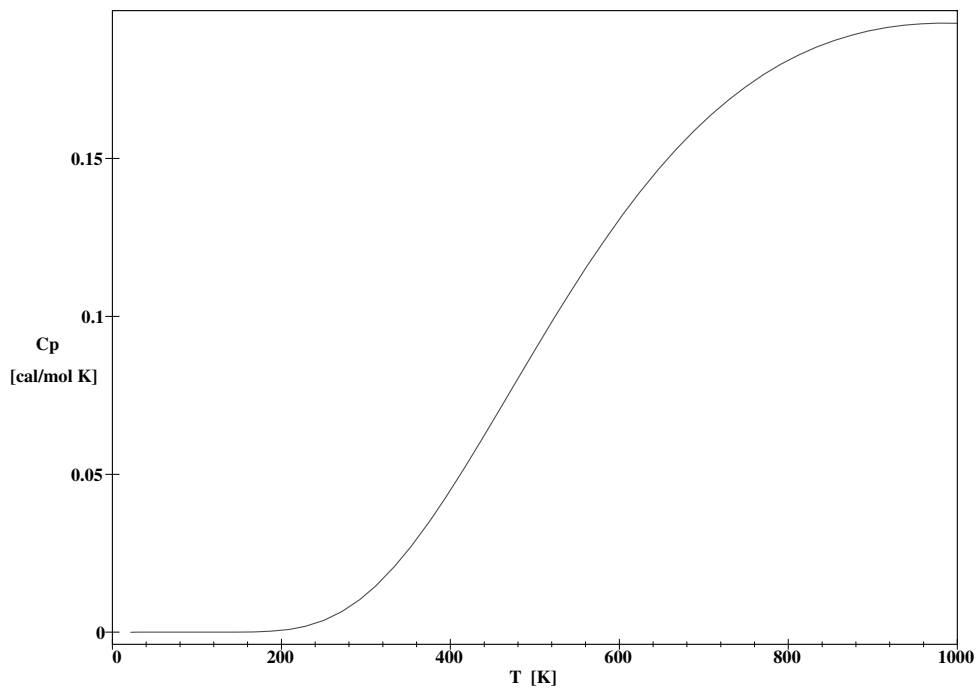


Figure 2. The curve $c_p(T)$ for $x = 0.1$.

The two- or three-dimensional character of the growth enables us to ask questions to which this model can give at least a qualitative answer. For example, it is interesting to follow the time development of the average density of free bonds on the surface of a growing cluster. In our model only the addition of the B -atoms leads to *one* new bond creation, whereas when an A -atom joins the cluster, the number of free bonds remains the same.

Thus, if at a given moment t the number of free bonds on the surface layer of a cluster was $N(t)$, on the next layer produced after the time interval τ the number of free bonds is $N(t + \tau) = (\sigma + 1)N(t)$, where σ is the characteristic exponent of growth, defined as

$$\sigma = \frac{d(\ln N)}{d(t/\tau)} = M_{vu} p_u + M_{uv} p_v + M_{uw} p_w. \quad (19)$$

If σ is greater than 1 (in two dimensions) or 2 (in three dimensions), then the density of free bonds on the surface will grow until they entangle with the result that further growth becomes impossible; in contrast, if it is smaller, then the density of free bonds will decrease with the result that at the end only thin filaments will remain. Thus, within this model, $\sigma + 1$ behaves like an effective fractal dimension. Finally, it can also be proved that $C_p(T)$ is proportional to $d\sigma/dT$, so the glass transition occurs when $d^3\sigma/d^3T = 0$. Within the model, this inflexion point can be interpreted as the one in which the clusters can reach almost infinite sizes since the conditions for growth are satisfied at that particular temperature. Thus, the change in c_p is due to the latent heat of cluster formation.

Our model extends naturally to the case where one has to take into account the effects of rapid cooling. In fact, since each action of M creates a new layer of atoms during the time τ , this enables us to replace M^n by $M^{t/\tau}$. Therefore, we may evaluate the time derivative of the probability distribution vector (denoted by $p(t)$) as follows:

$$\frac{d}{dt}p(t) = \frac{d}{dt}\left(M^{t/\tau}(T(t))p(0)\right) = \left(\frac{1}{\tau}\ln M + \frac{t}{\tau}\frac{dT}{dt}\frac{\partial \ln M}{\partial T}\right)p(t) \quad (20)$$

and then find the stationary configurations as the null eigenvectors, $dp(t)/dt = 0$.

In conclusion, we have described a model of the agglomeration processes that reproduces many of the features of the glass transition, like the modified Gibbs–DiMarzio equation and the shape of the specific heat. In the case of the Gibbs–DiMarzio equation, we showed that the system parameter depends on the logarithm of the ratio between the coordination numbers of each of the components of the glass. This result is in agreement with many experimental results.

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