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Section 3. Stability and crystallization

Theoretical method for non-crystalline growth

R. Paredes, G.G. Naumis *, R.A. Barrio

Instituto de Física, Universidad Nacional Autónoma de México (UNAM), Apartado Postal 20-364, Mexico DF 01000, Mexico

Abstract

A method of agglomeration of atomic units is developed to investigate some important features of the statistical processes that take place when a glass is formed. In particular, by allowing several free valences to be saturated in a single agglomeration step, the growth is non-dendritic. The process becomes non-linear, and it has to be treated self-consistently. The sites whose bonds are completely saturated in each step become important and their final concentration changes abruptly at the transition temperature for any value of the modifier concentration.

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1. Introduction

The glass transition is of considerable practical and technological importance; however, little is known about the thermodynamic and structural factors that determine it [1]. For instance, chalcogenide glasses have electric and infrared transmission properties that make them useful in technological applications [2]; consequently, a lot of effort has been devoted to correlate the glass transition temperature (T_g) with other physical and chemical properties, such as composition [3]. In this paper we shall focus our attention on this problem. For example, the properties of an A_xB_{1-x} glass as the chemical composition varies is far from trivial. T_g can be raised or lowered by increasing x, and the nature of the glass can be changed from fragile to strong [4]. The stochastic matrix method (SMM), introduced by Kerner and co-workers [5–7] to study glass formation, has succeeded in obtaining the empirical modified Gibbs–DiMarzio Law [8,9], that allows a calculation of the change in T_g for low concentrations of modifiers [2], but the main problem with the SMM is that it describes a dendritic growth process. Although this feature makes the model quite simple, it is likely to be accurate only for small x, when the correlations between pairs of impurities are negligible. Here we propose a scheme that deals with non-dendritic growth in an approximate way. This new approach allows to obtain the variation of T_g for a glass of the type A_xB_{1-x} in all the range of x resembling some unexplained experimental data.

2. Theory

The SMM describes the formation of a glass by assuming that small atomic-like units, existing in a

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* Corresponding author. Tel.: +52-56 22 5174; fax: +52-56 22 5008.

E-mail addresses: naumis@fisica.unam.mx (G.G. Naumis), barrio@fisica.unam.mx (R.A. Barrio).

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liquid, can be attached to the free bonds at the surface of solid clusters [5]. At a given time, one has a collection of clusters, and at their surfaces there is a finite number n of different local configurations. One can form a n-dimensional vector $v = (P_1, P_2, \ldots, P_n)$ whose entries are the probabilities of finding each one of these configurations [5]. The agglomeration process is represented by the transformation $\mathbf{S}\bar{v} = \bar{v}'$, where $\mathbf{S}$ is a stochastic matrix [6]. The matrix elements $S(i,j)$ contain the probabilities of starting with a configuration i and ending with a different configuration j, and are given by [5]

$$S(i,j) = M(i,j)/Q_i = \Omega_{ij} p_j(x) \mathrm{e}^{E_{ij}/k_\mathrm{B}T}/Q_i, \qquad (1)$$

where E_{ij} is the activation energy associated with the bond formed, $p_j(x)$ is the probability of having a unit of type j in the liquid, which is proportional to the concentration relation between units (x), Q_i is the normalizing factor $\sum_j \Omega_{ij} \mathrm{e}^{E_{ij}/k_\mathrm{B}T} p_j(x)$, and Ω_{ij} is the statistical factor counting the number of all equivalent processes that start with i and end with j. The macroscopic solid can be regarded as the result of applying this transformation a large number of times. It can be shown [5] that a stochastic matrix has at least one eigenvector (say $\hat{e}_1$) with eigenvalue 1, and the final distribution of configurations [6] is given by the elements of $\hat{e}_1 \equiv (P_1^\infty, P_2^\infty, \ldots, P_n^\infty)$. If it is assumed that only one bond can be attached to a given configuration, the sites at the surface are uncorrelated, and the growth process is necessarily dendritic. If one allows for simultaneous formation of two bonds, either one produces two-atom rings, which is usually considered unrealistic, or one attaches one single unit to various sites, in which case neighboring sites at the surface become correlated. In real systems, though, there is no reason preventing several bonds to form simultaneously. In what follows we present a simple way of dealing with this situation.

Consider a hypothetical $\mathrm{A}_x\mathrm{B}_{1-x}$ alloy, where B has coordination 2, and A coordination 3. There are three possible sites offering unsaturated bonds at the surface: a unit A with two unsaturated bonds, a unit A with one unsaturated bond, and a unit B with one unsaturated bond. We still avoid the formation of two-fold rings; simultaneous formation of two bonds will require two different sites at the surface. Since it is quite possible that there is no neighbor at the right distance offering an unsaturated bond, the sites with all bonds saturated must be considered as playing their own role in the growth process. The immediate consequence of considering two neighbor sites is that the elements of $\mathbf{S}$ will depend on the site probabilities R_i of having a neighbor of type i entering the agglomeration game. Therefore, the equation $\mathbf{S}(R_1,\ R_2, \ldots, R_n)^\infty \bar{v}_0 = \hat{e}_1 = (P_1, P_2, \ldots, P_n)$ that describes the full growth process has to be solved self-consistently, in order to assure that at the end one has $R_i = P_i^\infty$. Let us solve in detail our example, to illustrate the whole procedure.

In Fig. 1(a), the complete single site configurations for this case are shown, where the vertical bar represents the surface of the cluster. The empty site is named P_0. To write down the transformation rules for a given site, we need to know which types of site are available with bonds that can be saturated in a single agglomeration step, if any. We assume that the probability of encountering a site

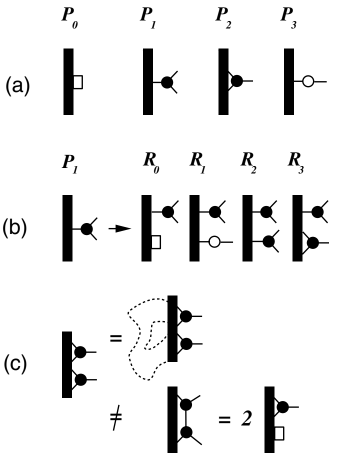

Fig. 1. (a) The four possible configurations at the surface. A square means a site with all bonds saturated. (b) If one considers configuration 1, there are four possibilities for a proper neighbor being of a certain kind, with different probabilities R_i. (c) Small membered rings should be avoided by correctly interpreting the two neighbor site representation.

of type i is R_i, which in principle is different from the true site probability P_i. For instance, take a site of type P_1, as in Fig. 1(b). To investigate the number of ways to obtain any of the four basic site configurations after one agglomeration step, one needs to consider all the contributions from the two-site situations depicted in the right hand side of Fig. 1(b).

There is a word of warning concerning the interpretation of the two-site diagrams. In Fig. 1(c) we show a diagram with a pair of sites of type 2. These sites are at the surface of the cluster and the two free bonds can be connected in a single step. They are surely already connected somewhere in the bulk, but it is not known how many sites in the bulk one should visit to go from one site to the other: there are *at least two* such paths, as shown in the figure with dotted lines. In dendritic growth all paths reach the starting cluster necessarily, but when rings are formed the minimal path is shorter, or even made by one link only, as shown in the lower part of Fig. 1(c). In this latter case, the configuration should be interpreted as twice P_2R_0, as shown in the figure. This is the reason why the original site probabilities P_i need not to be the same as the neighboring site probabilities R_i. The elements of **S** now depend on the site probabilities R_i. One also needs to consider three energy parameters, namely $e_1 = \mathrm{e}^{-E_{\mathrm{AA}}/k_{\mathrm{B}}T}$, $e_2 = \mathrm{e}^{-E_{\mathrm{AB}}/k_{\mathrm{B}}T}$, $e_3 = \mathrm{e}^{-E_{\mathrm{BB}}/k_{\mathrm{B}}T}$ to take into account the three types of bonds in the alloy.

Let us examine the bonding processes that occur when considering a P_1 site. We need to consider the combinations when having any type of site as neighbor, including the possibility of no neighbor. In Fig. 2 we show the final configurations obtained from Fig. 1(b). With these rules, one can write all the contributions to the matrix element in the second row and third column $S(2,3)$; that is, all the possible one-step agglomerations that result in creating a type 2 site from a type 1 site. In Fig. 2, these are labeled with P_2 and also the statistical energetic and configurational factors are indicated, thus one has to include them all, once they have been multiplied by the corresponding probabilities R_i. From the figure it is clear that

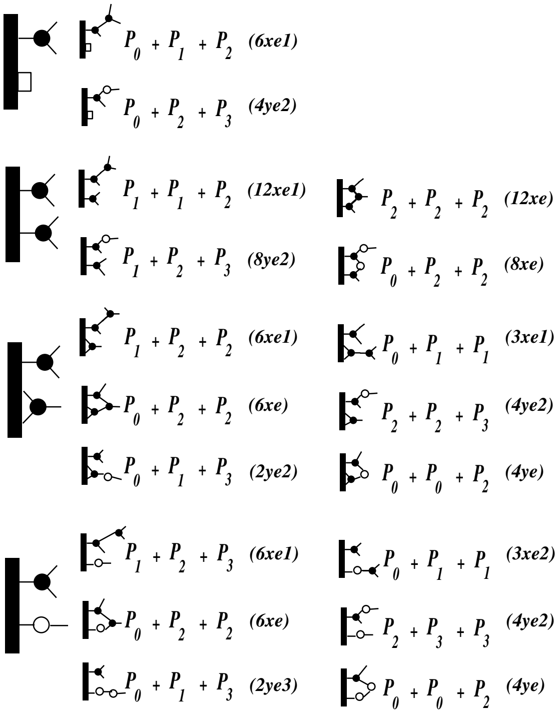

Fig. 2. Configurations obtained from a site P_1 when one considers a neighbor. The transition probabilities that give the elements of **S**, containing Boltzmann and degeneracy factors (where $y = 1 - x$), are written in parenthesis. One needs a further Boltzmann factor e when a ring is made.

$$\begin{aligned} M(P_1,P_2) &= S(2,3) \times Q_1 \\ &= R_0[6xe_1 + 4ye_2] + R_1 \\ &\quad \times [12xe_1 + 36xe + 8ye_2 + 16ye] \\ &\quad + R_2[12xe_1 + 12xe + 8ye_2 + 4ye] \\ &\quad + R_3[6xe_1 + 12xe + 4ye_2 + 4ye]. \end{aligned} \tag{2}$$

All the other elements can be obtained in a similar fashion. Now, the solution of the problem involves finding the eigenvalues of a 4×4 matrix, once the energy parameters, the concentration x and the temperature are fixed. Of special interest is the element $S(1,1)$, containing all the processes that start and result on an empty site.

$$\begin{aligned} M(P_0,P_0) &= S(1,1) \times Q_0 \\ &= 2R_0 + (R_1 + R_2 + R_3)[6xe_1 + 4ye_2]. \end{aligned}$$

Since there is no possibility of 'resurrecting' any saturated site, that is, there is no process that converts a square in Fig. 2 to any other configuration, the elements of column 1 have to be interpreted as the amount of bulk made. Observe that due to the inhomogeneous term $2R_0$, when the temperature is sufficiently low to make all the Boltzmann factors negligible, $\hat{e}_1 = [1, 0, 0, 0] \equiv \hat{e}_s$, which means that the solid is formed. For a given set of energy parameters, the appearance of this eigenvector should depend on concentration and temperature only. At low temperature, this is the only solution, but at high temperature the other sites are always present. Therefore, we shall interpret the temperature that signals the appearance of the solution $\hat{e}_s$ as T_g, since the solid cluster is in dynamical equilibrium with its surroundings.

Given the energy parameters, the concentration x and the temperature, one writes down **S** using an initial guess for the probabilities R_i, and finds $\hat{e}_1$. The components of the latter have to be considered as a new starting point, with which a new matrix **S** is written. The process is continued until the difference between the obtained vector does not differ from the previous, and one obtains a single solution $\hat{e}_F = [P_0^\infty, P_1^\infty, P_2^\infty, P_3^\infty]$. The result contains the final concentrations of A or B atoms in the cluster, and the number of bonds of each type (b_{AA}, b_{AB} and b_{BB}), because these are encoded in the elements $M(i,j)$. With this information, we can write the internal energy [6] as, $U(T) = (3NkT/2) + E_{\mathrm{AA}}b_{\mathrm{AA}} + E_{\mathrm{AB}}b_{\mathrm{AB}} + E_{\mathrm{BB}}b_{\mathrm{BB}}$, where the first term is the kinetic contribution.

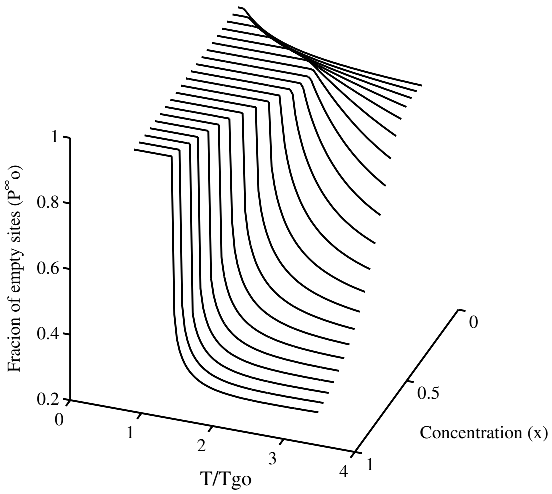

Fig. 3. Plot of the first element of $\hat{e}_F$, as a function of x and T, for the parameters indicated in the text.

3. Results and discussion

We can apply the method to an hypothetical A_xB_{1-x} compound. Usually, in many binary chalcogenide glasses, the bonds of type b_{AB} and b_{AA} are more favored than b_{BB} due to the energies involved. Let us choose arbitrary energy parameters to reflect this fact. The parameter E_{BB} has to give the correct transition temperature when $x = 0$, and if $k_BT_g(0) = k_BT_{g0}$ is taken as unity, the value $E_{\mathrm{BB}} = 10.805$ signals the transition temperature $T_{g0} = 1$. The parameter E_{AA} has to reflect the fact that this type of bond is stronger than the BB type; therefore we choose $E_{\mathrm{AA}} = 8.7E_{\mathrm{BB}}$. The more robust b_{AB} means that the remaining energy has to be larger, we choose $E_{\mathrm{AB}} = 12.5E_{\mathrm{BB}}$. In order to isolate the effect of considering two neighbor sites in the SMM, let us set the different ring forming energies, represented by the parameter e in Fig. 2, by the corresponding products e_ie_j for creating two uncorrelated bonds. In Fig. 3, the behavior of P_0^∞ in the (T, x) plane is shown. The solution $P_0^\infty = 1$ is found at low temperatures, and its value changes at T_g. Notice that T_g, as a function of x, is the curve defined by the points in which P_0^∞ ceases to have its maximum value. Observe that T_g rises in the small x region and that a maximum is attained in the stoichiometric concentration. The non-linear character of the approach is the reason to obtain this maximum, and thus non-dendritic growth plays an extremely important role in setting T_g. One can also verify that the specific heat ($C_p(T)$), calculated as the derivative of $U(T)$, also presents an inflexion point and a jump at T_g. This jump can be related to the minimum speed required to form the glass ('strong' or 'fragile' character), and was also predicted by simple thermodynamic rigidity arguments [10]. Our theory can be applied to any system fulfilling the

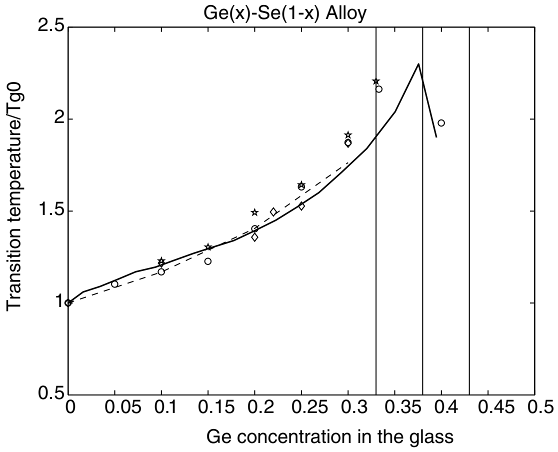

Fig. 4. Prediction of $T_g(x)$ in Ge_xSe_{1-x} (—). The symbols are experimental points from [2,11,12], and denoted as diamonds, circles, and stars, respectively. The vertical lines represent (from left to right) the stoichiometric concentration, the theoretical and experimental limits for glass formation. The Gibbs–DiMarzio equation is shown as a dashed line.

requirements, and the actual form of the transformation matrix depends very much on the particular problem at hand. For instance, one can study the system Ge_xSe_{1-x}, as an agglomeration of four-fold and two-fold coordinated atomic units. In this case, one obtains a 5×5 stochastic matrix. In Fig. 4, we show the result of the calculation for Ge_xSe_{1-x}, and data from different experimental groups. Observe that compared with the Gibbs–DiMarzio equation, our theory gives a more accurate description of T_g in the low x range, reproducing the shoulder found in the experimental data. It is clear that all the main experimental features are well reproduced by the theory in this particular system. However, the theory gives unphysical results (negative values of $C_p(T)$) beyond a certain value of the modifier concentration. The point at which this is seen depends on the values of the energy parameters, particularly on E_{AA}, and can be interpreted as a prediction for the limit of the glass formation region, since it occurs very near the experimental composition where the glass is not possible to form anymore.

4. Conclusions

We have presented a modified SMM with two novel features: (1) The agglomeration rules now depend on the situation of a neighboring site. (2) One is able to completely saturate surface bonds in a single agglomeration operation. This is extremely important, since one is allowing the formation of rings (relaxing the condition for dendritic growth), and one can keep track (in a rather approximate way, though) of the several units formed the solid. The price to pay is that one is forced to consider the possibility of finding a site without free bonds at the surface.

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