Glass transition temperature variation, cross-linking and structure in network glasses: A stochastic approach

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Abstract. – Stochastic network description provide useful information about the link between the glass transition temperature T_g and network connectivity. In multicomponent glasses, this permits to distinguish homogeneous compositions (random network) from inhomogeneous ones (local phase separation). The stochastic origin of the Gibbs-Di Marzio equation is predicted at low connectivity and the analytical expression of its parameter emerges naturally from the calculation.

Most inorganic solids can be made amorphous by vapor deposition onto cold substrates. However, only a very few of inorganic melts can be supercooled by a water or air quench to yield bulk glasses which solidify at the glass transition temperature T_g. Oxides as vitreous silica (SiO_2) and chalcogenides (*e.g.*, Ge_xSe_{1-x}) represent some of the best-known glass formers in nature. There have been numerous efforts to understand the nature of glass transition, and to relate T_g to some easily measurable quantities. Tanaka has proposed a relationship between T_g and the mean coordination number [1]. Gibbs and Di Marzio have developed a second-order phase transition model and obtained an empirical relationship (GDM equation) between the transition temperature and the density of cross-linking agents inserted inside a system of molecular chains [2]. However, there is still no universal relationship between T_g and the glass network connectivity, satisfied by allmost all kinds of glass formers. The first attempt of such a quantitative description has been given only very recently [3]. We present in this letter several important results concerning the glass transition temperature variation as a function of connectivity in network glasses.

Mean-field estimates of T_g work only at low connectivity, but they do not work at high connectivity because a stochastic description fails.

In the chalcogen limit (low connectivity), an adapted version of the GDM equation for chalcogenides [4] can be obtained analytically from the stochastic description of the network.

Consequently, the parameter β appearing in [4] can be computed in this limit from the coordination number for any glass system, with simple and elegant sum rules.

The combination of the GDM equation in [4] and the topological calculation of the parameter β yields the correct trends in the T_g variation up to $\bar{r} = 2.4$, in agreement with Phillips' constraint theory [5]. Moreover, it suggests that usual curve-fitting with GDM equation hides the stiffness transition at $\bar{r} \simeq 2.4$, when realized over the whole concentration range because of the occurrence of chemical ordering.

The prediction of the model is parameter-free and it can be easily extended from binary to ternary, quaternary and multicomponent network-forming materials. We should stress at this point that the model is not intended to describe the physics of glass transition, but rather the connectivity dependence of the temperature of this transition. To this end, the chalcogenide systems are of particular interest for the application of the model because of the minor role played by kinetics, compared to the larger role of connectivity in determining the value of the glass transition temperature [6]. For the reader's convenience, let us first sketch the main ideas of the stochastic model.

If the network of a certain glass system forms a random network, then one should be able to treat statistically with equivalent fashion different states of structural description. For example, in a binary $B_x A_{1-x}$ structure the mean probability $p_A^b = 1/2[2p_{AA} + p_{AB}]$ of finding an atom A among randomly distributed bonds A-A and A-B (with probability p_{AA} and p_{AB}) should be equal to the probability p_A^a of finding it among a random distribution of A and B atoms. Thus, $p_A^b = p_A^a$. We have excluded the possibility of a B-B bond which occurs only in a modifier-rich glass structure. The bond probabilities p_{ij} (with $(i,j) = (A,B)$) should be proportional to the concentration x and $(1-x)$ (or p_A^a and p_B^a), a statistical weight w_{ij} related to the coordination numbers of the atoms A and B (r_A and r_B), and a Boltzmann factor involving both the glass transition temperature T_g and the bond energies E_{ij}. The probabilities p_{AA} and p_{AB} can be written as follows:

$$p_{AA} = \frac{r_A^2}{\mathcal{Z}}(1-x)^2 e^{-E_{AA}/k_B T_g} , \tag{1}$$

$$p_{AB} = \frac{2r_A r_B}{\mathcal{Z}} x(1-x) e^{-E_{AB}/k_B T_g} ; \tag{2}$$

$\mathcal{Z}$ normalizes the bond probabilities. The statement: $1 - x = p_A^a = p_A^b$ can be solved in terms of the concentration x, because p_A^b is constructed with it:

$$x = \frac{r_B e^{-E_{AB}/k_B T_g} - r_A e^{-E_{AA}/k_B T_g}}{2r_B e^{-E_{AB}/k_B T_g} - r_A e^{-E_{AA}/k_B T_g}} . \tag{3}$$

Also, eq. (3) can be made parameter-free (*i.e.* without involving $\Delta\varepsilon = E_{AB} - E_{AA}$) by condidering the limit $x = 0$ (pure chalcogen) where $T_g(0) = T_0$. One gets from (3): $\Delta\varepsilon = E_{AB} - E_{AA} = k_B T_0 \ln[r_B/r_A]$. Finally and most importantly, the relationship (3) can be cast in a more compact presentation by performing the derivative of (3) with respect to T_g in the limit $x = 0$, and inserting the energy difference $\Delta\varepsilon$. We obtain then the following parameter-free slope equation which is the central result [3] to be used in the present work:

$$\left[\frac{dT_g}{dx}\right]_{x=0, T_g=T_0} = \frac{T_0}{\ln\left[\dfrac{r_B}{r_A}\right]} . \tag{4}$$

As $\bar{r}$ is defined by: $\bar{r} = r_A(1-x) + r_B x$, one can obtain the derivative of T_g with respect to $\bar{r}$

by replacing in all eqs. (1)-(3) x by $(\bar{r} - r_A)/(r_B - r_A)$:

$$\left[\frac{\mathrm{d}T_\mathrm{g}}{\mathrm{d}\bar{r}}\right]_{\bar{r}=r_A, T_\mathrm{g}=T_0} = \frac{T_0}{(r_B - r_A)\ln\left[\dfrac{r_B}{r_A}\right]} . \tag{5}$$

The value of the coordination number r_B can be determined in most of the situations by the $8 - N$ rule, where N is the number of outer shell electrons of the considered atom [7] (and of course, in the forthcoming, $r_A = 2$). From the second part of eq. (5), it is possible to demonstrate the stochastic origin of the heuristic GDM equation at low connectivity ($\bar{r} = 2$) and to show that the modified equation proposed by Varshneya and co-workers [4] is the correct expression as long as this equation remains linearly extrapolated. The GDM theory of glass transition (based on equilibrium principles) is intended to describe the variation of T_g of long polymer chains of equal length, with chain stiffness produced by cross-linking agents [2]. The T_g of the cross-linked glass is suggested to behave as: $T_\mathrm{g} = T_0(1 - \kappa X)^{-1}$, where X is the cross-link density and κ a constant. From the construction of the theory, it is easily conceivable that it might describe chalcogenide glasses as well, because the initial selenium network is also made of long polymeric chains, and the modifier atoms as Ge or As should play the cross-linking agents. To this end, the GDM equation has been recently adapted with success by Varshneya and co-workers in order to describe the T_g trends in chalcogenides [4]: $T_\mathrm{g} = T_0/(1 - \beta(\bar{r} - 2))^{-1}$ (which we will denote by VGDM equation). The parameter β is obtained from a least-squares fitting of the experimental data. Now, if one performs the derivative with respect to $\bar{r}$ of the first-order Taylor expansion (linear) of the latter expression in the vicinity of $\bar{r} = 2$, one obtains βT_0. This can be compared with the right-hand side of eq. (5) and yields an analytical expression for β: $\beta^{-1} = (r_B - 2)\ln[\frac{r_B}{2}]$. In a two-component chalcogenide glass (A, B), the constant β has a topological origin and can be easily computed from the coordination number of the modifier atom B.

We shall prove that the factor appearing in the expression of β has a universal character and can be extended to M-component glass system, yielding the value of the parameter β for any sytem, to be inserted in the VGDM equation. This result will still be obtained in the limit where the VGDM equation emerges naturally from a stochastic description of the network.

Before, we shall consider a glass system made of three different kinds of atoms (say A, B and C, with respective concentration $1 - x - y$, x and y), one of them being the chalcogenide atom of the chain-like initial structure (when $x = 0$ and $y = 0$). The coordination numbers of the involved atoms are $r_A = 2$, r_B and r_C. The average coordination number is $\bar{r} = r_B x + r_C y + 2(1 - x - y)$ and

$$\frac{\mathrm{d}\bar{r}}{\mathrm{d}T_\mathrm{g}} = (r_B - 2)\frac{\mathrm{d}x}{\mathrm{d}T_\mathrm{g}} + (r_C - 2)\frac{\mathrm{d}y}{\mathrm{d}T_\mathrm{g}}. \tag{6}$$

We can still identify the derivative of the first-order Taylor expansion of the VGDM equation in the vicinity of $\bar{r} = 2$ with the right-hand side of (6), where consequently $x = 0$ and $y = 0$ and where the quantities $\mathrm{d}x/\mathrm{d}T_\mathrm{g}$ and $\mathrm{d}y/\mathrm{d}T_\mathrm{g}$ have the form presented in eq. (4) (*i.e.* $\ln[r_B/r_A]/T_0$ and $\ln[r_C/r_A]/T_0$). By identification, this leads to the analytical expression of the parameter β in a glass made of three components: $\beta^{-1} = (r_B - 2)\ln[r_B/2] + (r_C - 2)\ln[r_C/2]$. The extension to multicomponent systems appears to be quite natural. β has the same sum rules as the resistance in a parallel circuit in electrokinetics, *i.e.* it is the sum of the $1/\beta$ of each related two-component system AB, AC, etc. Finally, for a system made of M different kinds of atoms with coordination numbers r_i, we just have to sum up the $M - 1$ contributions

$(r_i - 2) \ln[\frac{r_i}{2}]$ in order to obtain the theoretical value of β^{-1}:

$$\frac{1}{\beta} = \sum_{i=1}^{M-1} (r_i - 2) \ln\left[\frac{r_i}{2}\right]. \tag{7}$$

In this notation, m_M is the coordination number of the chain atom, equal to 2. However, when applied to ternary systems, the stochastic description with three kinds of atoms A, B and C is able to predict the VGDM equation up to $\bar{r} \simeq 2.3$ with the correct value of β, satisfying (7), starting from a system which satisfies $p_B^a = p_B^b$ and $p_C^a = p_C^b$ [8].

Comparison with experimental data. – In order to minimize the influence of the preparation techniques, we have carefully selected data of i) glass systems prepared with the same heating/cooling rate and ii) glass systems with more than five different compositions [9]. The initial value T_0 has been averaged over a set of data found in the literature (T_0 of v-Se has been taken as 316 K, of v-S as 245 K). We have plotted in fig. 1 several experimental data on binary, ternary and quaternary systems with the parameter β computed from the involved coordination numbers r_i and the VGDM equation (solid lines). The dotted lines correspond to the slope equation (5) and shows the stochastic origin of the VGDM equation at low connectivity ($\bar{r} \simeq 2$). For other systems, we have performed a least-squares fit of the parameter β from the VGDM equation, denoted as β_{exp}. Then, we have compared the results with the predicted parameter β_{pr} obtained from (7). In the system Si-As-Ge-Te the involved coordination numbers of the modifier atoms are $r_i = (4, 3, 4)$. Thus, $\beta_{\text{pr}} = (3 \ln 2 + \ln 3)^{-1} = 0.31$, in excellent agreement with the fit $\beta_{\text{exp}} = 0.30$ [13]. Examples displayed in fig. 1a show also that the slope (5) yields accurate trends in the variation of T_{g} with respect to the average coordination number $\bar{r}$ at low connectivity.

From fig. 1a, we can obviously see that the addition of a two-coordinated atom (as tellurium or sulphur, $r_i = 2$) in multicomponent glass systems does not affect the value of the parameter β (because of the rate $\ln[r_i/2]$). A quaternary system which involves a two-coordinated atom can therefore be considered as a ternary system. The simultaneous use of the VGDM equation and the stochastic prediction of (7) can give the value of the glass transition temperature of any composition, at least for $\bar{r} \leq 2.4$ which is the limit imposed by Maxwell rigidity [5]. We invite the reader to check on this basis that the T_{g} of $Ga_{10}B_{10}S_{80}$ is about 325 K. For greater values of $\bar{r}$, one has to take into account intermediate-range order effects such as the existence of rings [6, 14] or chemical ordering. However, the stochastic model suggests also that usual curve-fitting with the VGDM equation [4, 15] does not permit to distinguish between floppy and rigid regions (limited by $\bar{r} = 2.4$), whereas the combination of VGDM and (7) show direct evidence of the stiffness transition between these two regions. This is due to the fact that β is evaluated from the random network description and it fails around 2.4. To illustrate this observation, we have plotted in fig. 1b for the P-Ge-Se compound the least-squares fit of the VGDM equation (dotted line) ($\beta_{\text{exp}} = 0.66$, realized over the whole concentration range [16]) and the VGDM equation, combined with the sum rule (7) for $\beta_{\text{pr}} = 0.55$ (solid line). The deviation occurs at $\bar{r} = 2.43$, consistently with constraint counting arguments [5]. We have also plotted in the insert of fig. 1b the value β_{exp} computed from the VGDM equation, as a function of the average coordination number, in In-Ge-Se systems [15]. This clearly shows the threshold around $\bar{r} = 2.4$ between the values $\beta = 0.55$ (predicted from the model by the random network picture) and $\beta = 0.72$ (predicted from the model by the occurrence of chemical ordering, as we shall see below). A global fit of the VGDM equation (dotted line) with a unique value of β would not have given this information.
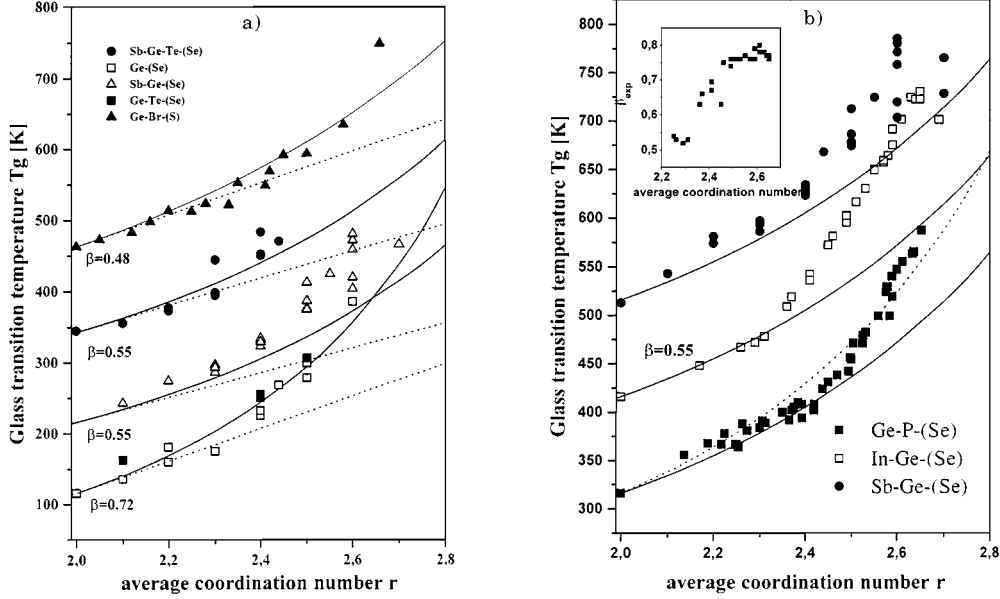
Fig. 1. – a) Comparison of the VGDM equation with the stochastic calculation of β (7) with experimental measurements in binary, ternary and quaternary glasses (solid line). The slope equation (5) corresponds to the dotted lines. Systems Ge-Te-(Se), $r_i = (4, 2)$ and Ge-(Se), $r_i = 4$ [17]: $\beta_{\mathrm{pr}} = 0.72$. System Sb-Ge-Te-(Se), $r_i = (3, 4, 2)$ and Sb-Ge-(Se), $r_i = (3, 4)$ [4]: $\beta_{\mathrm{pr}} = 0.55$. System Ge-Br-(S), $r_i = (4, 1)$ [18]: $\beta_{\mathrm{pr}} = 0.48$. b) Occurrence of chemical ordering in ternary selenides (data from [4, 16, 12]). The stochastic description yields for all $\beta_{\mathrm{pr}} = 0.55$, since $r_i = (3, 4)$ in the three systems. The solid line represents the combination of this description with the VGDM equation. The dotted line corresponds to the VGDM equation with β fitted from the whole concentration range, as realized in [4]. For $\bar{r} > 2.4$, the systems behave as a binary glass with $r_i = 4$ and $\beta_{\mathrm{pr}} \simeq 0.72$. The insert shows β_{exp} *vs.* the average coordination number $\bar{r}$ for the In-Ge-Se compound. All data sets have been displaced by 100 K for a clearer presentation.

Effect of chemical ordering. – In most of the chalcogenide systems, chemical ordering occurs for $\bar{r} \geq 2.4$, and therefore stochastic description fails, as shown in fig. 1. However, the description is still useful, if the network can be thought as a set of compound clusters inside a random network.

Again, let us consider a ternary glass system $A_{1-x-y}B_x C_y$ with the corresponding coordination numbers $r_A = 2$, r_B and r_C. If we assume that the general tendency of the glass is to form a demixed structure of A and B in stoichiometric proportions, then we can rewrite the system as: $(B_{r_A} A_{r_B})_{x/r_A} C_y A_{1-y-(r_A+r_B)x/r_A}$. For the glassy matrix, this defines an effective concentration of C atoms $y^{\mathrm{eff}} = \frac{y}{1-x(r_A+r_B)/r_A}$ and the average coordination number of the glassy matrix is given by

$$\bar{r} = r_A + \frac{(r_C - r_A)y}{1 - x\dfrac{(r_A + r_B)}{r_A}} \, . \tag{8}$$

If we proceed as before, *i.e.* performing the derivative with respect to T_{g} and looking at the limit $(x, y \to 0)$ in order to identify with the expansion of the VGDM equation, we can see that the corresponding parameter β is defined as $\beta^{-1} = (r_C - r_A) \ln[\frac{r_C}{r_A}]$. In other words, the parameter β of a ternary system which displays chemical ordering can be computed

by considering only the remaining two-component glass. We have checked the validity of this rule on a set of germanium-incorporated chalcogenides. We have considered all possible stoichiometric demixed structures at the tie-line composition (*e.g.*, in $Ge_xAs_ySe_{1-x-y}$, the possible structures are $GeSe_2$ and As_2Se_3). Most of the ternary III-IV-VI systems such as Sb-Ge-X glasses (X = S, $\beta_{exp} = 0.61$ [19]; X = Se, $\beta_{exp} = 0.78$ [20]; X = Te, $\beta_{exp} = 0.79$ [21]) behave as a single binary IV-VI glass (as Ge-Se) with parameter close to $\beta_{pr} = 0.72$ when $\bar{r} > 2.4$. This is explained by the presence of Sb_2X_3 clusters (X = S, Se, Te) inside the remaining random network of Se-Se and Ge-Se bonds. Also, data on Sn-Ge-Se systems show that $\beta_{exp} = 0.68$, when $SnSe_2$ clusters are assumed, close to $\beta_{pr} = 0.72$ [22]. Coming back to the illustrative In-Ge-Se compound (insert of fig. 1b), the behavior of T_g *versus* $\bar{r}$ can be explained as follows. For $\bar{r} < 2.4$, the structure can be described by a random network of Se-Se, Ge-Se, In-Se and Ge-In bonds. For this system, the VGDM equation and (7) describe the $T_g(\bar{r})$ behavior, with $\beta_{pr} = 0.55$ is computed from (7) with $r_i = (3, 4)$. For $\bar{r} > 2.4$, the network structure looses its random character because of the occurrence of In_2Se_3 clusters [15]. Thus, the system behaves as a pseudo-binary Ge-Se system with the effective concentration (8) and $\beta_{pr} = 0.72$.

<p align="center">***</p>

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[9] We have checked that the influence of the heating rate on the value of β could be neglected at the heating rates which were used in the preparation of the glasses we have investigated. To do this, we have used both Kissinger's formula [10] $\ln[\frac{T_g^2}{Q}] + \text{const} = \frac{E}{RT_g}$, which is very well adapted for the description of chalcogenide glasses, and the VGDM equation. Q is the heating rate, E the activation energy for glass transition and R the gas constant. Inserting typical values of $\bar{r}$, E and T_0 shows that β depends weakly on Q ($\Delta\beta/\beta \leq 5\%$). This verification has been also realized on systems for which the heating rate in DSC calorimetry was reported. For example, the parameter β of the glass As-Sb-Se lies in the range [1.14, 1.17] (computed from a least-squares fit) for cooling rates between $Q = 0.62$ K min^{-1} and 40 K min^{-1}, which corresponds to $\Delta\beta/\beta = 0.013$ [11]. In Ge-Sb-Se glasses, β varies as $\Delta\beta/\beta = 0.0014$ for glasses cooled through the transition at 10 K min^{-1} and quenched glasses [12].

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