Simple rules for the prediction of the value of the glass transition temperature in network glasses

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We give in this letter a set of general rules which allow the prediction of the value of the glass transition temperature $T_g$ in network glasses. Starting from the Gibbs-Di Marzio law which gives a very general relationship between this temperature and the average coordination number of a system, we explain how to compute from the valencies of the atoms of the glass, the parameter $\beta$ used in this law. We check the validity of the obtained expression and show that it is possible to predict the glass transition temperature for any composition in multicomponent chalcogenide glasses. The possibility of existence of a demixed structure is also discussed.

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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.

The origin of glass-forming tendency and the determination of the value of the glass transition temperature is a subject of great interest, not only for purely scientific reasons, but also for technological reasons, because the exact or the approximate value of \( T_g \) is needed in some situations in order to optimize the glass preparation process. Therefore, numerous efforts have been realized in order to understand the nature of glass transition, but also to relate the value of \( T_g \) to some easily measurable quantities. One of the best known relationships is the "two-third" rule proposed by Kauzmann, stating that \( T_g \) scales with the melting temperature as \( T_g \approx \frac{2}{3}T_m \) [1]. More recently, Tanaka has proposed an empirical relationship between \( T_g \) and the average coordination number. The relationship is readily satisfied in oxides, chalcogenides and organic glass-forming materials [2].

Importance of thermodynamic factors in glass formation have been discussed by Adam and Gibbs [3], and Gibbs and Di Marzio [4], suggesting that the glass transition may be a manifestation of a second-order phase transition, when both the Gibbs energy and its derivatives remain continuous (at the melting temperature, where the liquid crystallize, the derivatives of the Gibbs energy are discontinuous, but not the Gibbs energy). Applying the theory to a liquid made of molecular chains, the authors found a quantitative relationship between the transition temperature and the density of cross-linking agents inserted inside the system. Later on, the relationship was adapted to chalcogenide glasses, yielding the following equation, known as the Gibbs-Di Marzio law [5]-[6]:

\[
T_g = \frac{T_0}{1 - \beta(<r>-2)}
\]

(0.1)

where \( T_0 \) is the glass transition temperature of the chain-like glass (e.g. vitreous selenium with \( T_0 = 316 \text{ K} \)), \( \beta \) a system-dependent parameter and \( <r> \) the average coordination number.
number. The latter has been introduced by Phillips in his constraint theory \( [7] \) and is widely used in the investigation of network glasses \( [8] - [10] \). \( < r > \) is defined in a M-component glass by 
\[
< r > = \sum_{i=1}^{M} m_i x_i ,
\]
where \( m_i \) is the valence of an atom with concentration \( x_i \) (e.g. \( < r > = 2.67 \) in GeSe\(_2\)). Agreement of the Gibbs-Di Marzio law with experimental data could be obtained by fitting the parameter \( \beta \) for numerous glass systems \( [3] - [4] \). Thus, the Gibbs-Di Marzio law seems to describe very well the \( T_g \) trends as a function of the average coordination number \( < r > \), at least for concentrations corresponding to \( < r > \leq 2.7 \).

On the contrary, if one could compute exactly the parameter \( \beta \) of a given glass system, one could be able to predict its glass transition temperature \( T_g \) as a function of \( < r > \). The purpose of the present letter is to show that the parameter \( \beta \) is related to the local glass structure and can be easily computed for any chalcogenide glass system.

In a recent series of papers \( [11] - [14] \), R. Kerner and one of us have demonstrated by use of a model of statistical agglomeration that the glass transition temperature \( T_g \) displayed a very simple law (called ”slope equations” in weakly modified binary glass systems, such as \( Ge_xSe_{1-x} \) with \( x \) the concentration of the modifier atom less than 0.1.

\[
\left[ \frac{dT_g}{dx} \right]_{x=0,T_g=T_0} = \frac{T_0}{\ln \left[ \frac{m_B}{2} \right]} 
\]

(0.2)

where \( T_0 \) stands for the initial glass transition temperature and has the same meaning as the one appearing in equation (0.1). \( m_B \) is the coordination number (or valence) of the modifier atom (e.g. \( m_B = 4 \) is the valence of the germanium atom in \( Ge_xSe_{1-x} \) systems). The value of these coordination numbers 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 \( [15] \). Thus, the slope in equation (0.2) indicates how the value of the glass transition temperature will change if a small proportion of modifier atoms (such as Ge or As) is added to the initial network.

The relationship (0.2) is very well satisfied in more than 30 different glass systems such as chalcogenides and binary glasses (e.g. \( (1-x)SiO_2 - xLi_2O \) \( [13] \). Last but not least, if one uses the average coordination number of the network \( < r > = m_B x + 2(1 - x) \) and performs the first-order Taylor expansion of the Gibbs-Di Marzio law (0.1) in the vicinity of \( < r > = 2 \),
it is possible to obtain an analytical expression for the parameter $\beta$ in two-component glass: 

$$\frac{1}{\beta} = (m_B - 2) \ln \left[ \frac{m_B}{2} \right]$$  \hspace{1cm} (0.3)

Here again, the predicted value of the parameter $\beta$ computed from obvious structural considerations ($m_B = 4$, $m_B = 3$, etc.) is in excellent agreement with the value determined from experimental data [12]. We shall now prove that the factor appearing in the right-hand side of equation (0.3) has a universal character and can be easily extended to a multicomponent chalcogenide glass system, yielding the value of the parameter $\beta$ for any system, to be inserted in the Gibbs-Di Marzio law (0.1). To do this, we shall compute from available experimental data the value of the parameter $\beta$ and compare it to the predicted one.

Let us extend the expression (0.3) to a M-component glass. For the reader’s convenience, we shall first 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 atom of the chain-like initial structure (when $x = 0$ and $y = 0$). The valences of the involved atoms are $m_A = 2$, $m_B$ and $m_C$. The average coordination number is $< r > = m_B x + m_C y + 2 (1 - x - y)$. We can compute the derivative with respect to the glass transition temperature:

$$\frac{d < r >}{dT_g} = (m_B - 2) \frac{dx}{dT_g} + (m_C - 2) \frac{dy}{dT_g}$$  \hspace{1cm} (0.4)

and look at the limit when $< r > \simeq 2$ (i.e. $T_g \simeq T_0$, $x = 0$ and $y = 0$). Then, we can still identify the derivative of the first-order Taylor expansion of the Gibbs-Di Marzio law (1.1) with the right-hand side of equation (0.4), where the quantities $dx/dT_g$ and $dy/dT_g$ have the form presented in equation (0.2). Identifying all this and simplifying by $T_0$ leads to the analytical expression of the parameter $\beta$ in a glass made of three components:

$$\frac{1}{\beta} = (m_B - 2) \ln \left[ \frac{m_B}{2} \right] + (m_C - 2) \ln \left[ \frac{m_C}{2} \right]$$  \hspace{1cm} (0.5)

The extension to multicomponent systems appears to be quite natural. $\beta$ has the same sum rules as the resistance in a parallel circuit in electrokinetics, i.e. it is the sum of the
1/β of each related two-component system AB, AC, etc. For a given system made of $M$ different kinds of atoms with valencies $m_i$, we just have to sum up the $M - 1$ contributions $(m_i - 2) \ln \left( \frac{m_i}{2} \right)$ in order to obtain the theoretical value of $\beta^{-1}$.

\[
\frac{1}{\beta} = \sum_{i=1}^{M-1} (m_i - 2) \ln \left( \frac{m_i}{2} \right)
\]  

(0.6)

In this notation, $m_M$ is the coordination number of the chain atom, equal to 2. We have looked at the validity of this expression on a variety of different glass systems (ternary glasses as $As_xGe_ySe_{1-x-y}$ and multicomponent glasses such as $As - Si - Ge - Se$, etc.)

**Comparison with experimental data:** In order to minimize the influence of the preparation techniques and to obtain a meaningful correlation coefficient, we have carefully selected data of i) glass systems prepared with the same heating/cooling rate ii) glass systems with more than five different compositions. We have checked that the influence of the heating rate on the value of $\beta$ 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 the Kissinger’s formula

\[
\ln \left( \frac{T^2}{Q} \right) + \text{const.} = \frac{E}{RT_g}
\]  

(0.7)

which is very well adapted for the description of chalcogenide glasses, and the Gibbs-Di Marzio law. $Q$ is the heating rate, $E$ the activation energy for glass transition and $R$ the gas constant. Inserting typical values of $< r >$, $E$ and $T_0$ shows that $\beta$ depends weakly on $Q$ ($\Delta \beta/\beta \leq 5\%$). This verification has been also realized numerically on systems for which the heating rate in DSC calorimetry was reported. For example, the parameter $\beta$ 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 $\Delta \beta/\beta = 0.013$.

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 performed a least-squares fit of the Gibbs-Di Marzio law applied to the data. The results of the fit for the parameter $\beta$, denoted as $\beta_{exp}$, and the correlation coefficient are displayed in Table I with their corresponding reference. For completeness, we have reported in the first part of Table
I some results \[12\] for two-component systems, which satisfy \((0.3)\). The results can be compared with the predicted value of \(\beta\), denoted as \(\beta_{pr}\) in Table I, which has been computed from equation \((0.6)\). For example, in the system Si-As-Ge-Te the involved valencies of the modifier atoms are 4, 3 and 4 respectively. Thus, \(\beta_{pr}^{-1} = 3 \ln 2 + \ln 3\) and \(\beta_{pr} = 0.31\), in excellent agreement with the fit \(\beta_{exp} = 0.30\). The number of different glasses satisfying exactly or roughly the rule \((0.6)\) is impressive and proves that the agreement is not a matter of coincidence.

Let us now come to the prediction of glass transition temperature values. We can note that the addition of a two-valenced atom (as tellurium or sulphur) in multicomponent glass systems does not affect the value of the parameter \(\beta\). A 4-component system which involves a two-valenced atoms can therefore be considered as a ternary system (Table I) and \(T_0\) is then the glass transition temperature of the initial mixture (e.g. \(Se - Te\)). But for all the other elements of the columns III, IV and V, we can compute the value of \(\beta\) and represent \(T_g\) as a function of \(< r >\) (fig.1). The simultaneous use of equations \((0.1)\) and \((0.6)\) should give the value of the glass transition temperature of any composition, at least for \(< r > \leq 2.4\) (as shown on figure 1 for the comparison between the theoretical Gibbs-Di Marzio law and the experimental data). For greater values of \(< r >\), one should take into account intermediate range order effects such as the existence of rings \([9]\)-\([10]\). This extra influence has not been considered here.

**Influence of a demixed structure:** Nevertheless, there are still several systems for which the predicted value of \(\beta\) does not match with the computed one. The difference between \(\beta_{exp}\) and \(\beta_{pr}\) can be quantitatively discussed in terms of the presence of some demixed structure inside the network. This feature is generally used in order to explain the unusual variation of \(T_g\) in glasses, such as \(Bi_xSe_{1-x}\) or \(In_xSe_{1-x}\). In the former system, data obtained for the \(Bi - Se\) glass, show that glass transition temperature increases with \(Bi\) content for low modification, in perfect agreement with the slope equation \((0.2)\). But when \(x > 0.1\), \(T_g\) remains constant \([22]\). This behavior is attributed to the existence of a demixed structure of \(Bi_2Se_3\) microclusters. The same happens in the indium selenide compound at every
concentration, and evidence of $In_2Se_3$ clusters has also been discussed \[23\].

Again, let us consider as before a ternary glass system $A_{1-x-y}B_xC_y$ with the corresponding coordination numbers $m_A = 2$, $m_B$ and $m_C$. 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: $(B_{m_A}A_{m_B})x/mAC_{y}A_{1-y-((m_A+m_B)x/m_A)}$ which defines an effective concentration of $C$ atoms $y^{eff} = \frac{y}{1-x(m_A+m_B)/m_A}$ and the average coordination number of the system is given by:

$$<r> = m_A + \frac{(m_C - m_A)y}{1 - x(m_A+m_B)/m_A}$$  \hspace{1cm} (0.8)

If we proceed as before, i.e. taking 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 Gibbs-Di Marzio law, we can see that the corresponding parameter $\beta$ is defined as $\beta^{-1} = (m_C - m_A)\ln[m_C/m_A]$. In other words, the parameter $\beta$ of a ternary system which displays a demixed structure can be computed by considering only the remaining two-component glass. Here again, we have checked the validity of this rule on a set of germanium incorporated chalcogenides (Table II). 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 $As_2Se_3$). Again, we have computed the corresponding parameter $\beta_{pr}$ and compared it to the value $\beta_{exp}$ obtained from a least-squares fit. Table II shows that most of the $III - IV - VI$ systems such as $Sb - Ge - S$ glasses behave as a single $IV - VI$ glass (as $Ge - Se$) with parameter $\beta_{pr} = 0.72$. This is explained by the presence of $A_2X_3$ ($X = S, Se, Te$) clusters with $A$ an element of the column III or V.

In summary, we would like to recall the most important rules to be used if one wishes to determine a glass transition temperature of a multicomponent chalcogenide glass.

1. Consider all the possible demixed stoichiometric structures of the $M$-component chalcogenide glass. There is in general a strong evidence of demixing in the case of $Sb$ ternary based glasses \[29\].
2. Given the concentrations \( x_i \) of the atoms, compute the average coordination number \( < r > \), either directly, or by use of the effective concentration \( x_i^{eff} \) if there is some evidence of structural demixing.

3. Compute the parameter \( \beta \) from the coordination numbers of the remaining atoms (those which are not involved in the demixed structure).

4. Insert \( \beta \) and \( < r > \) in the Gibbs-Di Marzio law in order to obtain the glass transition temperature.

As illustrative examples of these rules, we give for the conclusion glass transition temperatures of systems, which have to our knowledge never been investigated.

Assuming that \( \Delta \beta/\beta \approx 0.1 \) (possibly produced by the heating rate effects, see above, or anything else) and if there is no demixing, the glass \( As_5Ga_5Si_{15}Se_{75} \) should have a transition temperature of about 385 ± 8 K since \( \beta = 0.45 \) is computed from the valencies \( m_i = (3, 3, 4) \) and \( < r > = 2.4 \). In the sulphide analog glass, one should measure 299 ± 7 K. Similarly, the glass \( Ga_{10}B_{10}S_{80} \) should have a transition temperature of \( T_g = 325 ± 11 \) K (\( \beta = 1.23 \) computed from the valencies \( m_i = (3, 3) \) and \( < r > = 2.2 \)).

The influence of intermediate range order on this set of rules will be discussed in a forthcoming article. Also, work devoted to the influence of the cooling/heating rate on the value of the glass transition temperature is in progress.

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| System                  | $\beta_{pr}$ | $\beta_{exp}$ | Correlation Reference |
|-------------------------|--------------|---------------|-----------------------|
| Ge-(Se)                 | 0.72         | 0.72          | 0.988 from [12]       |
| Ge-(S)                  | 0.72         | 0.73          | 0.998 from [12]       |
| Si-(Se)                 | 0.72         | 0.81          | 0.997 from [12]       |
| Ge-Sb-(Se)              | 0.56         | 0.66          | 0.972                 |
| Ga-Ge-(Se)              | 0.56         | 0.55          | 0.965 from [24]       |
| Ga-Ge-(S)               | 0.56         | 0.59          | 0.823 from [18]       |
| As-Sb-(Se)              | 1.23         | 1.17          | 0.995 from [19]       |
| Al-P-(Se)               | 0.32         | 0.21          | 0.952 from [20]       |
| Ge-Sb-Te-(Se)*          | 0.56         | 0.55          | 0.998                 |
| Si-As-Ge-(Te)           | 0.31         | 0.30          | 0.979 from [21]       |
| Ge-Sb-As-Te-(Se)*       | 0.45         | 0.55          | 0.989                 |

TABLE I. Different multicomponent glass systems. Comparison between the predicted value $\beta_{pr}$ obtained from equation (0.6) given the valencies of the involved atoms, and the value $\beta_{exp}$ computed from experimental data by a least-squares fit. The atom which corresponds to the chain-like entity corresponds to the chemical symbol inside the brackets. M-component glasses with an * can be considered as (M-1) component glasses for the computation of $\beta$, since they involve a two-valenced atom (Te).
| System       | $\beta_{exp}$ | Demixed Correlation Reference structure coefficient |
|--------------|---------------|-----------------------------------------------------|
| In-Ge-(Se)   | 0.77          | $In_2Se_3$                                          |
|              |               | 0.993 [24]                                           |
| Sb-Ge-(S)    | 0.61          | $Sb_2S_3$                                           |
|              |               | 0.932 [25]                                           |
| Sb-Ge-(Se)   | 0.78          | $Sb_2Se_3$                                          |
|              |               | 0.986 [26]                                           |
| Sb-Ge-(Te)   | 0.79          | $Sb_2Te_3$                                          |
|              |               | 0.992 [27]                                           |
| Sn-Ge-(Se)   | 0.68          | $SnSe_2$                                            |
|              |               | 0.973 [28]                                           |

**TABLE II.** Different multicomponent glass systems exhibiting a demixed structure. Comparison between the predicted value of $\beta_{pr} = 0.72$ obtained by considering the remaining $Ge - X$ system ($X = S, Se, Te$) and the value $\beta_{exp}$ computed from experimental data by a least-squares fit. The atom which corresponds to the chain-like entity corresponds to the chemical symbol inside the bracketts.
FIG. 1. Several Gibbs-Di Marzio laws with the computed value of $\beta$ in multicomponent chalcogenide glasses. Solid line: $m_i = (3, 4, 4)$ and $\beta = 0.31$. Dashed line: $m_i = (2, 3, 4)$ and $\beta = 0.56$ with the experimental data of the $Te - Sb - Ge - Se$ system [3] (boxes). Dotted line: $m_i = (3, 3, 3)$ and $\beta = 0.82$. 