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Models of Disorder*

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Abstract—The stochastic matrix method is used to describe the statistical processes that take place when a glass is formed. We stress the physical features of the model and the relevancy of the hypotheses made. The theory is applied to various types of binary and ternary chalcogenide glasses, and the predictions of the model are compared with the experimental data. We also reveal the influence of doping on the transition temperature. The theory is extended to the case of growing a disordered solid on a substrate.

INTRODUCTION

Glasses are common materials in nature and have been used by mankind since the beginning of times. However, there is very little theoretical understanding in this field [1], due to the essential role that disorder plays in dictating their peculiar physical properties. One of the basic questions about glasses is the persistence of a disordered structure at low temperatures, knowing that the thermodynamically stable state is the crystal. This fact has driven people to conclude that a glass is in a metastable state that eventually should transform to another more stable and ordered state [2]. This metastable state could be locked-in by a rapid quenching, preventing atoms from diffusing into more stable configurations, or by other steric hindrances arising from the complicated geometry of nucleated clusters of molecules. However, there are many examples of materials that prefer the vitreous state regardless of the process of formation. These are known as *good glass formers* and are usually compound materials with a definite chemical short-range order, such as SiO_2 or B_2O_3 [3]. Therefore, at least in these cases, one should recognize that there is more to the process of formation of a glass than only thermodynamic equilibrium considerations. The formation of a solid glass from the melt or the growth of an amorphous solid from a free surface are processes that take place far from equilibrium, and kinetics becomes very important.

The situation of good glass formers, in which the short-range chemical order is very robust [4], has been considered by the authors in previous papers [5, 6]. The important physical consideration is that there are two well separated time scales to reach equilibrium in the cooling melt. The time to form a chemical bond and reach local equilibrium is very fast, and the time it takes to equilibrate the whole system is much longer. Under these conditions, one could assign the Boltzmann factors to the process of formation of a bond, that is, to agglomerate a single atom to the surface of the growing solid. The other process can be regarded as a Markovian chain of events, each one having a statistical probability of occurrence, dictated by some configurational entropy (the number of ways to go from one initial configuration to a final one), and by some geometrical rules that specify the facility to obtain a given configuration from another one. The full details of this theory of glass growing through agglomeration are described elsewhere [5, 6]. However, in this paper, we will treat the detailed study of some features of chalcogenide glasses that allows us to compare the predictions of the theory with some experimental data. After that, we will consider a hypothetical situation in which one has a single kind of atom, but the bonding could be different. This extension of the theory could be applicable to amorphous semiconductors, like silicon or germanium, in which there exist dangling bonds trapped in the amorphous network. We conclude with some general considerations about glass formation and the relevance of this understanding on current issues of interest in the field.

MARKOV PROCESSES APPLIED TO CHALCOGENIDE GLASSES

Chalcogenide glasses usually grow from a hot melt that contains the basic atomic entities which form the glass. During the cooling process of the melt, these entities form clusters of different sizes that are the seeds from which the resulting glass grows as a successive agglomeration. This very basic physical observation can give us lots of information about the formation and properties of the glass, even though the glass transition is a very complicated phenomenon. In what follows, we will show how to use this simple idea in order to describe the growth of a typical glass in terms of a

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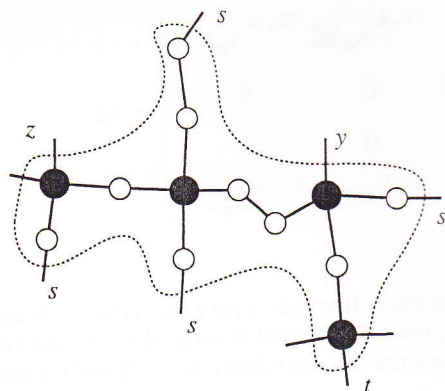* The article was submitted by the author in English.

Fig. 1. A typical cluster with four kinds of sites in the surface layer, indicated by the dashed line. Explanations are given in the text.

Markov process, which is a probabilistic way of describing the time evolution of the cluster surface.

Let us consider the particular case of vitreous Ge_xSe_{1-x}. This glass is made from a melt that contains atoms Ge and Se with concentrations c_B and $c_A \equiv 1 - c_B$, respectively (note 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 for creation of single bonds Se–Se, Se–Ge, and Ge–Ge. The bond creation is a rapid process and can be assumed to reach equilibrium in a very short time. Therefore, each bond created can be labeled by an activation energy that we denote by E_1, E_2, and E_3, respectively.

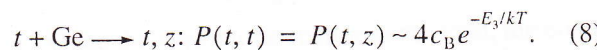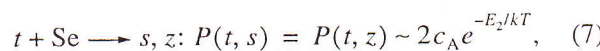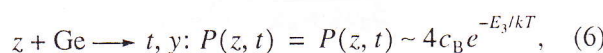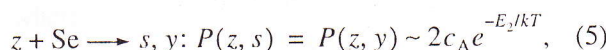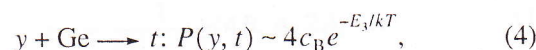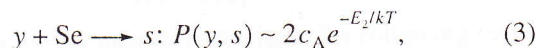When a new atom (Ge or Se) comes close to the cluster, it can be attached to one of the unsaturated bonds that are at the cluster surface. Since the coordination of Ge is four and that of Se is two, the new atom may encounter four kinds of environment sites corresponding to particular configurations of unsaturated bonds (these sites being explicitly shown in Fig. 1). Since any atom at the surface is necessarily in one of these configurations, a vector with four components is enough to define the composition of the surface if each component is the probability of finding a given configuration on it. The growth process can be described with a linear transformation, that is, by a matrix operator that gives the statistical result of agglomerating atoms at the surface. 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 matrix to 4×4, and it is only valid in the case of low concentration $x \ll 1$. This matrix has to be stochastic (all elements in a column add up to one) if one wants to describe the evolution of probabilities.

Each kind of site has a certain frequency of occurrence (denoted by s; y, z, t) at the surface 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 bond has a frequency y. Thus, *the distribution of each kind of unsaturated bonds* 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 to each of the free bonds on the surface. Once this atom sticks, a new site on the surface is created and the surface changes. For example, if a Ge or Se atom is added at a site s, the transformation is as follows:

$$s + Se \longrightarrow s: P(s, s) \sim 2c_A e^{-E_1/kT}, \qquad (1)$$

$$s + Ge \longrightarrow t: P(s, t) \sim 4c_B e^{-E_2/kT}, \qquad (2)$$
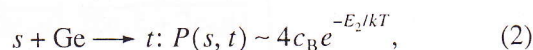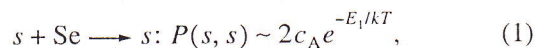
where the probabilities of each sticking process [represented by $P(s, s)$, $P(s, t)$] are given by two factors: one is the purely configurational entropy factor [the number of ways of joining the 4 (2) valences of Ge (Se) in each kind of site], and the other is the Boltzmann factor which takes into account the corresponding energy barrier to form a bond. Similar expressions can be found when the Ge and Se atoms are added to each of the other sites, that is,

$$y + Se \longrightarrow s: P(y, s) \sim 2c_A e^{-E_2/kT}, \qquad (3)$$

$$y + Ge \longrightarrow t: P(y, t) \sim 4c_B e^{-E_3/kT}, \qquad (4)$$

$$z + Se \longrightarrow s, y: P(z, s) = P(z, y) \sim 2c_A e^{-E_2/kT}, \qquad (5)$$

$$z + Ge \longrightarrow t, y: P(z, t) = P(z, t) \sim 4c_B e^{-E_3/kT}, \qquad (6)$$

$$t + Se \longrightarrow s, z: P(t, s) = P(t, z) \sim 2c_A e^{-E_2/kT}, \qquad (7)$$

$$t + Ge \longrightarrow t, z: P(t, t) = P(t, z) \sim 4c_B e^{-E_3/kT}. \qquad (8)$$

Note that, for some sites, there are two possible paths with different probabilities [for example, for creating one z site, there are two ways: (1) stick a Se on a t site or (2) 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.

This process can be written as a matrix whose elements represent the probabilities $P(i, j)$ of transforming a site i into a site j, because the total probability for all atoms to stick to a certain site is the sticking probability of the process multiplied by the frequency of occurrence in the surface of that kind of site. Inserting all the contributions, the explicit matrix is written as

$$M = \begin{pmatrix} 2c_A e^{-E_1/kT} & 2c_A e^{-E_2/kT} & 2c_A e^{-E_2/kT} & 2c_A e^{-E_2/kT} \\ 0 & 0 & 2c_A e^{-E_2/kT} + 4c_B e^{-E_3/kT} & 0 \\ 0 & 0 & 0 & 2c_A e^{-E_2/kT} + 4c_B e^{-E_3/kT} \\ 4c_B e^{-E_2/kT} & 4c_B e^{-E_3/kT} & 4c_B e^{-E_3/kT} & 4c_B e^{-E_3/kT} \end{pmatrix}. \tag{9}$$

Since this matrix acts on a vector that represents the probabilities of finding each class of site and, as stated previously, should be normalized, the sum of the elements in each column must be unity, so the vector obtained after applying the matrix is also normalized. After normalizing each column of the matrix, one gets

$$M = \begin{pmatrix} \dfrac{c_A}{(c_A + 2c_B\xi)} & \dfrac{c_A\xi}{(c_A\xi + 2c_B\mu)} & \dfrac{c_A\xi}{2(c_A\xi + 2c_B\mu)} & \dfrac{c_A\xi}{2(c_A\xi + 2c_B\mu)} \\ 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ \dfrac{2c_B\xi}{(c_A + 2c_B\xi)} & \dfrac{2c_B\mu}{(c_A\xi + 2c_B\mu)} & \dfrac{2c_B\mu}{2(c_A\xi + 2c_B\mu)} & \dfrac{2c_B\mu}{2(c_A\xi + 2c_B\mu)} \end{pmatrix}, \tag{10}$$

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

The growth of clusters is modeled by a successive application of the matrix on an arbitrary initial vector (v_0), which could be written as a linear combination of the four eigenvectors of this matrix. After applying the matrix j times, the final configuration of the rim is given by

$$\mathbf{v}_j = a_1\lambda_1^j\mathbf{e}_1 + a_2\lambda_2^j\mathbf{e}_2 + a_3\lambda_3^j\mathbf{e}_3 + a_4\lambda_4^j\mathbf{e}_4, \tag{11}$$

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 of this sort has at least one eigenvalue (in general, complex) with modulus equal to unity, while all the others have their moduli less than unity. This means that only the eigenvectors $\mathbf{e}_i$ with eigenvalue such that $|\lambda_i| = 1$ remain after successive applications of the stochastic matrix. If we suppose that M has only one such eigenvector (call it $\mathbf{e}_1$). Then, in the limit of $j \longrightarrow \infty$, $\mathbf{v}_j$ converges to precisely that eigenvector, since a_1 must be unity due to conservation of probability. Thus, the rim attains a stable statistical regime after enough successive steps of growing. This regime is governed solely by the statistics of the eigenvector with eigenvalue one. Note that before the growing process attains the stable regime, there are fluctuations in the first generations due to the eigenvalues different from unity, which are in general complex numbers.

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

$$(M - 1)\mathbf{e}_1 = 0, \tag{12}$$

which for the present case yields the following vector:

$$\mathbf{e}_1 = \frac{1}{4B + 7A}(4B, A, 2A, 4A), \tag{13}$$

where

$$A = \frac{2c_B\xi}{c_A + 2c_B\xi} \tag{14}$$

and

$$B = \frac{c_A}{c_A\xi + 2c_B\mu}. \tag{15}$$

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 given by the proportion of new Se atoms on the surface of the cluster

$$1 - x = 4B/(4B + 7A). \tag{16}$$

The concentration obtained from equation (16) is a function of the concentration in the melt (c_B). However, since the glass is growing at the expense of the surrounding medium, we can impose a condition of self-consistency, $x = c_B$, since the compositions of the melt and the glass are the same after the glass transition. If

one puts $c_B = x$ in the right-hand side of equation (16), three solutions are obtained, that is, $x = 0$, $x = 1$, and the following equation for the concentration:

$$x = \frac{1 - 2\xi}{1 - 4\xi + 4\mu}, \quad (17)$$

which gives a relation between the glass transition temperature, the concentration and the difference of energies for forming the bonds, as we will discuss in the next section.

PHYSICAL IMPLICATIONS FOR CHALCOGENIDE GLASSES

Equation (17) contains two free parameters, which are the differences in energies between the three kinds of bonds. But we can use the fact that bonds Ge–Ge are not observed in this glass [7, 8]. Thus, we may set $\mu = 0$, since the energetic cost for this bond is too high, and, thus, the only remaining parameter to fix is ξ. This parameter is fixed by observing that in the limit $x \longrightarrow 0$, the glass transition temperature of pure selenium is $T_{g_0} = 315$ K [8]. By making $x = 0$ in equation (17), we get

$$E_1 - E_2 = kT_{g_0}\ln(1/2) = 0.02 \text{ eV.} \quad (18)$$

which gives the corresponding energy difference between different kind of bonds. Using this for small x, equation (17) can be written as

$$T_g = \frac{T_{g_0}}{1 - \beta(\langle r \rangle - 2)}, \quad (19)$$

where $\langle r \rangle = 4x + 2(1 - x)$ is the average coordination number, and $\beta = (1/2\ln 2) = 0.72$.

Equation (19) is turns out to be the well-known modified Gibbs–Di Marzio equation, which is an empirical law that has been very successful for obtaining T_g in chalcogenide glasses [9]. Furthermore, the method presented here allows one to obtain theoretically the constant $\beta = 0.72$, which is very close to the observed one in experiments $\beta = 0.73$ [10].

Note that the origin of this constant is purely topological; i.e., it, depends only on the logarithm of the ratio between valences, as was first proposed by Kerner and Micoulaut [5]. This explain why the value of β is similar to that for other glasses with similar coordination numbers, like Ge_xS_{1-x} ($\beta = 0.73$) [11] and $Ge_xAs_ySe_{1-x-y}$ ($\beta = 0.73$) [10]. In this ternary glass, the As atoms enter with an effective coordination of four, since they occur in pairs connected by a selenium bond [12]; thus, it should behave as our example for a binary chalcogenide glass. This way for obtaining β is also valid for other binary glasses with different coordination number ratios [13].

For multicomponent glasses, we can obtain the value of β by using the values observed in the corresponding binary systems. For example, if we have a glass of the type $A_xB_yC_zD_{1-x-y-z}$ with coordinations m_A, m_B, m_C, and 2, respectively, where D is the chalcogenide element, the derivative of $\langle r \rangle = m_A x + m_B y + m_C z + 2(1 - x - y - z)$ with respect to T_g is

$$\frac{d\langle r \rangle}{dT_g} = (m_A - 2)\frac{dx}{dT_g} + (m_B - 2)\frac{dy}{dT_g}$$
$$+ (m_C - 2)\frac{dz}{dT_g}. \quad (20)$$

The binary glasses A_xD_{1-x}, B_yD_{1-y}, and C_zD_{1-z} follow the modified Gibbs–Di Marzio equation with constants β_1, β_2, and β_3, respectively. Then, if equation (20) is evaluated at $x = 0$, we obtain

$$1/\beta = 1/\beta_1 + 1/\beta_2 + 1/\beta_3, \quad (21)$$

where β is the constant of the multicomponent system. Clearly, this procedure can be applied to systems with an arbitrary number of chemical component n. Thus, the value of the constant follows a law that reminds the sum rule of resistances in a parallel circuit. Some glasses that obey this rules are listed in the table (reproduced from [14]).

It is worth emphasizing what this simple theory is able to predict with very little effort. We have derived an extremely important empirical relation used m glass research. This result was obtained basically with the assumption that chemical bonding and order are the main restrictions when agglomerating atoms from the melt.

Parameter β for various glasses

System	β_{pr}	β_{exp}	Correlation coefficient	References
Ge–(Se)	0.72	0.72	0.988	From [5]
Ge–(S)	0.72	0.73	0.998	From [5]
Si–(Se)	0.72	0.81	0.997	From [5]
Ge–Sb–(Se)	0.56	0.66	0.972	[10]
Ga–Ge–(Se)	0.56	0.55	0.965	[15]
Ga–Ge–(S)	0.56	0.59	0.823	[16]
Al–P–(Se)	0.32	0.21	0.952	[17]
Ge–Sb–Te–(Se)	0.56	0.55	0.998	[10]
Si–As–Ge–(Te)	0.31	0.30	0.979	[18]
Ge–Sb–As–Te–(Se)	0.45	0.55		[10]

A SIMPLE MODEL FOR DIFFUSIVE EPITAXY

There are cases when these facilitating physical considerations are not present. One important case is when one obtains an amorphous film grown on a substrate by some chemical deposition method. It is true that the final composition of the solid depends not only on the concentrations of the chemicals in the vapor, but also on the substrate properties and temperature. For

instance, when growing an amorphous silicon film, the porosity of the material depends crucially on the substrate temperature, and the number and size of internal voids can be modified by subsequent thermal annealing. On the contrary, amorphous Ge films cannot be thermally annealed, but the porosity can be reduced if some bombardment with neutral atoms is combined during the growing process [19].

In this case, there is only one sort of atom, and usually the substrate imposes some lattice mismatch restrictions on the configurations of the adatoms. The important feature that distinguishes between the Si, and Ge cases should be the strength of the directional covalent bonding, and the mobility of the adatoms on the surface. This lead us to conclude that a good model for this kind of process should be an extension of our theory to the bond binary alloy. One may suggest that an atom can stick to the surface in two different ways: either it is bonded strongly and becomes a part of the solid, or it binds itself in a weak way such that, in a short time, it could become an adatom by increasing the strength of the bond, or diffuse away to another place, or even be evaporated from the surface. The case of Si or Ge is difficult to model, since the formation of rings should be very important. A simple model to illustrate this extension of the theory is to consider a one-dimensional solid growing in one direction. There is a strong bond with energy E_1 that defines a Boltzmann factor $\alpha = \exp(-E_1/kT)$, and a weak bond with energy E_2 and Boltzmann factor $\beta = \exp(-E_2/kT)$. If a strong bond is formed, it remains unchanged and eventually forms a perfect solid. Now, if a weak bond attaches, three situations could arise before coming to local equilibrium: (i) it could be evaporated with rate u/β, since one has to break a bond of strength β; (ii) it could be transformed into a strong bond with rate $v\alpha/\beta$, since one needs an extra energy factor of α/β; and (iii) it could remain unchanged with rate w. The factors u, v, and w should depend on the mobility of the atoms, i.e., the diffusion coefficient and the initial kinetic energy with which they strike the surface. In this simple model, nothing else can happen; thus, one has that

$$u/\beta + v\alpha/\beta + w = 1. \qquad (22)$$

The possible transformation rules are illustrated in Fig. 2. Notice that one has to consider an intermediate step to take into account the possible rapid changes of the weak bonds due to diffusion. The final stochastic matrix of the model is

$$M = \frac{1}{d} \begin{pmatrix} u + w\beta & 0 & w\beta & 0 \\ v\alpha + \alpha & u & v\alpha + \alpha & 0 \\ 0 & w\beta & u & w\beta \\ 0 & v\alpha + \alpha & 0 & v\alpha + \alpha + u \end{pmatrix}, \quad (23)$$
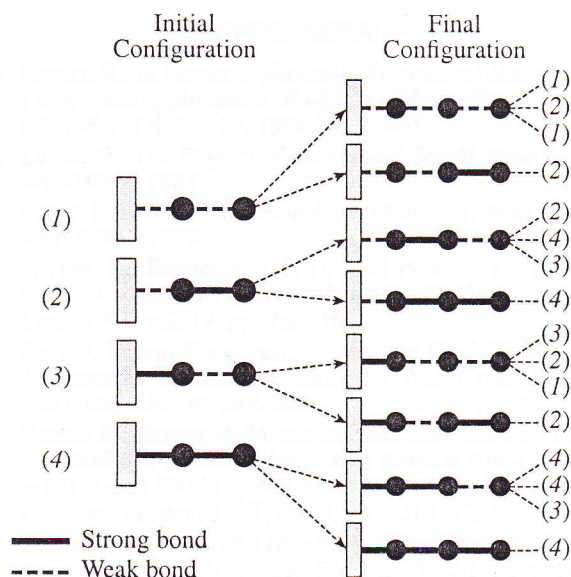

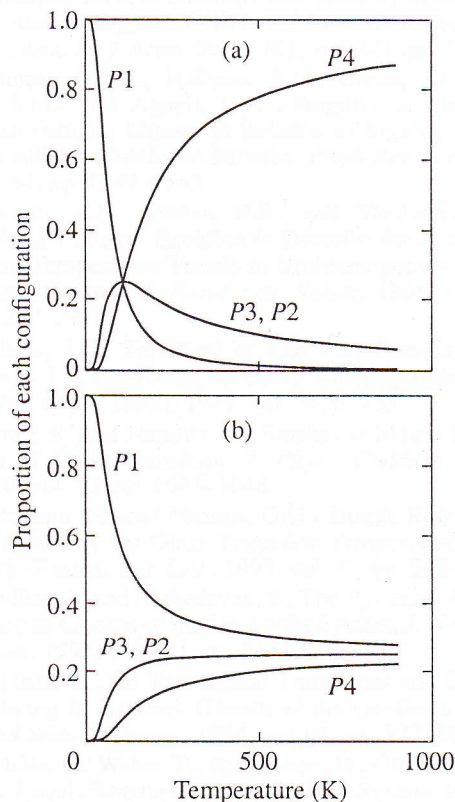**Fig. 2.** Diagram showing all the possible transformations in the model.

Fig. 3. Temperature dependence of the components of the eigenvector with eigenvalue one for the simple linear chain model, with reasonable values of the parameters $E_1 - E_2 = 0.01$ and $u = 0$: (a) bond conversion rate $v = 0.1$ and (b) $v = 1$. Observe that for the first case $P3$ diminishes quadratically, while for the second case, it grows almost linearly.

where the normalization factor is $d = u + w\beta + \alpha(v + 1)$. This matrix has a single eigenvalue one with eigenvector

$$\mathbf{e}_1 = (1, \chi, \chi, \chi^2)/(1 + \chi)^2, \qquad (24)$$

where $\chi = (v + 1)\alpha/w\beta$. Note that this eigenvector does not depend on evaporation rate u, since this term puts the system in the initial state regardless of the configuration and only appears in the diagonal term. Its influence is indirect only in the normalization condition of equation (22). From this solution, one can extract information about the number of defects (weak bonds) left in the structure as a function of the temperature and the diffusion parameters contained in the parameter χ. It is not worth trying to fit these parameters to a real case, because the model is exceedingly simple. This problem was solved only to illustrate a different kind of situation in the field of disordered solids. Nevertheless, one can see that the main physics is already in the model. In Fig. 3, we have plotted the components of the limit eigenvector in equation (24) for two different values of the "mobility" v with $u = 0$ and for a fixed value of α/β. Note that, at normal substrate temperatures, the dependence of the number of defects, or "porosity," could be almost linear or quadratic, and the porosity could change appreciably or not. These two behaviors are documented experimentally for Si and Ge [19]. Certainly, a more sophisticated model is needed for a quantitative comparison with experimental data.

CONCLUSION

The stochastic matrix method for studying a covalent network glass has been applied to the case of chalcogenide multicomponent glasses. The model turns out to be extremely simple but allows one to get important information about the glass forming processes. The 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 has been applied to model other systems like vitreous B_2O_3 and quasicrystals. In this paper, we have exposed a simple extension of the model to consider totally different situations when growing disordered solids. Future work is needed to investigate the wealth of theoretical knowledge that can be extracted with this method.

ACKNOWLEDGMENTS

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