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Evaluation of the concentration of boroxol rings in vitreous B_2O_3 by the stochastic matrix method

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Abstract. A statistical model in which the stochastic matrix method is applied is used to find the fraction of boron atoms belonging to boroxol rings in a boron oxide (B_2O_3) glass. The method also enables one to evaluate the characteristic energies related to the formation of a single B–O–B unit in an oxygen bridge or in a boroxol ring. The qualitative behaviour of the heat capacity $C_p(T)$ during the glass transition is reproduced, with the inflexion point at the temperature given by the experiment. 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.

1. Introduction

The structure of glasses, and of amorphous solids in general, can be viewed as the absence of long-range order. However, as discussed by Galeener [1], one usually finds local order dictated by the chemical bond, and also some kind of intermediate-range order, in the form of rings or other small regular clusters. In the case of vitreous B_2O_3 we know that the chemical order is very strong; there are only O–B–O bonds with no experimental evidence of wrong bonds. The continuous random network of the glass could be formed by situating every boron atom at the centre of a triangle of oxygen atoms, with the oxygen atoms acting as bridges between pairs of boron atoms.

There are various kinds of experiment that seem to suggest the existence of intermediate-range order in B_2O_3 in the form of boroxol rings. These are six-membered planar and regular rings, B_3–O_3, in which there should be a substantial reduction of the oxygen-bridge angle, since the average O–B–O angle in the network is 130°. The abundance of boroxol rings in the network should be substantial to explain the experiments, yet it has been difficult to settle this matter, due to the fact that recent molecular dynamics calculations have found it difficult to produce boroxol rings, and the claim has been made that they are not needed to explain most of the experimental data [2, 3]. One should mention that there is not yet a model of a structure containing many boroxol rings able to predict the density of the material.

Among the most conspicuous features attributed to boroxol rings are the extremely sharp peaks found in vibrational spectroscopic studies, such as ones based on infrared and Raman scattering [4, 5]. There is no convincing explanation for these sharp peaks if one denies the existence of intermediate-range order. There exist various kinds of theoretical calculation,

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ranging from effective-medium models [6] to more detailed ones [8], which are able to explain all of the experimental features only if one assumes large quantities of boroxol rings in the disordered network. A more definite argument in favour of the existence of boroxol rings comes from recent neutron scattering experiments [7], which can be explained coherently only if ∼80% of the boron atoms belong to rings.

Evidently, the formation of rings should be a consequence of the way in which the solid is grown, since they are not present in any of the crystalline forms of B_2O_3, and some kinetic models are needed to explain their formation. Molecular dynamics is unlikely to give definite answers, since the main reason for the formation of rings should be a peculiar three-body force that allows modification of the bridge angle. On the other hand, a fundamental idea advanced by Galeener is that a six-membered ring should be planar and somehow trapped in an 'energetic bottle-neck', in such a way that it could be stable under small thermal fluctuations. This allows one to think that the bonding energy of a normal oxygen bridge should be somewhat smaller than the bonding energy of the same entity in a boroxol ring. As a corollary, one may believe that the final proportion of atoms in boroxol rings is mainly governed by the conditions of the growing process. More generally, one finds that near the glass transition, either the density or the viscosity changes abruptly, but they are not discontinuous, suggesting that at any stage of solidification one should find clusters of bonded atoms whose average size increases continuously as the temperature approaches the glass transition temperature from above. These clusters do not need to be in equilibrium, since local variations of the size of the clusters are likely to be large.

In a series of earlier papers [9–14] we introduced a model of agglomeration to study the growth and structure of solids, which succeeds in making useful predictions for covalent network glasses. The model was based on the computation of probabilities of creation of large clusters of atoms by consecutive one-by-one agglomeration of stable elementary entities, forming first *doublets*, then *triplets*, and so forth, i.e. clusters composed of two, three, and more such entities.

At each step of the agglomeration process, consisting in adding one more entity, one calculates the probability factors, including the statistical weight (multiplicity) of the step, and the Boltzmann factor, which takes into account the corresponding energy barrier.

In this paper we shall use the same ideas to build up a model of growth which is simpler and more powerful that the previous one, to investigate the process of growth and the origin of boroxol rings in vitreous B_2O_3.

Instead of tracing along all possible pathways that lead to the creation of a given type of cluster, starting from the formation of doublets, and then computing their probability distribution, here we propose to follow a totally probabilistic description of the agglomeration process. From the beginning, we consider an *ensemble* of all of the clusters of various sizes, and look at the probability distribution of different types of *site* at their rims. Then we evaluate the probabilities of transformations of these sites due to the gradual agglomeration of new singlets, and establish the recurrent linear transformations ruling this process. The eigenvectors of these transformations corresponding to the unit eigenvalue give the asymptotic statistics of local configurations in the network.

With this probability distribution we can evaluate several physically pertinent quantities, such as the internal energy stored in the bonds, and the characteristic exponent ruling the growth of the number of free valencies at the rim of an average cluster, which seems to give rise to a dominant contribution to the observed exponential behaviour of the viscosity during the glass transition.

2. The stochastic matrix description of the growth process

Here we propose to investigate the thermodynamic properties of vitreous B_2O_3 using the *stochastic matrix method*, introduced recently by one of the authors (Kerner [15]). This method is more general than the previous one, using non-linear differential systems and their singular solutions, and it is based on the assumption that the dominant phenomenon during the glass transition is a rapid agglomeration of small clusters into bigger ones, leading to the formation of a global random network.

During the growth through agglomeration, many complicated and competing processes take place, but, gradually, bigger clusters and parts of the network appear everywhere. Whatever their shape, one thing seems to be obvious: at each particular stage of their evolution, they can be divided in two parts: the *rim* (or the *border*), composed of all of the entities that offer a potential possibility for a new entity to stick and agglomerate, and the *bulk* (or the *interior*)—that is, all of the units that have formed all their bonds already, as shown in figure 1 below.

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

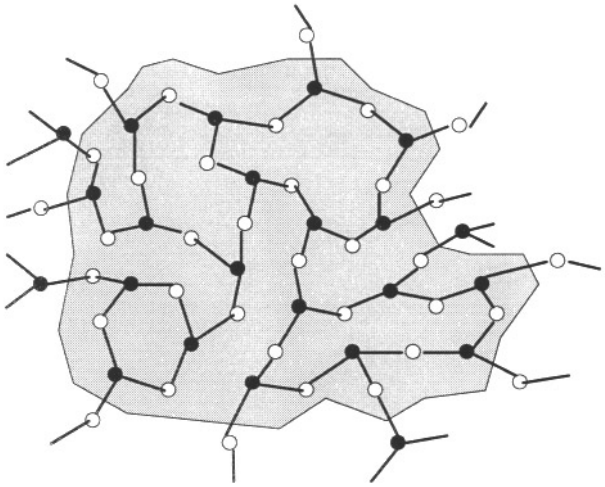

Figure 1. A cluster composed of two types of atom. The bulk is identified as the shaded part.

While the temperature slowly decreases, the average size of the clusters grows, due to the progressive agglomeration of new atoms that stick to the rim. After a characteristic time τ (which, of course, depends on the physical conditions imposed on the sample and on its composition), a new layer of atoms is created, thus transforming the probabilities of observing various sites on the rim.

The process of growth at the rim can be described by a matrix acting on a vector. In order to do this, the sites at the rim of a cluster are denoted by appropriate symbols and represented as a vector whose components are the probabilities of finding a given site at the rim of a cluster of a certain size. 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. Now, each sticking process has a certain probability of occurring; thus, 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 to forming a certain kind of bond.

For B_2O_3, the most elementary building block is a triangle, $B(O_{1/2})_3$ (there is clear experimental evidence for this fact [13]). In what follows, we shall refer to it as a 'singlet'.

Two singlets can be connected only as a chain, called a 'doublet', since other ways of connecting two units would produce a twofold ring (a dimer), which would be energetically costly and is not seen in experiments [16]. Otherwise, it would produce in x-ray or neutron diffraction patterns a sharp and characteristic peak, corresponding to the B–B bond length [17]. Let us say that the energy cost of forming this chain is E_1. After a doublet is produced, two situations can occur if a new singlet is added: the newly arriving singlet can form a longer chain (a 'triplet') or it can close a ring, with a different energetic cost (E_2). The agglomeration process occurs at a given temperature T, at which the individual bonds reach equilibrium. Therefore, we shall use the notation

$$e^{-\epsilon} = e^{-E_1/kT}$$

and

$$e^{-\eta} = e^{-E_2/kT}.$$

A short inspection of the possible configurations at the rim of the clusters resulting from agglomeration of the boron–oxygen singlets shows that whenever a new singlet is coming close to the rim, it can attach itself to one of the sites presenting free valence ions; it may encounter one of the *six* situations shown in figure 1. We shall denote these configurations by x, y, z, t, u, and w, with x meaning an isolated singlet at the rim with only one free valence ion available, y corresponding to a singlet at the rim with two free valence ions available, z denoting two singlets in a chain, with four valence ions, and finally t corresponding to three singlets in a chain.

In principle we could have also considered longer chains of singlets, but this would lead to the multiplication of sites and transitions. It can be argued that the probability of creation of longer chains in covalent glasses is negligible, because if the contrary was the case, it would lead to local 'voids' which, in turn, would create density fluctuations which are not observed in real glasses.

The terminations u each correspond to a free bond of a boron atom trapped in a ring, while a w-termination corresponds to two valence ions of two different boron atoms trapped in the same ring.

Let us assume that, at a given temperature, the hot liquid can be regarded as a mixture of clusters of various sizes, and that the chemical interactions are largely between single units and bigger clusters, because of the low mobility of the latter.

During a slow cooling process, a new boron–oxygen unit comes close to one of these clusters and attaches itself to the free valence ions at the rim of the cluster, in one of the *six* ways mentioned before. We shall evaluate the evolution of the probabilities x, y, z, t, u, and w as functions of the cluster size (also interpreted as the number of elementary agglomeration steps leading to its creation).

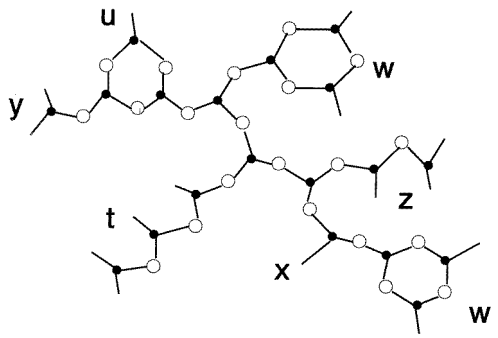

Figure 2. A typical cluster in B_2O_3 with six types of site on the rim.

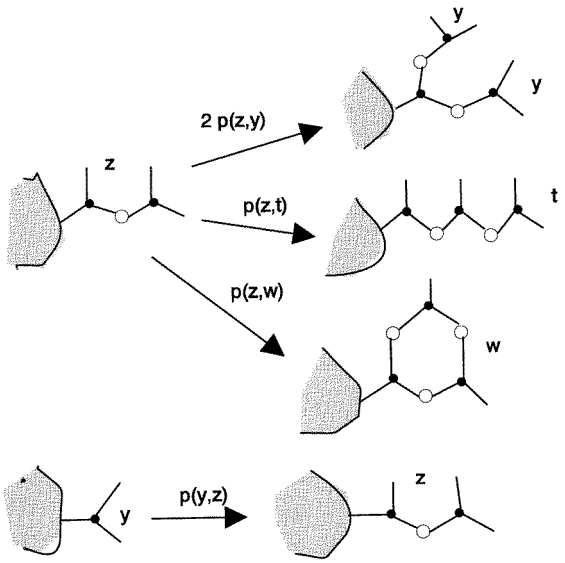

Figure 3. Two examples of site-transforming transitions via the addition of one single atom to the rim.

It should be stressed that this one-to-one agglomeration of elementary steps might not occur in reality, and it is only useful as a mental representation. Most probably, such singlets are rare in the liquid melt close to the glass transition temperature T_g. However, the attribution of transition probabilities for each elementary step can be given a meaning in the following way.

At any moment, the melt contains billions of various clusters composed of N_k atoms, whose 'centre of gravity' evolves towards higher values of $\langle N \rangle$ as the temperature decreases. Consider one of these clusters, labelled $C_{N_k}^{(1)}$, belonging to the family formed by all clusters with N_k atoms. Once the choice of this particular cluster $C_{N_k}^{(1)}$ has been made, consider, among all of the clusters with $N_k + 1$ atoms, only those which have the cluster $C_{N_k}^{(1)}$ as a sub-cluster. Depending on the particular choice (i.e. the shape and the number of free valence ions at the rim of $C_{N_k}^{(1)}$), we shall have a whole spectrum of such clusters, denoted

by $C^{\alpha}_{(N+1)_k}$, with $\alpha = 1, 2, \ldots, L$. Each of them could be produced from the cluster $C^{(1)}_{N_k}$ by addition of just one singlet to one particular site on the rim, although, in reality, many different creation pathways, mostly via agglomeration of clusters of lesser dimensions, could effectively occur.

However, if one considers the relative abundance of all possible types of cluster with $N + 1$ boron atoms that could have evolved from the cluster $C^{(1)}_{N_k}$, one should get the same probability distribution as is the result of attributing appropriate Boltzmann factors corresponding to the characteristic energies needed to create either a single O–B–O bridge, or a boroxol ring, and containing also the statistical factors depending on the multiplicity of a given agglomeration step.

With this in mind, it is easy to find the contributions to the probability factors of all possible transitions. The result is given below in the form of a table in which all transformations of sites via one elementary agglomeration step are displayed. The way to count the multiplicities of each transition becomes clear when one looks at the examples shown in figure 3.

Here we took into account the purely statistical factors according to the number of free bonds and the multiplicity available for each transition, which can be quite easily found from purely geometrical considerations, and the Boltzmann factors taking into account the corresponding energy barriers, defined above, as follows: $\mathrm{e}^{-E_1/kT}$ for a simple bond, $\mathrm{e}^{-E_2/kT}$ for a ring creation. The 'table' is as follows.

$$
\begin{aligned}
&x \Rightarrow y: && P(x, y) \sim 3\mathrm{e}^{-\epsilon}\\
&y \Rightarrow z: && P(y, z) \sim 6\mathrm{e}^{-\epsilon}\\
&z \Rightarrow \begin{cases} y: & P(z, y) \sim 2 \times 3\mathrm{e}^{-\epsilon}\\ \text{or } t: & P(z, t) \sim 6\mathrm{e}^{-\epsilon}\\ \text{or } w: & P(z, w) \sim 12\mathrm{e}^{-\eta} \end{cases}\\
&t \Rightarrow \begin{cases} y + z: & P_1(t, y) \text{ and } P(t, z) \sim 3\mathrm{e}^{-\epsilon}\\ \text{or } x + y: & P_1(t, x) \text{ and } P_2(t, y) \sim 3\mathrm{e}^{-\epsilon}\\ \text{or } y + u: & P_3(t, y) \text{ and } P(t, u) \sim 6\mathrm{e}^{-\eta}\\ \text{or } x + w: & P_2(t, x) \text{ and } P(t, w) \sim 12\mathrm{e}^{-\eta} \end{cases}\\
&u \Rightarrow y: && P(u, y) \sim 3\mathrm{e}^{-\epsilon}\\
&w \Rightarrow y + u: && P(w, y) \text{ and } P(w, u) \sim 6\mathrm{e}^{-\epsilon}.
\end{aligned}
$$

The factors $P(x, x)$, $P(x, y), \ldots$ that define the statistical weights of the transitions resulting in the corresponding *transformations of sites* can be displayed as a 6×6 matrix:

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

Note that the zeros correspond to the absence of many transitions, e.g. $x \Rightarrow x$, and $y \Rightarrow x$. In this matrix each of the entries symbolizes the sum of all partial probabilities whenever there is more than one pathway leading to the given configuration, e.g. $P(t, x) = P_1(t, x) + P_2(t, x)$.

Inserting all of the contributions, the explicit form of the matrix is

$$\begin{pmatrix} 0 & 0 & 0 & 3e^{-\epsilon}+12e^{-\eta} & 0 & 0 \\ 3e^{-\epsilon} & 0 & 6e^{-\epsilon} & 9e^{-\epsilon}+6e^{-\eta} & 3e^{-\epsilon} & 6e^{-\epsilon} \\ 0 & 6e^{-\epsilon} & 0 & 3e^{-\epsilon} & 0 & 0 \\ 0 & 0 & 6e^{-\epsilon} & 0 & 0 & 0 \\ 0 & 0 & 0 & 6e^{-\eta} & 0 & 6e^{-\epsilon} \\ 0 & 0 & 12e^{-\eta} & 12e^{-\eta} & 0 & 0 \end{pmatrix}. \tag{1}$$

Let us recall that the above matrix is supposed to act on a column vector representing the probabilities p_x, p_y, p_z, p_t, p_u, and p_w satisfying the normalization condition $p_x + p_y + p_z + p_t + p_u + p_w = 1$; and that we want to obtain a new distribution of probabilities satisfying the same normalization condition. In order to ensure this, the sum of the entries in each column of the above matrix must be equal to one, also. This is why one must divide each element of a column by the sum of all of the elements of that column.

After normalization, we get the following stochastic matrix that transforms the probabilities of finding one configuration at the rim of a cluster, $(p_x, p_y, p_z, p_t, p_u, p_w)$ into a new set of probabilities $(p'_x, p'_y, p'_z, p'_t, p'_u, p'_w)$ after the characteristic time τ during which an entire new layer of atoms has been grown, with *one new atom at each available site:*

$$\mathbf{M} = \begin{pmatrix} 0 & 0 & 0 & \dfrac{1+4\xi}{5+12\xi} & 0 & 0 \\ 1 & 0 & \dfrac{1}{2+2\xi} & \dfrac{3+2\xi}{5+12\xi} & 1 & \dfrac{1}{2} \\ 0 & 1 & 0 & \dfrac{1}{5+12\xi} & 0 & 0 \\ 0 & 0 & \dfrac{1}{2+2\xi} & 0 & 0 & 0 \\ 0 & 0 & 0 & \dfrac{2\xi}{5+12\xi} & 0 & \dfrac{1}{2} \\ 0 & 0 & \dfrac{2\xi}{2+2\xi} & \dfrac{4\xi}{5+12\xi} & 0 & 0 \end{pmatrix} \qquad \text{where } \xi = e^{\epsilon-\eta}.$$

3. Mathematical analysis of the agglomeration process

Using the above matrix, the growth of clusters is modelled by the successive application of the matrix to an arbitrary initial vector $\boldsymbol{v}_0$. Thus, the evolution of the probabilities at the rim after j steps is given by

$$\boldsymbol{v}_j = \mathbf{M}^j \boldsymbol{v}_0. \tag{2}$$

The final configuration depends only on the eigenvectors of the stochastic matrix. In order to show this, we decompose the vector $\boldsymbol{v}_0$ as

$$\boldsymbol{v}_0 = c_1\boldsymbol{e}_1 + c_2\boldsymbol{e}_2 + c_3\boldsymbol{e}_3 + c_4\boldsymbol{e}_4 + c_5\boldsymbol{e}_5 + c_6\boldsymbol{e}_6 \tag{3}$$

where $\boldsymbol{e}_i$ is the eigenvector of $\mathbf{M}$ corresponding to the eigenvalue λ_i, and c_i is the projection of $\boldsymbol{v}_0$ onto $\boldsymbol{e}_i$. By inserting (3) into (2) we get

$$\boldsymbol{v}_j = c_1\lambda_1^j\boldsymbol{e}_1 + c_2\lambda_2^j\boldsymbol{e}_2 + c_3\lambda_3^j\boldsymbol{e}_3 + c_4\lambda_4^j\boldsymbol{e}_4 + c_5\lambda_5^j\boldsymbol{e}_5 + c_6\lambda_6^j\boldsymbol{e}_6. \tag{4}$$

It is easy to prove that a matrix with all of its 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. The complex eigenvalues indicate the presence of

an *oscillatory regime* of growth, usually damped by the norm of the eigenvalue, which is always less than 1. The imaginary part can be interpreted as a circular frequency measured in radians per unit time (i.e. the number of layers), or the real time divided by the characteristic time τ. Due to exponential damping, only eigenvectors with norm one remain after many applications of the stochastic matrix. If we suppose that $\mathbf{M}$ has only one eigenvalue 1 (corresponding to $\lambda_1 = 1$), then, in the limit of large j, $\boldsymbol{v}_j$ converges to

$$\boldsymbol{v}_j = \boldsymbol{e}_1 = \boldsymbol{u}, \text{ the eigenvector with } \lambda_1 = 1.$$

since $c_1 = 1$ due to probability conservation. Observe that this result is independent of the initial conditions, as expected.

As a matter of fact, among the eigenvectors of a stochastic matrix, only those belonging to the eigenvalue 1 have a trace equal to 1, whereas all other eigenvectors have null trace. This is because, by construction, a stochastic matrix preserves the trace of a vector:

$$\mathrm{Tr}(\mathbf{M}\boldsymbol{v}) = \sum_{k=1}^{n} (\mathbf{M}\boldsymbol{v})^k = \sum_{k=1}^{N} \left(\sum_{i=1}^{n} M_i^k v^i \right) = \sum_{i=1}^{n} v^i = \mathrm{Tr}(\boldsymbol{v})$$

because $\sum_{k=1}^{n} M_i^k = 1$ for any value of i by definition of the stochastic matrix.

Therefore, for an eigenvector $\boldsymbol{e}_\alpha$ corresponding to the eigenvalue $\lambda_\alpha \neq 1$, we have

$$\mathrm{Tr}(\mathbf{M}\boldsymbol{e}_\alpha) = \mathrm{Tr}(\lambda_\alpha \boldsymbol{e}_\alpha) = \mathrm{Tr}(\boldsymbol{e}_\alpha) = 0 \qquad \text{if } \lambda_\alpha \neq 0.$$

For the same reason, in the situation in which there is only one eigenvector with eigenvalue 1, its trace must be equal to one if we remain in the domain of probabilistic distributions: if we denote this vector by $\boldsymbol{u}$, with $\mathbf{M}\boldsymbol{u} = \boldsymbol{u}$, and if

$$\boldsymbol{v} = c_1 \boldsymbol{u} + \sum_{\alpha} c_\alpha \boldsymbol{e}_\alpha$$

with $\mathrm{Tr}(\boldsymbol{v}) = 1$, then obviously, because all of the vectors $\boldsymbol{e}_\alpha$ are traceless,

$$\mathrm{Tr}(\boldsymbol{v}) = 1 = \mathrm{Tr}\left(c_1 \boldsymbol{u} + \sum_{k=1}^{n} c_\alpha \boldsymbol{v}_\alpha \right) = c_1 \,\mathrm{Tr}(\boldsymbol{u}) = c_1$$

so one must have $c_1 = 1$ independently of the initial conditions. This is why the limit after many consecutive actions of the matrix $\mathbf{M}$ on any initial vector $\boldsymbol{v}$ is always the same.

As a consequence, the evolution of the rim attains a stable statistical regime after successive steps of growth; this regime is governed solely by the statistics represented by the eigenvector with eigenvalue one. The eigenvector corresponding to the eigenvalue 1 determines the distribution $(p_x, p_y, p_z, p_t, p_u, p_w)_\infty$ to which the average statistic tends asymptotically. This is also the statistics of the bulk if the clusters are really large. For clusters of intermediate size, one should instead average over the sum of many layers. (Here too, like in differential geometry, the surface is in some sense the *differential* of the volume, and the circumference is a differential of an area.)

The stochastic matrix model can in principle describe also the growth of ordered structures. In a general case, this may occur when the stochastic matrix characterizing the agglomeration process has a particular set of complex eigenvalues. It may happen (if the number of sites is large enough) that among the eigenvalues there is one pair (or more) of complex conjugate eigenvalues with absolute value 1, which can be denoted by $\mathrm{e}^{\mathrm{i}\omega}$ and $\mathrm{e}^{-\mathrm{i}\omega}$. Then, in a real basis, one will observe asymptotic rotation around the unit eigenvector, without damping: when all other components are squeezed because the corresponding eigenvalues have a negative real part, the action of the matrix $\mathbf{M}$ becomes as follows:

$$\mathbf{M}\boldsymbol{v} = \mathbf{M}(\boldsymbol{u} + c_1 \boldsymbol{e}_1 + c_2 \boldsymbol{e}_2) = \boldsymbol{u} + c_1 \cos\omega \boldsymbol{e}_1 + c_2 \sin\omega \boldsymbol{e}_2.$$

The circular frequency ω, like all of the other eigenvalues, is a function of the temperature and the characteristic energies E_1 and E_2. In more complicated models it may also depend on the concentration of various modifiers, and other parameters. If ω is an arbitrary real number incommensurate with π, the consecutive positions of vectors obtained from the initial one after k steps, $\mathbf{M}^{(k)}\boldsymbol{v}_0$, will densely cover a circle around the axis given by the unit vector $\boldsymbol{u}$. This behaviour can be called 'chaotic'. But it may happen (for a precise choice of values of the essential parameters, and in particular for a precise value of the temperature T) that ω is equal to $2\pi/n$, with an integer (and not too large) value of n. Then one will observe a periodic repetition of the same sequence of several configurations, characteristic for a crystalline state.

4. The characteristic energy and statistics of boroxol rings

In our statistical model for the B_2O_3 glass, the only free parameter is ξ, or the excess free energy when closing a ring $(E_1 - E_2) = kT\ln(\xi) = \mathcal{F}$.

In order to fix this parameter, we shall study the behaviour of the internal energy U, and the specific heat, c_p, near the glass transition temperature. We shall take this temperature from experiment.

The internal energy of the glass is obtained by observing that, in the rim, the average potential energy involved in the growing process is simply the probability of forming a new bond on a certain kind of site multiplied by the energetic cost of this. Each time a boroxol ring is created, there is an energy cost given by E_2, while adding a bond to create a chain costs an energy E_1. There is also a contribution from the kinetic energy, which contributes $3kT/2$. Thus, if we neglect other contributions like rotational or vibrational modes, the energetic cost of the agglomeration at the jth rim $(U_R(j))$ is

$$U_R(j) = \frac{3kT}{2} + E_2 P_B^j(T) + E_1(1 - P_B^j(T))$$

where $P_B^j(T)$ is the probability of forming a ring when passing from the jth layer to the $(j+1)$th one, and is simply given by counting the proportion of rings that were formed between the step j and the step $j+1$. This information is encoded in the matrix as the probability of the processes $z_j \to w_{j+1}$ and $t_j \to u_{j+1}, w_{j+1}$, so

$$P_B^j(T) = p_{z_j}(M_{63}) + p_{t_j}(M_{54} + M_{64}).$$

Now, the internal energy is an extensive parameter, and the total energy after N steps of growth is the sum of the energy in each layer of growth:

$$U(T) = \frac{3NkT}{2} + E_1 N + (E_2 - E_1)\sum_{j=1}^{N} P_B^j(T). \tag{5}$$

The specific heat is obtained by taking the derivative of U with respect to the temperature:

$$c_p(T) = \frac{3Nk}{2} + (E_2 - E_1)\sum_{j=1}^{N} \frac{\mathrm{d}P_B^j(T)}{\mathrm{d}T} \tag{6}$$

and if we calculate $c_p(T)$ for a large number of steps of growth, then $P_B(T)$ can be replaced by its limit value in the stationary regime:

$$c_p(T) = \frac{3Nk}{2} + (E_2 - E_1)N\frac{\mathrm{d}P_B^{\infty}(T)}{\mathrm{d}T}. \tag{7}$$

In glasses, it is generally observed that there is an inflexion point and a precipitous decrease in the heat capacity [18] at the glass transition temperature (T_g). Then, we will demand that $\partial^2 c_p(T)/\partial T^2$ must be zero at T_g:

$$\frac{\partial^2}{\partial^2 T}\left[c_p(T)\right]_{T=T_g} = 0$$

and by using (7) we get

$$\frac{\mathrm{d}^3}{\mathrm{d}^3 T}\left[P_B^{\infty}(T)\right]_{T=T_g} = 0. \tag{8}$$

The latter condition fixes the parameter ξ at T_g, and this quantity is well known from various experiments to vary from $T_g = 470$ K to 530 K [19]. For $T_g = 470$ K, we have found that condition (8) is satisfied for two values; one of these is

$$E_1 - E_2 = 0.214 \text{ eV} = 4.927 \text{ kcal mol}^{-1}.$$

and the other one is

$$E_1 - E_2 = 0.068 \text{ eV} = 1.566 \text{ kcal mol}^{-1}.$$

However, only one of these values corresponds to the real glass. When using the second value to draw the specific heat versus temperature curve, the first inflexion point that appears as one raises the temperature from zero occurs at a temperature much lower than $T_g = 470$ K. Only the first energy difference leads to the correct behaviour of $c_p(T)$. In figure 4 we show the contribution to c_p coming from the second term in (7) using an energy difference of 0.214 eV.

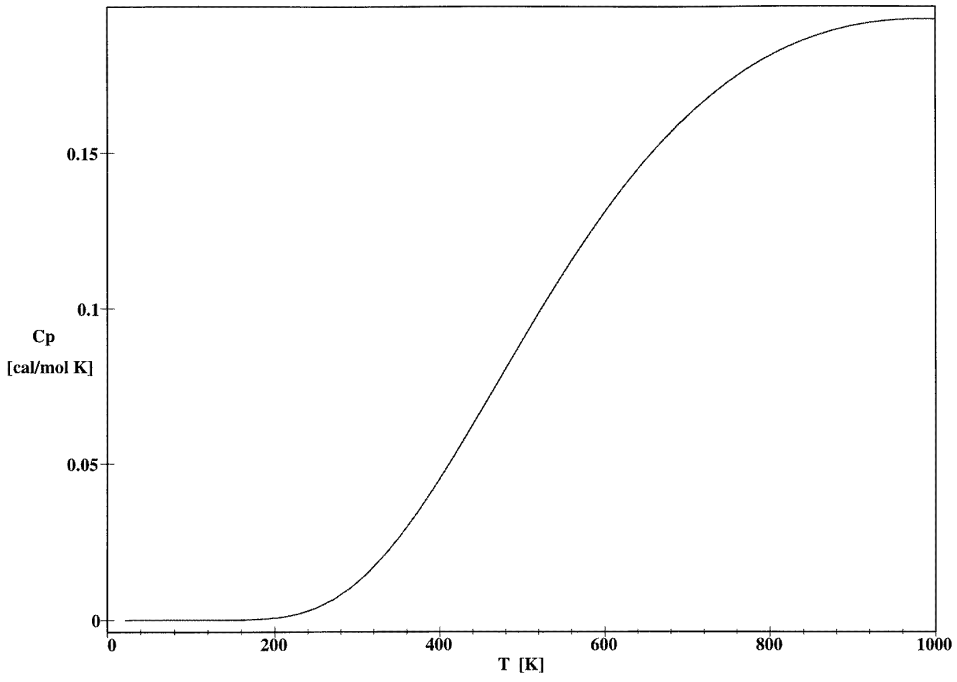

Figure 4. The specific heat as a function of T.

Another fit is possible when $T_g = 530$ K, which gives

$$E_1 - E_2 = 0.242 \text{ eV} = 5.572 \text{ kcal mol}^{-1}.$$

These values are very close to other estimates found in the literature. Walrafen and co-workers [19] have found 5.0 ± 0.04 kcal mol^{-1}, obtained from experimental data. Snyder [20] estimated 6.0 kcal mol^{-1}, on the basis of *ab initio* quantum mechanical calculations.

After the energy difference $(E_1 - E_2)$ is fixed, we can calculate the fraction of boron atoms in the glass that are contained in boroxol rings ($F_B = N_B/N_T$). At this point, we must remember that, in principle, the evolution of the vector $\boldsymbol{v}_j$ only gives information on the evolution of the probabilities on the rim, while the fraction F_B is a property of the bulk.

However, this bulk is formed by the addition of consecutive layers. Therefore, by adding the number of atoms that are trapped into boroxol rings in each step of growth we can find N_B. Still, another problem remains to be solved. The creation of a ring needs three steps of agglomeration. Then, to decide whether an atom is inside a boroxol ring, we must consider more than one step of agglomeration.

This counting can be achieved in the following way. We can count the number of rings that are closed in the jth step (a u-site contributes one atom, and a w-site contributes two) and consider that the sites that are contained in the chains of the type y and t can be trapped into a boroxol ring of the next generation, which is given by the probability of the processes $z_j \to w_{j+1}$ and $t_j \to u_{j+1}, w_{j+1}$. Using these criteria, the number of atoms in boroxol rings in the jth step is

$$N_B^j = u_i + w_j + 2z_j(M_{63}) + 2t_i(M_{54} + M_{64}).$$

To calculate the fraction of atoms inside boroxol rings (F_B), we must divide N_B^j by the total number of atoms that are at the rim (N_T), which can be evaluated as the sum of the probabilities of all kinds of site, weighted by the corresponding number of atoms with free bonds. Thus we get

$$F_B = \frac{u_j + w_j + 2z_j(M_{63}) + 2t_j(M_{54} + M_{64})}{x_j + y_j + 2z_j + 3t_j + u_j + 2w_j}. \tag{9}$$

In figure 5 we show the evolution of F_B as a function of the number of elementary steps of growth, with the energy difference fixed at $E_1 - E_2 = 0.214$ eV for two different (arbitrarily chosen) initial conditions. Note that, as predicted, some damped oscillations are clearly visible at the initial stages, but they rapidly disappear after the system reaches the stationary regime, a few steps later.

This is important because it tells us that the final structure of the glass is determined just by few local configurations of a very small size. This explains the lack of long-range correlations in a glass, and also justifies the notion of medium-range order introduced by Galeener [1].

Notice also that the oscillations present a period of roughly three steps. This is due to the fact that for completing one boroxol ring, at least three steps of growth are necessary. Then, if the initial configuration is only a cluster with x- and y-terminations, the rings appear after three steps. But after completing most of the rings, the number of chains that can give new rings is reduced, so the formation of rings is inhibited again for three generations, and so on.

The stationary value is near 80% of boron atoms trapped in boroxol rings. This number can be obtained more exactly if we use the eigenvector $\boldsymbol{e}_1 = \boldsymbol{u}$, which is the only one that remains at the end.

After many steps of agglomeration, the value of F_B is given by the asymptotic expression

$$F_B = F_B^\infty \tag{10}$$

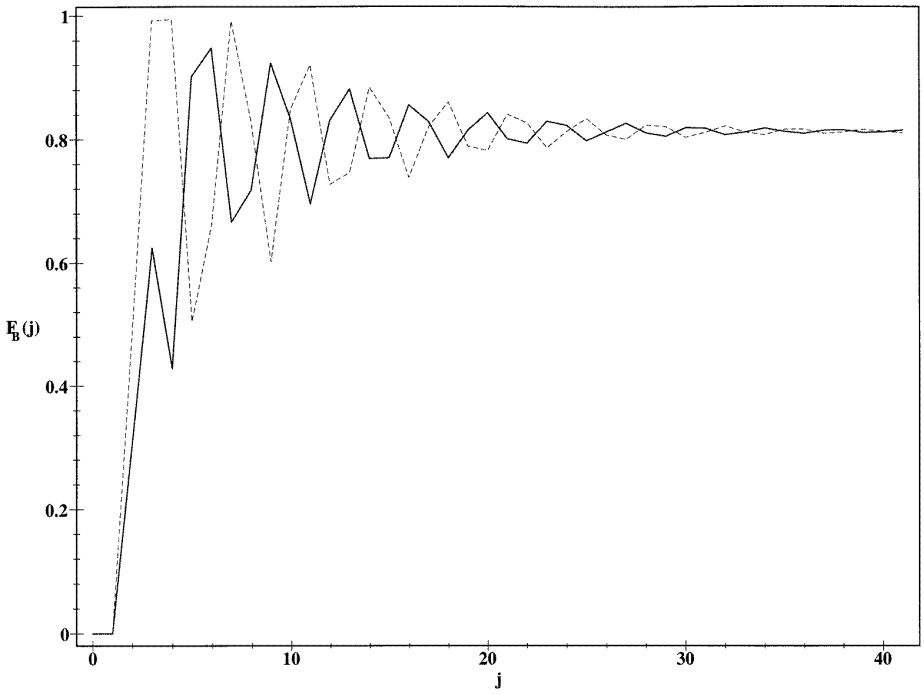

Figure 5. Two examples of the evolution of N_B^k for two different sets of initial conditions.

where F_B^∞ is obtained by substituting the components of the eigenvector with eigenvalue one into (9). In this model, the eigenvector is

$$\boldsymbol{e}_1 = \frac{1}{84\xi^2 + 107\xi + 25} \begin{pmatrix} 1 + 4\xi \\ 24\xi^2 + 34\xi + 9 \\ 24\xi^2 + 34\xi + 10 \\ 12\xi + 5 \\ 3\xi(4\xi + 3) \\ 2\xi(12\xi + 7) \end{pmatrix}.$$

Inserting the values $E_1 - E_2 = 0.21$ eV and $T_g = 470$ K into the last expression and substituting in (10) we get that $F = 81.3\%$. This result is in very good agreement with other theoretical and experimental results like the 83% proposed by Jellison *et al* [21], 80% proposed by Hannon *et al* [22] and 84% proposed by Micoulaut *et al* [13].

In the case of B_2O_3, we can observe this phenomenon in an approximate way if we exclude the formation of boroxol rings. This is equivalent to a reduction of the dimension of probabilistic vectors and the stochastic matrix, leaving only the variables p_y, p_z, and p_t, because without any rings the site 'x' will never appear. With this assumption the stochastic matrix becomes

$$\begin{pmatrix} 0 & \frac{1}{2} & \frac{3}{4} \\ 1 & 0 & \frac{1}{4} \\ 0 & \frac{1}{2} & 0 \end{pmatrix}$$

and has one eigenvalue 1 and two complex conjugate eigenvalues:

$$\lambda_{1,2} = -\frac{1}{2} \pm \frac{\mathrm{i}}{2\sqrt{2}}.$$

This does not lead to periodicity, because the angle is incommensurate with π and the damping factor is quite important. But we observe a periodic behaviour in the simplified case with the variable p_t suppressed, too. Then the matrix reduces to

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

which corresponds to the periodic exchange of all the sites y transforming into sites z, and vice versa. Similar oscillating behaviour may be expected in the case in which two or more eigenvectors of eigenvalue 1 are present, and the repeated action of the corresponding stochastic matrix amounts to the consecutive oscillations of the probability vector between these two (or more) eigenvectors.

In any case, in order to describe a genuine crystallization process, one must go much further, introducing more types of site, which would eventually contain elementary cells that can generate a crystalline state via translation symmetry.

5. The characteristic exponent σ and the glass transition

The two- or three-dimensional character of the growth enables us to address more pertinent questions to which this model can give, at least, qualitative answers. For example, it is interesting to follow the time development of the average density of free bonds on the surface of growing clusters. In our model only the adjunction of boron atoms in chains leads to *one* new bond in the rim, whereas when a boron atom closes a ring, the number of free bonds is reduced by one.

If at a given moment t_j, the number of free bonds on the surface layer of a cluster was $N_f(t_j)$, on the next layer produced after the characteristic time interval Δt, the number of free bonds $N_f(t_{j+1}) = N_f(t_j + \Delta t)$ is computed as follows:

$$N_f(t_{j+1}) = N_f(t_j + \Delta t) = N_f(t_j) + N_f(t_j)(1 - P_B^{(1)}(T)) - N_f(t_j)P_B^{(j)}(T) \tag{11}$$

because each time one of the sites x, y, z or t is produced by adjunction of a new singlet $B(O_{1/2})_3$, the number of free (dangling) bonds increases by one. The overall probability for one of these transformations to occur at the rims of huge clusters is proportional to $1 - P_B^{\infty}(T)$, and the total number of newly created dangling bonds at the rim is therefore $N_f(t)[1 - P_B^{\infty}(T)]$.

Similarly, each time a boroxol ring is closed on the rim, the number of free bonds *decreases* by 1, which is taken into account by the term $-N_f(t)P_B^{\infty}(T)$.

Developing the difference $N_f(t + \Delta t) - N_f(t)$ in a Taylor series, one can write, up to first order in Δt, and defining σ as the characteristic exponent of the growth (since the number of dangling bonds grows with the time t like t^{σ}):

$$\sigma = \frac{\mathrm{d} \ln N_f(t)}{\mathrm{d}t}\Delta t = \frac{\mathrm{d} \ln N_f}{\mathrm{d}s} = 1 - 2P_B^{\infty}(T) \tag{12}$$

where we have introduced the dimensionless derivative $\mathrm{d}/\mathrm{d}s = \Delta t\, \mathrm{d}/\mathrm{d}t$ (with respect to the dimensionless parameter s, i.e. the '*number of steps*' of agglomeration, each step representing a new layer added to an average cluster).

The characteristic exponent σ defined above is positive when the number of free bonds is increasing, and negative otherwise. If the growth is supposed to follow a steady rate (on

average, one new layer after time Δt), then in two dimensions the circumference should grow proportionally to t, while in three dimensions the surface grows roughly as t^2, the characteristic exponents being 1 and 2, respectively. This is why we define the *fractal dimension* of the network as $d_F = \sigma + 1$.

It is obvious that in three dimensions d_F should be close to 2, because in the case where it becomes too low (i.e. when $\sigma \to 0$) the density of dangling bonds on the surface of clusters in the process of forming will rapidly decrease, so only thin filaments will remain, thus creating voids in the structure which are not observed in real glasses whose homogeneity attains the molecular level.

If d_F becomes higher than 2, then the density of free bonds on the surface of growing clusters will grow too rapidly, until they become so entangled that further growth becomes impossible, or new bigger rings must be created, which also should not happen in good glass formers.

For the B_2O_3 glass, just before one reaches T_g, the characteristic exponent has the constant value 0.43, which corresponds to the fractal dimension 1.43. We also note that the expression for the characteristic exponent is similar to the contribution of the energy stored in the B–O–B-bridges and boroxol rings to the internal energy of the glass; it only differs by a constant factor. Let us evaluate first the particular contribution to the internal energy, $U_B(T)$, coming from the bond creation processes as a function of σ. According to (5) and (12), the energy stored in N bonds during the agglomeration process is given by

$$U_B(T) = \frac{E_1 - E_2}{2} N\sigma + \frac{E_1 + E_2}{2} N. \tag{13}$$

By taking the derivative of equation (13) with respect to temperature, one gets an expression for the specific heat as a function of σ:

$$c_p = \frac{3}{2} Nk + \frac{E_1 - E_2}{2} N \frac{\mathrm{d}\sigma}{\mathrm{d}T}. \tag{14}$$

Thus, the curve describing the behaviour of $\mathrm{d}N_f/\mathrm{d}t$ is the primitive function of c_p, as is shown in figure 6 below.

From the last equation, it is clear that the derivative of the exponent with respect to the temperature has an inflexion point at T_g, and it also must display a rapid increase for $T > T_g$. The fractal dimension follows exactly the same behaviour, since the derivatives of σ and d_f with respect to the temperature are equal. Thus, according to equation (14), the jump of the heat capacity at T_g when the temperature is decreasing yields a rapid decrease of the fractal dimension of the lattice. Furthermore, the shape of the curve of $U_B(T)$ is similar to the one observed for the specific volume [18] $V^*/N = 1/\rho$, since in it there is an abrupt change of the derivative at T_g.

The behaviour of the average number of free valencies at the rim of the clusters is crucial for a better understanding of the behaviour of the viscosity during the glass transition, which is well described by an Arrhenius law for B_2O_3 [23]. In fact, this average number is crucial for the mechanical interaction between the clusters, which determines the shear viscosity.

In a first approximation, we can consider that the main contribution to this quantity is the average force with which a cluster belonging to an infinitesimally thin layer of the melt acts on another cluster belonging to a thin layer next to it. This force is proportional to the sum of elementary forces created between the free bonds at the rims of both clusters, which should be proportional to the *square* of the average number of free bonds at the rim of an average cluster: $\eta \sim N^2$.

The Arrhenius behaviour of the shear viscosity (and also of the bulk viscosity, which

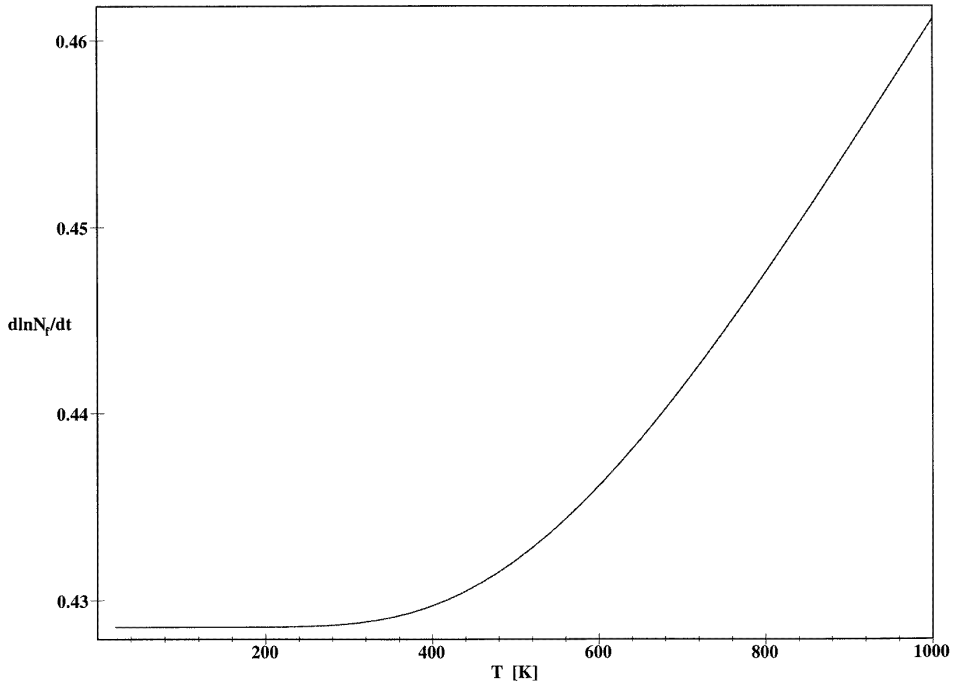

Figure 6. The curve for $\mathrm{d}N_f/\mathrm{d}t$ as a function of T.

in covalent glasses is of the same order of magnitude) reads

$$\eta(T) = \eta_0 \mathrm{e}^{A/kT} \tag{15}$$

where A is often called the *apparent activation energy* needed to break the covalent bonds in order to make the thermally activated atomic diffusion possible. In the group of strong covalent glasses (following Angell's definition [23]) to which B_2O_3 glass belongs (together with SiO_2 and GeO_2 glasses and most of the covalently bonded glass systems), the Arrhenius law for the viscosity is quite well satisfied, i.e. in the vicinity of the glass transition temperature T_g the logarithm of the viscosity (measured in poise) is a linear function of T_g/T, with the coefficient close to 20:

$$\log(\eta) \simeq \log(\eta_0) + 20(T_g/T)$$

with $\log(\eta_0)$ of the order of 10^{13}, which means that when the temperature T decreases from $2T_g$ to T_g, the viscosity increases by the factor of 10^{10}. Also the activation energy A can be evaluated as being roughly equal to $A \simeq 20kT_g$.

This suggests what the explicit dependence of N on the temperature T looks like, when one takes into account large timescales, neglected in the first approximation that we have used previously.

6. Conclusions

We have shown how with a few simple assumptions one can reproduce the most striking features of the glass transition process for the particular example of B_2O_3 glass. We have

obtained the energy of creation of a boroxol ring and the fraction of boron atoms trapped in boroxol rings. The numerical values are comparable with those obtained from experiments and various other models.

We have also deduced the characteristic behaviour of the internal energy and the specific heat. This and other thermodynamical quantities can be written in terms of the so-called characteristic exponent of growth (σ), which is related to the density of free bonds on the growing surface. In some sense, σ can be considered as an order parameter for the glass transition.

An important point to be stressed is that the method shows how very short correlations can lead to intermediate short-range order. This gives validity to calculations done with few atoms [13], although it opposes the concept of a phase-space landscape in which the glass is trapped in a metastable state.

Most of the ideas and methods presented in this article can be applied to other non-crystalline materials such as covalent network glasses (Ge_xSe_{1-x}, As_2Se_3, etc), and also to other forms of condensed matter—for example, nanotubules, microclusters—and other types of material which will be given attention in forthcoming papers.

References

[1] Galeener F L 1990 *J. Non-Cryst. Solids* **123** 182
[2] Soppe W and Den Hartog H 1989 *J. Phys. C: Solid State Phys.* **21** L689
[3] Teter M P 1987 *Am. Ceram. Soc. Bull.* **66** 562
[4] Galeener F L, Lucovsky G and Mikkelsen J C Jr 1980 *Phys. Rev.* B **22** 3983
[5] Massot M and Balkanski M 1991 *Microionics, Solid State Integrable Batteries* ed M Balkanski (Amsterdam: North-Holland) p 139
[6] Barrio R A, Castillo-Alvarado F L and Galeener F L 1991 *Phys. Rev.* B **44** 7313
[7] Hannon A C, Wright A C, Blackman J A and Sinclair R N 1995 *J. Non-Cryst. Solids* **182** 78
[8] Uchida N, Maekawa T and Tokokawa T 1985 *J. Non-Cryst. Solids* **74** 25
[9] Kerner R 1991 *J. Non-Cryst. Solids* **135** 155
[10] Kerner R and Micoulaut M 1994 *J. Non-Cryst. Solids* **176** 271
[11] Kerner R 1995 *Physica* B **215** 267
[12] dos Santos-Loff D M, Kerner R and Micoulaut M 1994 *Europhys. Lett.* **28** 573
[13] Micoulaut M, Kerner R and dos Santos-Loff D M 1995 *J. Phys.: Condens. Matter* **7** 8035
[14] Micoulaut M and Kerner R 1997 *J. Phys.: Condens. Matter.* **9** 2551
[15] Kerner R 1997 Stochastic matrix method for modelling growth and agglomeration processes, at press
[16] Galeener F L and Thorpe M 1983 *Phys. Rev.* B **28** 5802
[17] Mozzi R L and Warren B E 1970 *J. Appl. Crystallogr.* **3** 251
[18] Elliot S R 1990 *Physics of Amorphous Materials* (New York: Longman)
[19] Walrafen G E, Samanta S R and Krishnan P N 1980 *J. Chem. Phys.* **72** 113
[20] Snyder L C 1978 *Bull. Am. Ceram. Soc.* **57** 825
[21] Jellison G E, Panek L W, Bray P J and Rouse G B 1977 *J. Chem. Phys.* **66** 802
[22] Hannon A C, Sinclair R N and Wright A C 1993 *Physica* A **201** 375
[23] Angell C A 1988 *J. Non-Cryst. Solids* **102** 205