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The slope equations: A universal relationship between local structure and glass transition temperature

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Abstract. In this article, we present a universal relationship between the glass transition temperature T_{g} and the local glass structure. The derivation of the simplest expression of this relationship and some comparisons with experimental T_{g} values have already been reported in a recent letter. We give here the analytical expression of the parameter β of the Gibbs-Di Marzio equation and also new experimental probes for the validity of the relationship, especially in low modified binary glasses. The influence of medium range order is presented and the unusual behavior of T_{g} in binary B_2S_3 and P_2S_5 systems explained by the presence of modifier-rich clusters (denoted by B−B doublets).

PACS. 61.20.Ne Structure of simple liquids – 81.20.Zx Other methods of materials synthesis and materials processing

1 Introduction

It is well-known that the formation of glasses requires cooling to a sufficiently low temperature — below the glass transition — without the occurrence of detectable crystallization. In treating this phenomenon, it is has been suggested by different authors that specific structural features or physical properties will result in glasses being formed [1–6]. Various models have been proposed in order to describe this transition, which can appear superficially to be a second-order thermodynamic phase transition. These models generally involve factors (thermodynamic, structural, kinetic) which are viewed as decisive in the formation of glasses.

The best known structural model of glass formation and glass formation ability is that due to Zachariasen [7] and others [8,9] who proposed a classification of oxide materials in terms of glass-formers (*e.g.* SiO_2), modifiers (*e.g.* Li_2O) and intermediates (*e.g.* PbO). This led to the random network concept [10] which received support from X-ray diffraction studies of a variety of glasses, although these studies did not establish the model as unique representation of the structure [11–13]. In these models, the relationship with the glass transition temperature is lacking.

The importance of thermodynamic factors in glass formation has been pointed out by Gibbs and Di Marzio and by Adam and Gibbs [14,15]. These authors suggested that the glassy state is thus defined in terms of thermodynamic variables (temperature, volume, ...) and related ones (bulk compressibility, heat capacity, ...), but it is not necessarily implied that the glassy state is one of even metastable equilibrium (with reference to a possible crystalline phase). It can be stated that a glass-forming material has equilibrium properties, even if it may be difficult to realize. The theory developed by Adam and Gibbs on this basis, was able to predict a second-order phase transition and also a quantitative relationship between glass transition temperature and the cross-linking density in some linear molecular chains.

Nevertheless, when the glass transition temperature is measured under standard conditions (for example calorimetrically at a fixed heating rate), an important question concerns the relationship of T_{g} with some other physical and measurable factors. Various proposals have been made in the past which suggested for example that T_{g} scales with the melting temperature (the "*two-third rule*" proposed by Kauzmann [16]), the boiling temperature, the Debye temperature of the phonon spectrum, *etc.* [17]. Besides the influence of these thermodynamic factors, attention has been brought to structural factors, in particular to the valence of the involved atoms in the glass-forming material. Tanaka [18] has given an empirical relationship between T_{g} and Z, the average coordination number per atom: $\ln\ T_{\mathrm{g}} \simeq 1.6Z + 2.3$. This proposal agrees for various glass-forming systems including chalcogenide materials and organic polymeric materials. However, the relationship between structural factors and T_{g} becomes more complicated if the composition of the glass-forming alloy is changing. For example, in Ge_xSe_{1-x} network glasses,

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the glass transition temperature does not vary monotically with x, and exhibit even some characteristic behavior (maximum at $x = 0.33$ [19], which corresponds to the stoichiometric composition $GeSe_2$, anomaly at $x = 0.2$, where the average coordination number $\langle r \rangle$ is equal to 2.4). Obviously, T_g is sensitive to the chemistry involved, and a maximum in T_g at the stoichiometric composition may result from the formation of a chemically ordered network in which only the Ge–Se bonds are present. In other systems, a generally accepted rule states that T_g increases when the connectivity of the network increases, and *vice-versa*. Besides these rather qualitative relationships between structure and glass transition temperature, there exists a firm rule for predicting T_g in particular glassy materials, namely chalcogenide network glasses. The equation relating the glass transition temperature to some structural factor is due to Gibbs and Di Marzio [14]. Varshneya and co-workers have shown recently that a similar equation was particularly well adapted for predicting T_g in multicomponent chalcogenide glass systems [20]. Indeed, one can consider the chalcogenide glass system as a network of chains (*e.g.* of selenium atoms) in which cross-linking units (such as germanium atoms) are inserted. The increase of T_g is produced by the growing presence of these cross-linking agents, which can be roughly explained by the growth in network connectivity. In the former version, Gibbs and Di Marzio successfully applied their equation in order to explain the T_g data in polymers [21]. A modified theory constructed by Di Marzio [22] has shown that for glass systems with some chain stiffness, the glass transition temperature *versus* cross-linking density X could be expressed as:

$$T_g = \frac{T_0}{1 - \kappa X} \tag{1}$$

where T_0 is the glass transition temperature of the initial polymeric chain and κ a constant. In this article, we shall present several relationships between the glass transition temperature and the local structure in glass-forming materials, by using the agglomeration model, created by Kerner and Dos Santos [23] and applied with success to various glass-forming systems [24]. The physical basis of the model can be found in references [25,26]. Different situations will be reviewed in this article and previous results, reported in [27], will be inserted for completeness. In Section 2, we present the construction with star-like entities and obtain the first slope equation for corner-sharing structures (single bonded network, *i.e.* absence of dimers). Comparison with experimental data is presented in Section 3 for chalcogenide network glasses and for binary glasses. The relationship with the Gibbs-Di Marzio equation is also given in a forthcoming subsection. The influence of other structural contributions, such as the edge-sharing tendency between two local structures (two-membered rings, or dimers), which modifies slightly the slope equation, is presented, as well as the influence of particular bonds, leading to a second set of slope equations. These equations can describe the unusual behavior of T_g in B_2S_3 and P_2S_5 based glasses. Finally, Section 4 summarizes the most important results of the paper.

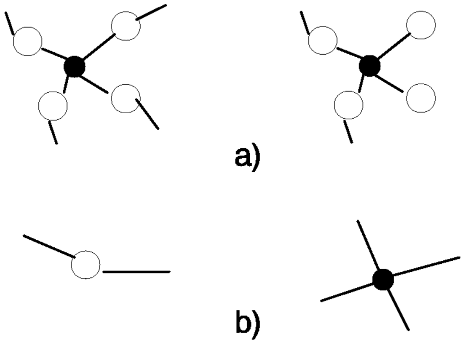

Fig. 1. A schematic representation of a choice of local configurations. a) Possible SRO star-like configurations in SiO_2-Li_2O glasses: a "*regular*" tetrahedron $SiO_{4/2}$ (a $Q^{(4)}$ structure) and an "*altered*" tetrahedron $SiO^{\ominus}_{4/2}$ (a $Q^{(3)}$ structure). b) Ge_xSe_{1-x} glass: a "*regular*" atom Se and an "*altered*" atom Ge.

2 Construction with star-like entities

2.1 A very simple structural consideration

For the reader's convenience, we shall first present the simplest possible construction of the agglomeration model, with two star-like entities. The vocabulary introduced in this section will be illustrated, whenever possible, by two archetypal glass systems which are binary SiO_2 systems and Ge_xSe_{1-x} glasses.

The simplest way of describing short range order (SRO) in glasses can be made on the basis of star-like entities (we shall also call *singlets* or local configurations [26]). These local configurations share a central atom and they provide clear, unambiguous experimental evidence and a well-defined coordination number (Fig. 1). The nature of the coordination can eventually be revealed by X-ray or inelastic neutron diffraction techniques [28,29] which exhibit sharp and characteristic peaks at the corresponding bond lengths and give information about the number of nearest possible neighbors of a central atom. Typical examples are: the tetrahedron which is the lowest possible SRO structure in glasses such as SiO_2 or $SiSe_2$ [29] and their binary compounds (Fig. 1a), or a two-valenced selenium atom in Ge_xSe_{1-x} network glasses (Fig. 1b) [30]. Starting from a system with a single type of *singlet*, called "*regular*" local configuration, one can modify the system (and thus the structure) by adding a second kind of star-like entity, denoted by "*altered*" local configuration.

In the liquid and supercooled state, and finally in the glassy state, the probability of finding a "*regular*" local configuration A with coordination number m can be denoted by p (*e.g.* $SiO_{4/2}$ tetrahedra in SiO_2-Li_2O systems and of course $m = 4$), whereas the one related to an "*altered*" local configuration B with coordination number m' can be denoted by $1 - p$. p is a function of temperature. The coordination number m' can correspond either to the valence (in the case where B represents an atom), or to the number of covalent bonds which connect the local configuration to the rest of the glass network. In IV-VI based glasses, the number of coordination can be obtained by considering NMR spectroscopy patterns [31,32]. For example, when adding the modifier Li_2O in SiO_2, the number of covalent Si−O−Si bonds decreases, because of the creation of so-called "*non-bridging atoms*" (NBO) due to the high ionicity of lithium (creation of ionic $Li^{\oplus}O^{\ominus}$ bonds). The local configuration B should be the $SiO^{\ominus}_{4/2}Li^{\oplus}$ tetrahedron [31], and obviously $m' = 3$ (Fig. 1a). The creation of such a new local structure can be proposed on the basis of ^{29}Si MAS NMR experiments. The peaks attributed to the $SiO_{4/2}$ tetrahedra in v−SiO_2 (assigned to $Q^{(4)}$ structures in NMR notation where "4" stands for the number of Si−O−Si bridges on a tetrahedron) are slightly shifted with addition of Li_2O, and a typical chemical shift occurs due to the presence of $Q^{(3)}$ species (the $SiO^{\ominus}_{4/2}$ tetrahedron [31]). This chemical shift is compared to the one obtained from the corresponding crystalline compound (here the disilicate $Li_4Si_4O_{10}$ made of 100% $Q^{(3)}$) and identified. Finally, the local structure in binary SiO_2−Li_2O systems can be described in terms of $Q^{(k)}$ functions over the whole concentration range [33] (where $4 - k$ is the number of NBO's on a tetrahedron). With these examples, it is easy to see that the local configurations A and B can describe very well the structural change induced by the addition of Li_2O in silica based glasses, at least for small concentrations of Li_2O. In the network glasses A_xB_{1-x}, the number of coordination can be given by the $8 - N$ rule (where N is the number of outer shell electrons) [34].

We shall show how the glass transition temperature varies as a function of m and m'.

The aim of the construction is to evaluate the time dependence of the local configuration probability, and derive an equation which leads to the stationary régime of these probabilities [23]. One can reasonably assume that the variation of p remains important as long as the system is in the liquid or the supercooled state, where the low viscosity still allows the (A, B) configuration interchange by movement, diffusion, bond destruction and creation or cation switching (in case of the presence of an alkali modifier). This in turn, should produce a variation of the local probability with respect to the time and the temperature. Although we do not know exactly the relationship between viscosity and the temporal fluctuations of structure (*via* p), one should expect a vanishing of the fluctuations, when the viscosity has increased markedly with decreasing temperature. Then, the local probabilities reach a stationary value (no more fluctuations of A and B) and can be identified with a stable (crystal) or a meta-stable solid (glass) configuration. When p is very small (corresponding to a system with high proportion of A configurations), there are only two possible elementary processes of single bond formation (Fig. 2), *i.e.* A−A and A−B, the second *doublet* being identical to B−A.

The probabilities of these *doublets* may be proportional to the products of the probabilities of *singlets*, a Boltzmann factor which takes into account the energy of creation of the respective bond formation (*i.e.* E_1 for A−A and E_2 for A−B) and a statistical factor which may be regarded as the degeneracy of the corresponding stored energy, because there are several equivalent ways to join together two coordinated local configurations [26]. In the single bond formation, the statistical factor is simply the product of the corresponding coordination numbers (see Fig. 2). The probability of finding the constructed *doublets* is then:

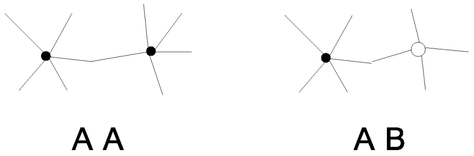

Fig. 2. Two possible connections of A and B configurations. With labelled bridges, there are $2 \times m \times m'$ ways to form the same doublet A−B.

$$p_{\mathrm{AA1}} = \frac{m^2}{\mathcal{Z}_1}(1-p)^2 \mathrm{e}^{-\beta E_1} \tag{2}$$

$$p_{\mathrm{AB1}} = \frac{2mm'}{\mathcal{Z}_1} p(1-p) \mathrm{e}^{-\beta E_2} \tag{3}$$

where β stands for $1/k_{\mathrm{B}}T$ with k_{B} the Boltzmann constant and $\mathcal{Z}_1$ is the normalizing factor given by:

$$\mathcal{Z}_1 = m^2(1-p)^2\mathrm{e}^{-\beta E_1} + 2mm'p(1-p)\mathrm{e}^{-\beta E_2}. \tag{4}$$

We have not considered here the possibility of creation of a bond between two "*altered*" configurations B. We shall indeed first focus our interest either on glass systems with a very low amount of local configurations B or on systems which do not possess the ability in creating these bonds. These situations are observed in glasses with a small concentration of modifier, *e.g.* $x\mathrm{Li_2O} - (1-x)\mathrm{SiO_2}$ systems with $x < 0.2$ (existence of $Q^{(4)}$ and $Q^{(3)}$ species only [31]) or Ge_xSe_{1-x} glasses with $x < 0.33$ (existence of Se−Se and Ge−Se bonds only [19]). The influence of B − B bonds will be presented in a forthcoming section. We have also excluded the possibility of a simultaneous creation of two bonds A−A or A−B which leads to the formation of two-membered rings (dimers); such a possibility does exist in binary chalcogenide glasses (*e.g.* SiS_2 based glasses), and will be also taken into account below. Anyhow, the analysis remains exactly the same. The relative probability of finding an A configuration among the doublets is then:

$$1 - p^{(1)} = \frac{1}{2}(2p_{\mathrm{AA1}} + p_{\mathrm{AB1}}). \tag{5}$$

If one denotes the average time needed to form a new bond by τ, we can evaluate the time derivative of p:

$$\frac{\mathrm{d}p}{\mathrm{d}t} = \frac{1}{\tau}\Big[p^{(1)} - p\Big]. \tag{6}$$

We have neglected the dependence of the cooling rate $q = \mathrm{d}T/\mathrm{d}t$ in the equation (6) because network chalcogenide glasses A_xB_{1-x} or binary oxides such as B_2O_3 or SiO_2 based glasses form very easily, and have critical cooling

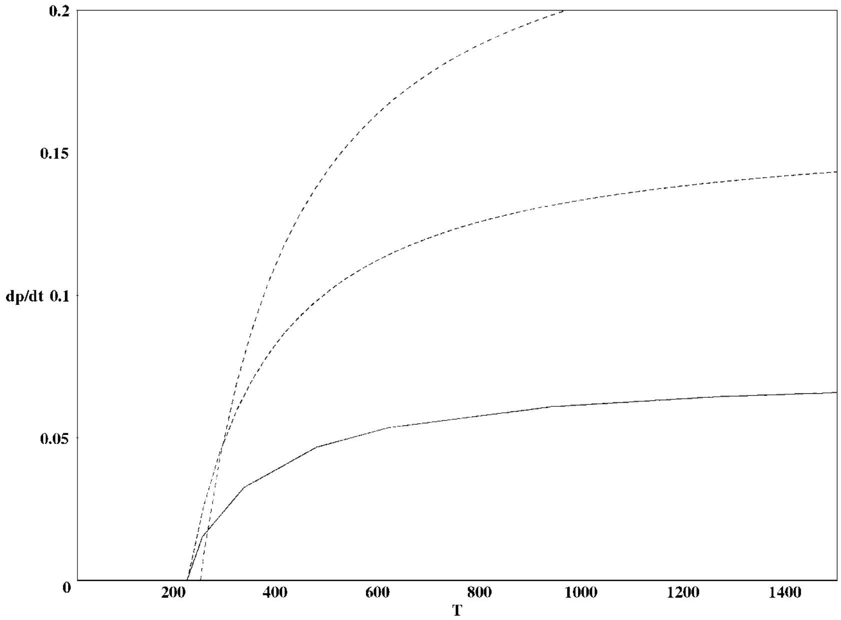

Fig. 3. An example of the arrest of the temporal fluctuations of structure. The plot represents the equation (6) with $m = 2$, $m' = 4$, $E_2 - E_1 = 0.0189$ eV ($T_0 = 316$ K, $\mathrm{Ge}_x\mathrm{Se}_{1-x}$ glass) and $p = 0.02$ (solid line), $p = 0.05$ (dashed line) and $p = 0.10$ (dotted line).

rates of the order of 10^{-4} K s^{-1} [35–37]. For these systems, it seems reasonable to neglect an additional cooling term.

In general, the composition of the mix is conserved during the cooling process. For example, the concentration x (and therefore p if one refers to the confgurations) of germanium atoms in $\mathrm{Ge}_x\mathrm{Se}_{1-x}$ is fixed before the preparation of the glass. However this does not prevent possible fluctuations provoked by agglomeration (which is characterized by Eq. (6)). When the temporal variation of the structure vanishes at T_g (high viscosity state yielding an arrest of the fluctuations) and $t \to \infty$, the above expression should be equal to 0, which amounts to finding the *stationary* or *singular* solutions of the differential equation (6) (Fig. 3). This leads to:

$$p(1-p)\Big[m(1-p)(m'\mathrm{e}^{-E_2/k_\mathrm{B}T_\mathrm{g}} - m\mathrm{e}^{-E_1/k_\mathrm{B}T_\mathrm{g}}) - pmm'\mathrm{e}^{-E_2/k_\mathrm{B}T_\mathrm{g}})\Big] = 0. \tag{7}$$

There are always two singular solutions at the points $p = 0$ and $p = 1$; but also a third solution can exist, given by the following expression:

$$p_{am} = \frac{mm'\mathrm{e}^{-E_2/k_\mathrm{B}T_\mathrm{g}} - m^2\mathrm{e}^{-E_1/k_\mathrm{B}T_\mathrm{g}}}{2mm'\mathrm{e}^{-E_2/k_\mathrm{B}T_\mathrm{g}} - m^2\mathrm{e}^{-E_1/k_\mathrm{B}T_\mathrm{g}}}\cdot \tag{8}$$

We do not consider here relaxation processes taking place just before or at T_g, but we can see how structural fluctuations behave with T in the vicinity of the stationary solutions.

Let us consider a fluctuation ξ in the vicinity of the solution $p = 0$. The linearized equation (6) reads:

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{1}{\tau}\left(1 - \frac{m'}{m}\mathrm{e}^{\frac{E_1-E_2}{kT}}\right)\xi = \frac{\xi}{\mathcal{T}}\cdot \tag{9}$$

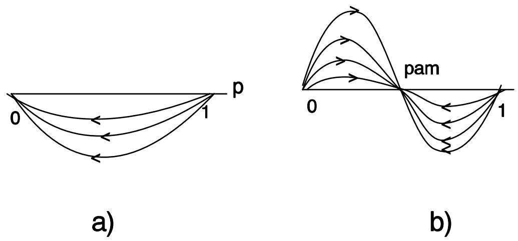

Fig. 4. The phase diagrams of equation (6): a) $m'/m < \mathrm{e}^{\alpha}$ (phase separation). b) $m'/m > \mathrm{e}^{\alpha}$ (glass formation).

If the right-hand side of (9) is negative, the fluctuation ξ tends to vanish with growing time, and the agglomeration process falls on the attractor $p = 0$. In other words, after a while, the process is governed at the microscopic level by A–A agglomeration only (Fig. 4a). This happens when:

$$\frac{m'}{m} > \mathrm{e}^{\frac{E_2-E_1}{kT}}. \tag{10}$$

In this situation, there is no intermediate solution, made of A and B configurations. The evolution of the fluctuation is governed by a characteristic time $\mathcal{T}$ (see Eq. (9)). At some temperature T_0, satisfying $m'/m = \mathrm{e}^{(E_1-E_2)/kT}$, $\mathcal{T} \to \infty$ and the fluctuation ξ needs an infinite time to fall again on the attractor $p = 0$. In the model, this temperature is identified with the glass transition temperature. T_0 then represents the glass transition temperature with solution $p = 0$, which corresponds to the glass made of 100% A configuration. The glass transition temperature T_g defined by (8) is defined on the same way. Note that due to the homogeneity of the expression (8), only one energy difference is essential here: $\alpha = (E_2 - E_1)/kT$ and that the absence of a B–B *doublet* yields automatically a repulsive solution for $p = 1$ (there is no possibility to obtain a structure with 100% B configuration). The phase portraits of the differential equation (6) are shown in Figure 4.

2.2 The first slope equation

In order to give a more realistic meaning to the solution (8), we have to relate the probability p_{am} of finding an "*altered*" local configuration B, with the modifier concentration x. In the case of network glasses A_xB_{1-x} (*e.g.* Ge_xSe_{1-x}), the identification is obvious: $p_{\mathrm{am}} = x$. For binary glass systems $(1-x)A_rX_s + xM_qX$ (or $A_rX_s + RM_qX$ following the notation), we have to recall the charge conservation law [26,38]. The concentration x of $M^{\oplus}$ cations must be equal to the anionic contribution located on each particular local configuration, expressed in terms of p_{am}:

$$\frac{1}{r}x \;=\; \frac{1}{q}(1-x)\Big[n_{\mathrm{B}}p_{\mathrm{am}} + n_{\mathrm{A}}(1-p_{\mathrm{am}})\Big] \tag{11}$$

where n_{B} and n_{A} are the anionic contributions of the B and A configurations. The factors q and r are given by the stoichiometry. For example, in low modified $(1-x)SiO_2 - xLi_2O$ systems ($x < 0.33$), equation (11) becomes:

$$R \;=\; \frac{x}{1-x} \;=\; \frac{1}{2}p_{\mathrm{am}} \tag{12}$$

where p_{am} is the probability of finding $Q^{(3)}$ species and R the reduced concentration [38]. Since x and p_{am} are now related, there should be various glass formers displaying a tendency towards the solution p_{am} in a wide range of modifier concentration, also when it tends to zero ($x \to 0$, *i.e.* $p_{\mathrm{am}} \to 0$). In this limit, we can obtain from (8) a condition concerning the energy difference $E_2 - E_1$:

$$E_2 - E_1 = kT_0 \ln\left[\frac{m'}{m}\right] \tag{13}$$

where T_0 is the glass transition temperature previously introduced and which is related to the solution $p = 0$. This corresponds to the limit when the modifier concentration x goes to zero, corresponding to a pure A glass (v−Se and $T_0 \simeq 316$ K) or a pure network former (SiO_2 and $T_0 \simeq 1450$ K).

This equation exhibits a relation between the *statistical* and *energetic* factors that are crucial for the glass forming tendency to appear. It tells us that in a good binary glass former whenever $m' > m$ (and $\ln(m'/m) > 0$), one should expect $E_2 > E_1$, and *vice versa*, in order to satisfy (10). This condition is what should be intuitively expected. Indeed, when a system displays the tendency towards amorphisation, it behaves in a "frustrated" way in the sense that the two main contributions to the probabilities of *doublets* act in the opposite directions. Whenever the modifier raises the coordination number ($m' > m$), thus creating more degeneracy of the given energies E_i (*i.e.* much more possibilities of linking the two entities A and B) and increasing the probability of agglomeration, the corresponding Boltzmann factor $\mathrm{e}^{-E_2/k_{\mathrm{B}}T}$ is smaller than for the non-modified atoms, $\mathrm{e}^{-E_1/k_{\mathrm{B}}T}$, reducing the probability of agglomeration, and *vice versa.*

Recalling that the stable solution corresponding to the glass-forming tendency in (7) defines an implicit function, $T_{\mathrm{g}}(p_{\mathrm{am}})$, *via* the relation

$$\begin{aligned}\Phi(p_{\mathrm{am}}, T_{\mathrm{g}}) = m(1-p_{\mathrm{am}})(m'\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}} - m\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}})\\ -mm'p_{\mathrm{am}}\,\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}}) = 0\end{aligned} \tag{14}$$

we can evaluate the derivative of T_{g} with respect to the reduced concentration $R = \frac{x}{1-x}$. This idea was first proposed in borate systems some years ago by Kerner [39].

$$\frac{\mathrm{d}T_{\mathrm{g}}}{\mathrm{d}R} \;=-\frac{q}{r}\left[\left(\frac{\partial\Phi}{\partial p_{\mathrm{am}}}\right)\Big/\left(\frac{\partial\Phi}{\partial T_{\mathrm{g}}}\right)\right]_{\Phi(p_{\mathrm{am}},T_{\mathrm{g}})=0}. \tag{15}$$

In the limit $R = 0$ ($x = 0$) the result has a particularly simple form:

$$\begin{aligned}\left[\frac{\mathrm{d}T_{\mathrm{g}}}{\mathrm{d}R}\right]_{R=0} &= \frac{q}{r}\left[\frac{\mathrm{d}p_{\mathrm{am}}}{\mathrm{d}T_{\mathrm{g}}}\right]^{-1}_{T_{\mathrm{g}}=T_0}\\ &= \frac{q}{r}\left[\frac{(2\,(m'/m)\,\mathrm{e}^{\frac{E_1-E_2}{kT_{\mathrm{g}}}}-1)^2}{\frac{E_2-E_1}{kT_{\mathrm{g}}^2}}\right]_{T_{\mathrm{g}}=T_0}.\end{aligned} \tag{16}$$

Inserting the condition (13), we obtain the first slope equation which is a general relation for binary glasses $A_rX_q + R\ M_qX$ and which can be regarded as a universal law:

$$\left[\frac{\mathrm{d}T_{\mathrm{g}}}{\mathrm{d}R}\right]_{R=0} \;=\; \frac{q}{r}\frac{T_0}{\ln\left[\dfrac{m'}{m}\right]}. \tag{17}$$

For network glasses A_xB_{1-x}, the following formula has been obtained in [27]:

$$\left[\frac{\mathrm{d}T_{\mathrm{g}}}{\mathrm{d}x}\right]_{x=0} \;=\; \frac{T_0}{\ln\left[\dfrac{m'}{m}\right]}. \tag{18}$$

Equations (17, 18) give the mathematical transcription of the well-known rule mentioned at the beginning of this article [40]. The glass transition temperature T_{g} increases with the addition of a modifier that increases the local coordination number ($m' > m$) (*e.g.* B_2O_3 based glasses [41] or Ge_xSe_{1-x} [19]), and decreases with the addition of a modifier that decreases the local coordination number ($m' < m$) (*e.g.* SiO_2 based glasses [42]).

3 Application and discussion

The equations (17, 18) can be quite easily compared with the experimental data. We compare the slope at the origin $x = 0$ ($R = 0$) with a set of experimental data among which the T_0 value and a T_g measurement for the lowest possible concentration x (or R), in order to produce approximate linearity, to be compared with the constant slope of (17, 18). Therefore, we have tried to find, whenever possible, reported glass transition temperatures of glass-forming systems which were composed of a very high fraction of "*regular*" local configurations A (*e.g.* $Q^{(4)}$

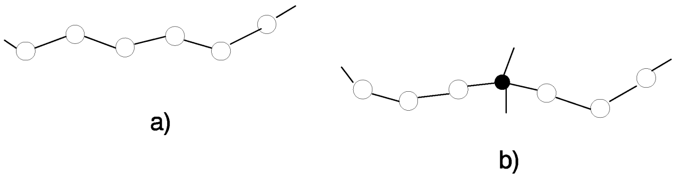

Fig. 5. (a) A selenium chain. (b) A selenium chain with a cross-linking silicon atom.

species in $SiO_2 - Li_2O$ or Se atoms in Ge_xSe_{1-x}). The lowest possible concentration is close to 5% in most cases, so that we can roughly approach the limit value $x \to 0$ of formula (17, 18). From the T_g and T_0 values, we can compute an "*experimental value*" of m'/m and compare it to the theoretical one, deduced from purely structural considerations. In reference [43], Kerner has demonstrated a good agreement of a close relationship with the behavior of dT_g/dx at $x = 0$ for the alkali-borate glass $(1-x)B_2O_3 - xLi_2O$ and the silicate glass $(1-x)SiO_2 - xCaO$. He predicted $m'/m \simeq 3/2$ in the first case, which leads to a positive derivative, and $m'/m \simeq 1/3$ giving a negative one in the second one. Nevertheless, the formula was incomplete because the factor q/r was missing, but the obtained values were correct since $q/r = 1$ in these systems.

3.1 Single-bonded systems

3.1.1 Chalcogenide network glasses

Various experimental probes for equation (18) can be obtained in very simple simple glass forming systems, namely chalcogenide network glasses, for which numerous experimental data are available in the literature, and $m = 2$. For completeness, we report some values which have already been presented elsewhere [27]. We have extended the list of investigated systems in order to prove beyond any doubt that the impressive agreement of (18) with experimental data is not a matter of coincidence. Within the ranges (close to $x = 0$, whenever possible) found in various references, the formula agrees very well with the experimental data for the sulphur, tellurium and selenium based glasses (Tabs. 1 and 2). Indeed, the computation of the slope of T_g at $x = 0$ obtained from the measured glass transition temperatures, leads to experimental values of m'/m, which in turn can be compared to the predicted ones, *e.g.* $m'/m = 2$ in Ge_xSe_{1-x} glasses or $m'/m = 3/2$ in As_xS_{1-x} systems. The structural change induced by the growing proportion of a modifier atom is obvious here. At $x = 0$, the two-valenced atoms ($m = 2$) of the VIth group form a network of chains with various length; this is particularly clear in vitreous selenium. For very low x concentration, the atoms of modifier (Ge, As, Si, ...) produce cross-linking between the chains as suggested by Boolchand and Varshneya [53,54], thus creating a new stable structural unit with coordination number $m' = 4$ for germanium or silicon atoms (Fig. 5), or $m' = 3$ for arsenic.

Table 1. Different tellurium and sulphur based glasses. Comparison between the theoretical value of m'/m and the experimental value of m'/m deduced from the slope using data of T_g for the lowest available concentration x. T_0 has been taken as 343 K in tellurium and 245 K in sulphur.

Compound	$\left(\frac{m'}{m}\right)_{th}$	$\left(\frac{m'}{m}\right)_{exp}$	Obtained from		Reference
			x	$T_g[K]$	
Si_xTe_{1-x}	2.0	2.11	0.10	389	[44]
Ge_xTe_{1-x}	2.0	1.97	0.15	419	[45]
Ga_xTe_{1-x}	1.5	1.45	0.20	528	[46]
As_xS_{1-x}	1.5	1.54	0.11	307	[47]
Ge_xS_{1-x}	2.0	1.72	0.10	290	[48]

Table 2. Different selenium based glasses. Comparison between the theoretical value of m'/m and the experimental value deduced from the slope using data of T_g for the lowest available concentration x. T_0 has been taken as 316 K.

Compound	$\left(\frac{m'}{m}\right)_{th}$	$\left(\frac{m'}{m}\right)_{exp}$	Obtained from		Reference
			x	$T_g[K]$	
Ge_xSe_{1-x}	2.0	2.04	0.05	336	[19]
Si_xSe_{1-x}	2.0	2.04	0.05	336	[49]
As_xSe_{1-x}	1.5	1.54	0.003	318	[50]
Sb_xSe_{1-x}	1.5	1.31	0.15	493	[51]
P_xSe_{1-x}	2.5	2.53	0.05	333	[52]

For the computation of the rates m'/m, we have used standard T_0 values, found in the literature, or averaged over a set of reported glass transition temperatures, so $T_0 = 316$ K for selenium [40], $T_0 = 245$ K [40] for sulphur and $T_0 \simeq 343$ K for tellurium [45]. As mentioned above, the sign of the derivative of T_g with respect to x depends on the sign of $\ln(m'/m)$. In all reported chalcogenide glasses, the rate m'/m is greater than one, the systems display therefore an increase of the glass transition temperature with increasing x, starting from T_0. Different systems are represented in Figure 6 and show that the linear approximation of (18) can give a correct estimation of T_g up to $x \simeq 0.4$ in certain glass formers, *e.g.* As_xS_{1-x}, whereas the substantial increase of T_g in Ge_xSe_{1-x} systems yields a satisfying description only for $x \leq 0.15$.

A problem arises in the systems for which the glass-forming region can not be extended towards $x = 0$ (existence of a minimal value of x for the glass-forming region); it is obvious that our formula can not be applied when glass can not be formed in the limit $x = 0$. Nevertheless, the formula can sometimes be extrapolated down to $x = 0$, when the variation of T_g *versus* x is linear for greater values of x. For example, the (m'/m) value shown in Table 1 for Ga_xTe_{1-x} glasses has been obtained by this method, because T_g exhibit linearity over a wide range of x and can be extrapolated linearly down to T_0 [46]. The constant slope allows then a comparison with (18).

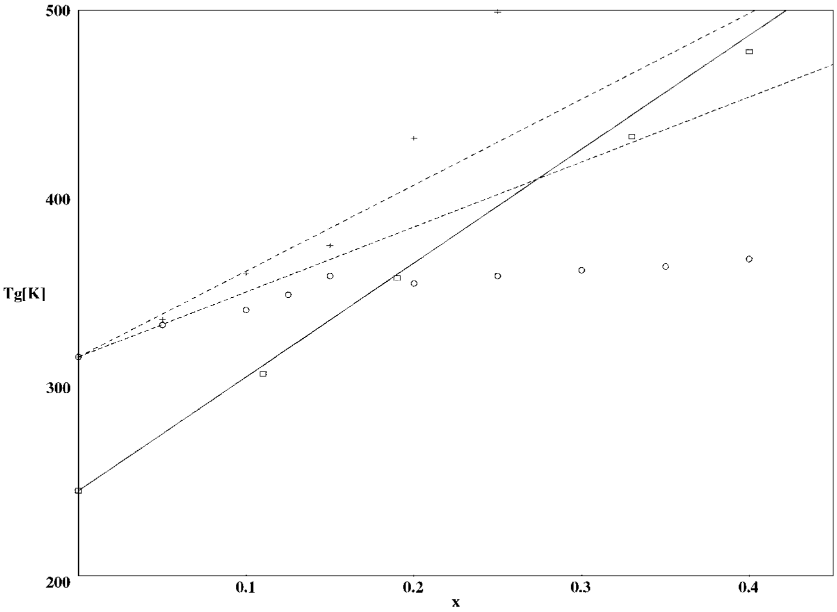

Fig. 6. Glass transition temperature (in K) *versus* concentration x for typical glass systems, As_xS_{1-x} [□], P_xSe_{1-x} [○] and Ge_xSe_{1-x} [+]. The plotted values are reported in [20, 47, 52]. The straight lines correspond respectively to the equations $T_g = 245(1 + \frac{x}{\ln(3/2)})$ (solid line), $T_g = 316(1 + \frac{x}{\ln(5/2)})$ (dashed line) and $T_g = 316(1 + \frac{x}{\ln(2)})$ (dotted line).

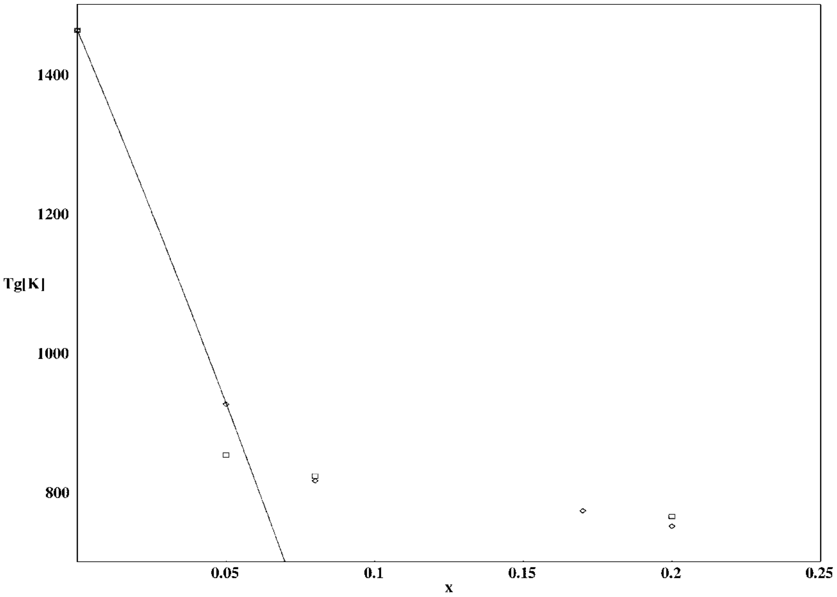

Fig. 7. Glass transition temperature (in K) of $(1-x)SiO_2 - xNa_2O$ [◇] and $(1-x)SiO_2 - xK_2O$ [□] systems *versus* the concentration x. The line represents the slope equation $T_g = 1463(1 + \frac{2x}{(1-x)\ln(3/4)})$ The plotted T_g data are taken from [42, 56].

3.1.2 Binary glasses

As pointed out in reference [43], the slope equation (17) seems to be supported in binary glass-formers. The most common single-bonded systems are the oxide binary glasses which use the typical network formers such as SiO_2, GeO_2, P_2O_5 or B_2O_3. The structural change which occurs when adding a modifier is well understood in terms of the modified random network concept [55]. It suggests that when alkali oxide is introduced into the glass former, the network is depolymerized through the formation of sites bearing non-bridging oxygens (NBO). Indeed, each molecule of the modifier M_2O [$M = Li, Na, K, ...$] creates two ionic $O^{\ominus}M^{\oplus}$ sites in the network, thus converting the covalent or partly covalent network into a size-decreasing structure. For large amounts of modifier, the structure generally reduces to isolated ionic species (*e.g.* $SiO^{4\ominus}$ units, the amorphous analogue of orthosilicates [33]).

- SiO$_2$ based glasses

In silica based glasses, the creation of $Q^{(3)}$ species with three covalent bridges ($m' = 3$) is proposed when adding a modifier. Therefore $m'/m = 0.75$ in these systems. Table 3 show a very good agreement of (17) with the experimental data for various types of modifier.

Since this glass can form continuously down to $x = 0$ ($R = 0$), it is possible to find T_g measurements for very low concentrations, yielding a better agreement with the predicted value of m'/m reported in the table. One can also remark that the dramatic decrease of the glass transition temperature when adding a very few modifiers can

Table 3. The m'/m rate deduced from experimental data, compared to the theoretical value of 0.75 in SiO_2 based glasses, with the average value of $T_0 = 1463$ K.

System	Na_2O	K_2O	Rb_2O	PbO
$\left(\frac{m'}{m}\right)_{\mathrm{exp}}$	0.75	0.78	0.66	0.74
obtained from the concentration x	0.05	0.05	0.08	extra-polation
Reference	[42]	[56]	[57]	[58]

Table 4. The m'/m rate deduced from experimental data, compared to the theoretical value of 0.75 in GeO_2 based glasses, with the average value of $T_0 = 820$ K.

System	Li_2O	K_2O	Rb_2O	Cs_2O
$\left(\frac{m'}{m}\right)_{\mathrm{exp}}$	0.85	0.73	0.71	0.68
obtained from the concentration x	0.01	0.02	0.02	0.02
Reference	[67]	[68]	[68]	[68]

be mathematically explained by the presence of the factor T_0 in the slope equation (Fig. 7).

The higher the initial glass transition temperature T_0 of the network former, the more pronounced will be the decrease of T_g. Of course, silica based glasses, which has one of the highest T_0 values among glass materials, show this characteristic feature very well. The fabrication of glass by ancient Egyptians is due to this fact. With the heating techniques of that time, it was impossible to form glass from the desert sand, made almost of pure SiO_2. Nevertheless, with the addition of 10 to 20% of K_2O, obtained from the ashes of burned algae, they could produce it quite easily, because of the sharp decrease of the glass transition temperature.

- GeO_2 based glasses

Another system behaves very similarly to the silica based glasses, namely GeO_2-M_2O systems. It has been extensively studied because of its unique physical properties, such as the so-called "*density anomaly*". Ivanov and Estropiev first reported [59] that the density of these glasses increases with the addition of alkali oxide. Further studies showed that density, as well as refractive index reach a maximum around 15−16% added Na_2O and then decrease [60–62]. Numerous structural studies have been carried out in order to elucidate the reason for this anomaly, leading to suggestions of the presence of GeO_6 octahedra within the network [63] in order to explain the density maximum. However, recent EXAFS studies [64] have clearly shown that pressure-induced coordination changes in v−GeO_2 are reversible and that Ge(6) should not be observed at room pressure. Other authors believe that the anomaly should result from an alternative structural reorganization [65]. Micro-Raman experiments have been performed and results have been obtained in this sense: the increase of the density with a low amount of modifier can be related to the existence of rings of particular sizes, namely 4- and 3-membered rings, the growing proportion of the latter one being responsible of the density anomaly [66].

From the available data, we can obtain the m'/m rate which is very close to 0.75 in most of the systems (Tab. 4). This suggests that for a very small concentration of modifier M_2O, the coordination number of the basic $GeO_{4/2}$ tetrahedra changes into $m' = 3$, as in the silicate glass (Fig. 8a). But in contrast with the latter glass system, the proportion of $Q^{(3)}$ structures does not increase any more

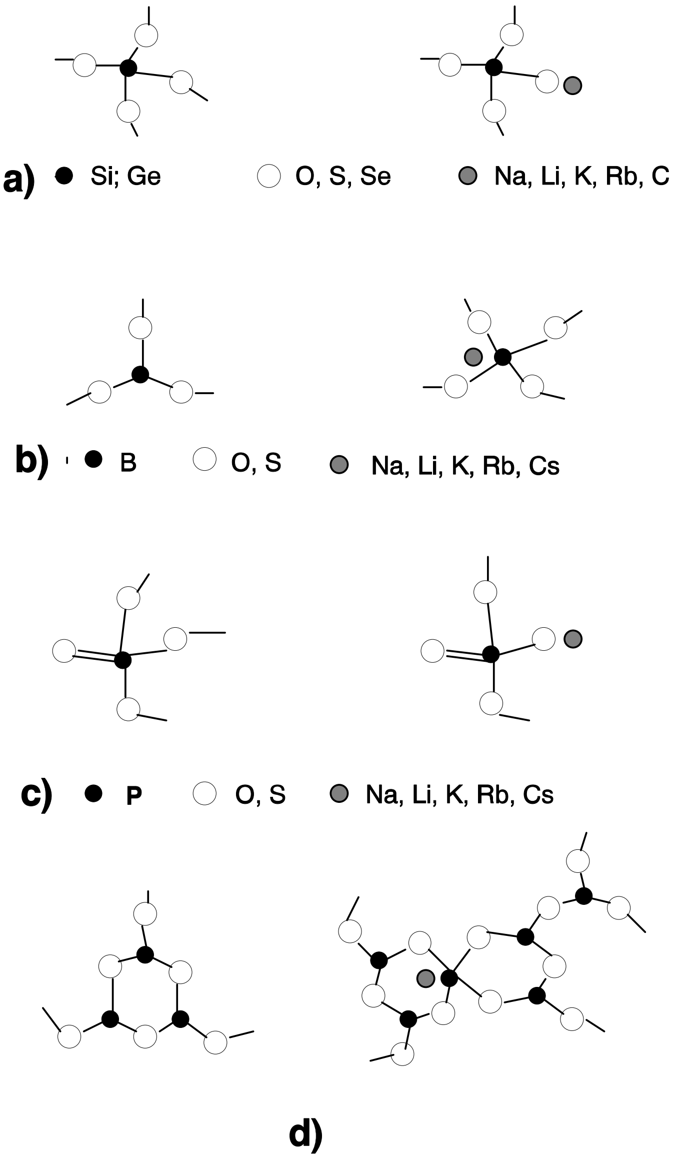

Fig. 8. a) IV-VI binary glasses. The SRO structures are the $Q^{(4)}$ and $Q^{(3)}$ tetrahedra and eventually the $Q^{(2)}$ tetrahedra with two non-bridging atoms ($m = 4$, $m' = 3$). b) SRO structures of a boron glass. A $BX_{3/2}$ triangle (X = O, S) and a four-coordinated boron (N4 unit) ($m = 3$, $m' = 4$). c) SRO structure of phosphor based glasses P_2X_5 (X = O, S) ($m = 3$, $m' = 2$). d) Possible MRO in B_2O_3 based glasses. The boroxol ring ($m = 3$) and the tetraborate group ($m' = 5$).

when x is growing, as shown indirectly in Figure 9. Indeed, the glass transition temperature shows a minimum around $x = 0.02$ and then increases. The positive derivative of T_g *versus* x for $x > 0.02$, means that the local coordination number of the "*altered*" configuration is now greater than that of the "*regular*" configuration (supposed to be composed of a mixture of $Q^{(3)}$ and $Q^{(4)}$ structures), thus confirming the growing presence of GeO_6 octahedra (with $m' = 6$). Note that the crystalline form of GeO_2 has the rutile structure, composed of GeO_6 octahedra, and that the nucleation of such units appears to take place at larger values of $x > 0.02$, where the Porai-Koshits picture [12] becomes possible.

- P_2O_5 based glasses

Other glass systems display the same agreement between the predicted value of m'/m and the one obtained from experimental data [69–71]. This is realized in P_2O_5 based glasses. The available T_g measurements of $(1-x)P_2O_5{-}xM_2O$ systems are represented in Figure 10 and compared to the equation $T_g = T_0[1+\frac{x}{1-x}\frac{1}{\ln\ 2/3}]$. The rate of m'/m should be equal to 2/3 in these glass systems (Fig. 8c). The basic network former P_2O_5 is made of phosphor tetrahedra with four P$-$O bonds, among which one is double bonded, so that it is not connected to the rest of the network, therefore $m = 3$ ($Q^{(3)}$ structure). At the beginning, the addition of a modifier produces the usual creation of one NBO, as in silicate and germanate glasses ($Q^{(2)}$ structure, $m' = 2$). The rate of this structure is increasing with the modifier concentration and reaches unity for $x = 0.5$, yielding the metaphosphate chain structure, made of corner-sharing polymeric $PO_4^{\ominus}$ tetrahedra [72]. On this basis, we predict $T_g = 620$ K for the 0.98 $P_2O_5{-}0.02$ Li_2O glass, when $T_0 = 653$ K [71].

- B_2O_3 based glasses

All the data presented up to now exhibit a decrease of T_g with growing modifier concentration x, in agreement with the slope equation (17) and the currently accepted rule which states that the increase of the coordination number (*i.e.* the connectivity of the network) produces an increase of the glass transition temperature. The well-known symmetrical example of this rule is given by the B_2O_3 based glass, which presents a positive derivative of T_g at the origin [41]. The addition of M_2O [M = Li, Na, ...] transforms the $BO_{3/2}$ triangles ($m = 3$), which represent the basic SRO structural unit of B_2O_3, into $BO_4^{\ominus}$ tetrahedra ($m' = 4$, N4 species [73], Fig. 8b). The linear increase of T_g *versus* the modifier concentration in these glasses is explained by the conversion of a three-valenced network into a four-valenced one, thus increasing the connectivity [74]. The nature of the cation $M^{\oplus}$ seems to have no influence for low concentration, when $T_g \simeq T_0$ [41]. Systems with the same concentration but with a different modifier cation, display still very close T_g data (Fig. 11). The rate of N4 species is growing linearly with R up to $R \simeq 0.5$ whatever the involved $M^{\oplus}$ cation [38]. For $R > 0.5$, the glass transition temperature decreases due to the growing presence of $BO_{3/2}^{\ominus}$ triangles sharing one NBO ($m' = 2$) [41]. When comparing the rate m'/m obtained from experiments with the theoretical one derived from the local structure consideration, one obtains $m'/m = 1.63$ instead of $4/3 = 1.33$.

Nevertheless, an alternative structural proposal supports the experimental value of $1.63 \simeq 5/3$. The structure of B_2O_3 is indeed a typical example of well-characterized medium-range order. There is a strong experimental evidence for the existence of larger structural groups than the local SRO $BO_{3/2}$ triangles, namely the boroxol ring B_3O_3, made of three connected $BO_{3/2}$ triangles [75–78]. The spectroscopic patterns of Raman investigation, NMR and neutron diffraction exhibit for this compound, sharp and well-characterized peaks, which can be attributed either to the breathing modes of the oxygens inside the boroxol ring (in case of Raman studies, at 808 cm^{-1} [79, 80]) or to the B$-$O$-$B bond length inside a boroxol ring (in the case of diffraction [28,77]). Whatever the proportion of this structural unit in the network former (0.8 is the currently accepted value [75–78]), the coordination number remains $m = 3$. The addition of the modifier leads to the creation of the so-called tetraborate group, even at the very beginning [73]. This structural group is made of several three-membered rings (as the boroxol group) sharing N4 species, with coordination number $m' = 5$. This yields a rate of $m'/m = 1.67$ (Fig. 8d).

3.2 Relationship with the Gibbs-Di Marzio equation

We have mentioned at the beginning of this article that Gibbs and Di Marzio have given a formula relating T_g to some structural factor, on the basis of thermodynamical considerations (Eq. (1)). Varshneya and co-workers have modified this equation in order to test its validity on chalcogenide network glasses [20,81]. These systems satisfy all the required conditions of Gibbs and Di Marzio's model, namely the presence of polymeric atomic chains (as Se chains in v$-$Se) which can be cross-linked by other atomic species, such as germanium. They have expressed T_g in terms of the network average coordination number $\langle r\rangle$, rather than the concentration x. $\langle r\rangle$ is widely used for the description of network glasses since Phillips and others have introduced this concept in the constraint theory [82]. Varshneya *et al.* have redefined for multicomponent chalcogenide glasses the cross-linking density X of Gibbs and Di Marzio equation (1) as being equal to the average coordination number of the cross-linked chain less the coordination number of the initial chain, *i.e.*: $X = \langle r\rangle - 2$, and the Gibbs-Di Marzio equation can in this situation be rewritten as:

$$T_g = \frac{T_0}{1-\beta(\langle r\rangle - 2)} \tag{19}$$

where β is a system dependent constant, whereas it was suggested that the constant κ of the initial equation (1) is universal [22]. Sreeram *et al.* fitted the constant β to their T_g measurements by least-squares fit [81] and obtained a value which depends on the considered system and the atoms involved.

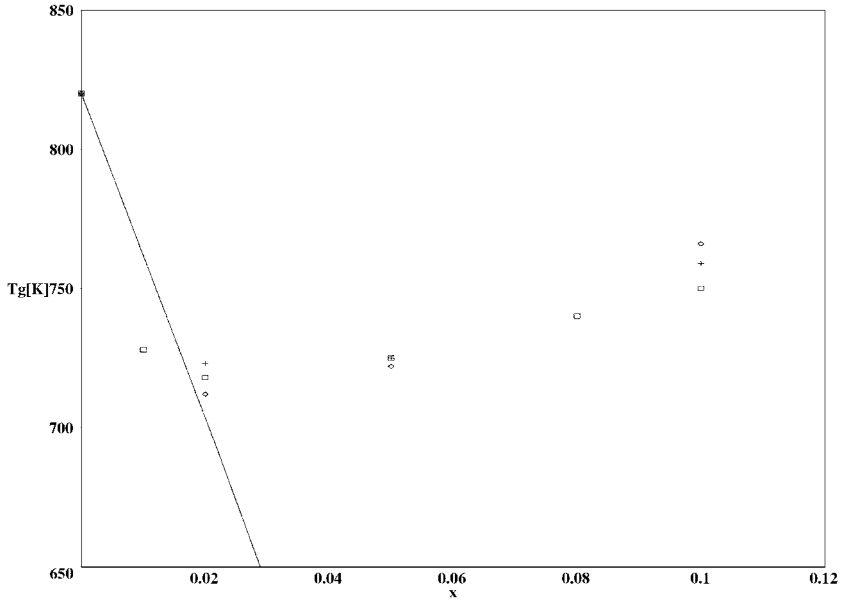

Fig. 9. Glass transition temperature (in K) *versus* the concentration x in $(1-x)\mathrm{GeO}_2 - x\mathrm{M}_2\mathrm{O}$ glasses with M = Li [□], K [◇] and Rb [+]. The line represents the equation $T_{\mathrm{g}} = 820(1+\frac{2x}{(1-x)\ln(3/4)})$. The data are reported in [67, 68].

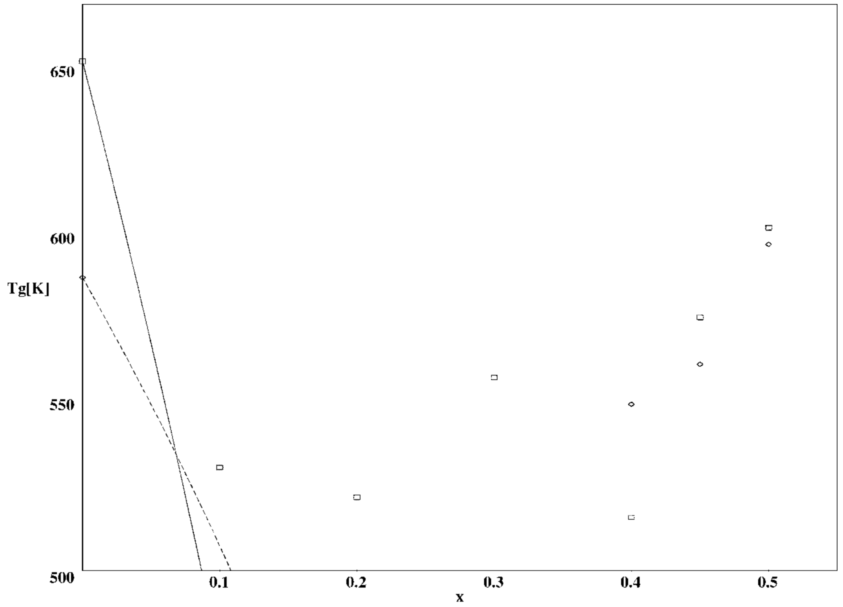

Fig. 10. Glass transition temperature (in K) of $(1-x)\mathrm{P}_2\mathrm{O}_5 - x\mathrm{M}_2\mathrm{O}$ glasses *versus* modifier concentration x with M = Li [□], $\mathrm{Pb}_{1/2}$ [◇]. The lines represented correspond to $T_{\mathrm{g}} = 653(1+\frac{x}{(1-x)\ln(2/3)})$ (solid line, M = Li) and to $T_{\mathrm{g}} = 588(1+\frac{x}{2(1-x)\ln(2/3)})$ (dotted line, $\mathrm{M} = \mathrm{Pb}_{1/2}$). The plotted data are given in references [69, 71].

The slope equation (18) can be related to the Gibbs-Di Marzio equation in the pure chalcogen limit and gives, after identification, an analytical expression for β.

According to Phillips [82], one can express the average coordination number $\langle r\rangle$ in terms of the coordination number of the covalently bonded atoms, *i.e.* the coordination numbers m and m' of the A (chalcogen atom) and B configuration (modifier atom)

$$\langle r\rangle \;=\; 2(1-x)+m'x. \tag{20}$$

The slope at the origin, where $x=0$ (and $\langle r\rangle = 2$) is then:

$$\left[\frac{\mathrm{d}T_{\mathrm{g}}}{\mathrm{d}\langle r\rangle}\right]_{\langle r\rangle=2} \;=\; \frac{T_0}{(m'-2)\;\ln\frac{m'}{2}}. \tag{21}$$

In the vicinity of the pure chalcogen region ($x\rightarrow 0$), a first order development of the Gibbs-Di Marzio equation has the following form:

$$T_{\mathrm{g}} \;\simeq\; T_0\left[1+\beta\;(\langle r\rangle-2)\right] \tag{22}$$

which leads by identifying (21, 22) to an analytical expression of the constant β, involving only the coordination number m' of the modifier atom.

$$\frac{1}{\beta} \;=\; (m'-2)\;\ln(\frac{m'}{2}). \tag{23}$$

The value of β can now be computed for different glass systems for which the coordination number of the modifier atoms are well-known, *e.g.* for chalcogenide based glasses. The possible values for β are 0.36 (for $m'=5$), 2.47 (for $m'=3$) and 0.72 (for $m'=4$). The latter situation corresponds to the glass $\mathrm{Ge}_x\mathrm{Se}_{1-x}$ and the agreement

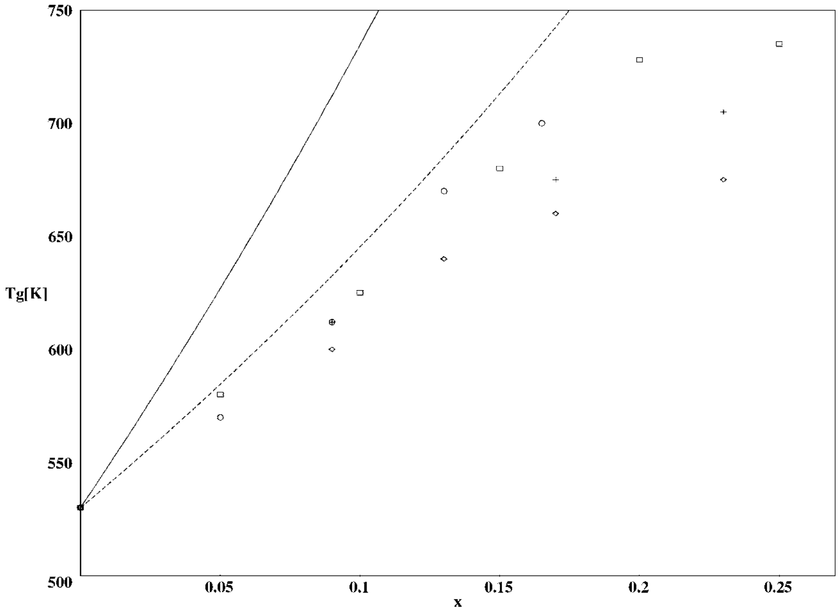

Fig. 11. Glass transition temperature (in K) *versus* the concentration x in $(1-x)B_2O_3 - xM_2O$ glasses, with M = Li [*o*], Na [□], K [+], Rb [◇] and Cs [.]. The lines represent the equations $T_g = 530(1+\frac{x}{(1-x)\ln(5/3)})$ (dotted line) and $T_g = 530(1+\frac{x}{(1-x)\ln(4/3)})$ (solid line). The plotted values are taken from [41].

Table 5. Computed values of the constant β of the modified Gibbs-Di Marzio equation, obtained from a least-squares fit, for different chalcogenide glass systems. They can be compared to $\beta = 0.72$ ($m' = 4$) or $\beta = 0.36$ ($m' = 5$). Some data are taken from [27].

System	β_{fit}	Correlation coefficient	Reference
Ge_xSe_{1-x}	0.74	0.993	[19]
Ge_xSe_{1-x}	0.72	0.988	[20]
Ge_xSe_{1-x}	0.65	0.993	[81]
Ge_xS_{1-x}	0.73	0.998	[48]
Si_xSe_{1-x}	0.81	0.997	[49]
P_xSe_{1-x}	0.14	0.902	[52]

of $\beta = \frac{1}{2\ln 2} = 0.72$ with the value obtained by a least-squares fit of the glass transition temperatures data *versus* $\langle r\rangle$, is very good and close to the measurements of Varshneya and co-workers. Other IV-VI systems behave very similarly, as seen in Table 5. However, expression (23) is valid for binary network glasses only, but we believe that it can be generalized for multicomponent chalcogenide network glasses, involving at least three different types of atoms.

3.3 Other structural contributions

3.3.1 Edge-sharing tendency

One of the possible corrections of the equation (17) can be produced by the influence due to the edge-sharing character of the local configurations. Binary chalcogenide glasses are the most representative systems of such a tendency. They form two-membered rings (dimers) very easily and the fraction of dimers can be either very low (such as in P_2S_5 [83]) or very high as in SiS_2 based glasses [32]. Indeed, the proposed long range structure in these latter systems is a chain of polymeric edge-sharing $SiS_{4/2}$ tetrahedra which are cross-linked by corner-sharing tetrahedra [84,85]. Thus, one can consider that the local glass structure of SiS_2 and $SiSe_2$ is made of pure edge-sharing $SiX_{4/2}$ tetrahedra. This result has been given by Tenhover on the basis of NMR spectroscopy [84], but also obtained by Sugai (Raman investigation and modelization) [86], Vashishta and co-workers (molecular dynamics) [87] and Gladden and Elliott (radial distribution function calculation) [29]. We have seen that the statistical factors which appeared at the very beginning of the construction in the expression of the probabilities of *doublets* (2, 4) are responsible for the presence of the term $\ln(m'/m)$ in (17, 18). If there is an edge-sharing tendency, the number of ways in joining together two *singlets* will be different and will modify the logarithmic expression.

The number of ways of joining by edges a *singlet* A with coordination number m with a *singlet* B with coordination number m' is $2\times 2\times \binom{m}{2}\times\binom{m'}{2}$ in three dimensions and the probabilities can be rewritten in the pure edge-sharing situation as:

$$p_{AA2} = \frac{2}{\mathcal{Z}_2}\left[\frac{m(m-1)}{2}\right]^2 (1-p)^2 e^{-\beta E_1+\beta E_e} \qquad (24)$$

$$p_{AB2} = \\ = \frac{4}{\mathcal{Z}_2}\left[\frac{m(m-1)}{2}\right]\left[\frac{m'(m'-1)}{2}\right] p(1-p) e^{-\beta E_2+\beta E_e} \qquad (25)$$

where E_e is an energetical correcting factor which takes into account the fact that the energy stored in an edge-sharing *doublet* is not equal to a single bond energy E_i.

$$\mathcal{Z}_2 = 2\left[\frac{m(m-1)}{2}\right]^2 (1-p)^2 \mathrm{e}^{-\beta E_1 + \beta E_{\mathrm{e}}} + 4\left[\frac{m(m-1)}{2}\right]\left[\frac{m'(m'-1)}{2}\right] p(1-p)\mathrm{e}^{-\beta E_2 + \beta E_{\mathrm{e}}}. \quad (26)$$

The construction is performed along the same scheme as equations (5-7). The amorphous singular solution is given by:

$$p_{\mathrm{am}} = = \frac{m'(m'-1)(m-1)\mathrm{e}^{-E_2/kT} - m(m-1)^2\mathrm{e}^{-E_1/kT}}{2m'(m'-1)^2\mathrm{e}^{-E_2/kT} - m(m-1)^2\mathrm{e}^{-E_1/kT}} \quad (27)$$

which exists only if:

$$\frac{m'(m'-1)}{m(m-1)} > \mathrm{e}^{(E_2-E_1)/kT} \quad (28)$$

and the general feature of the phase diagram (Fig. 4) remains the same in this situation. The solution can be, as before, examined in the limit condition ($x \to 0$ or $R \to 0$), where the pure A-network exists and $p_{\mathrm{am}} \to 0$. This yields the energy difference:

$$E_2 - E_1 = kT_0 \ \ln\left[\frac{m'(m'-1)}{m(m-1)}\right] \quad (29)$$

where T_0 is still the glass transition temperature of a pure A configuration glass, but with pure edge-sharing local configurations. One should note that the energetical correcting factor E_{e} does not appear in (27) and in the forthcoming equations. The slope at the origin is then consequently modified, but the derivation of the slope equation remains similar to the one presented above:

$$\left[\frac{\mathrm{d}T}{\mathrm{d}R}\right]_{R=0} = \frac{q}{r}\frac{T_0}{\ln\left[\dfrac{m'(m'-1)}{m(m-1)}\right]}. \quad (30)$$

Unfortunately, there are very few experimental data at our disposal in systems displaying a strong edge-sharing tendency, because they seem very difficult to form for very small modifier concentrations [88–90]. This is due to the strong edge-sharing tendency which is also responsible for crystallization ease [32].

Nevertheless, some data are represented in Figure 12 and they concern $\mathrm{SiSe_2}$ and $\mathrm{SiS_2}$ based glasses. As explained above, these systems possess a high proportion of dimers in the basic network former and some of the previously cited theoretical and experimental studies propose an approximate fraction of dimers of 53%, in terms of $E^{(k)}$ NMR functions [84–86] ($E^{(k)}$ is identified with a tetrahedron sharing k common edges with its neighbors, hence k runs from 0 to 2). The currently accepted repartition of the $E^{(k)}$ functions for $\mathrm{SiX_2}$ ($\mathrm{X} = \mathrm{S}, \mathrm{Se}$) is: $E^{(2)} = 0.29$, $E^{(1)} = 0.48$, $E^{(0)} = 0.23$. Figure 12 displays the available experimental data about the binary chalcogenide systems. The different straight lines using the slope equation (30) and corresponding to possibilities of structural modification are also plotted. The solid line corresponds to a pure corner-sharing situation (with $m = 4$ and $m' = 3$), whereas the dotted and dashed lines represent a pure edge-sharing situation slope equation with respectively $m = 4$ and $m' = 2$, and $m = 4$ and $m' = 3$. Although precise information about the glass transition temperature is lacking in the very low modification regime (low x concentration) [88–90], one can observe that a $\mathrm{Q}^{(4)} \to \mathrm{Q}^{(3)}$ conversion (solid line in Fig. 12) using pure corner-sharing tetrahedra (slope Eq. (17) with $m = 4$ and $m' = 3$) seems not adapted for the description of T_{g} at the origin $x = 0$. The two other possibilities seem more accurate and also support what is proposed on the basis of NMR spectroscopy by Eckert [91] and Martin [92]. In $\mathrm{SiS_2{-}Li_2S}$ glasses, the addition of lithium sulphide produces the conversion of $\mathrm{Q}^{(4)}$ into $\mathrm{Q}^{(2)}$ species (a structure with two non-bridging sulphur atoms, *i.e.* a tetrahedron $\mathrm{SiS}_{4/2}^{2\ominus}$), thus producing a growing rate of the $\mathrm{Li_2SiS_3}$ phases, identified with $\mathrm{Q}^{(2)}$ edge-sharing dimers (the HT form of $\mathrm{c{-}Li_2SiS_3}$ [91]) and $\mathrm{Q}^{(2)}$ corner-sharing polymers (the LT form of $\mathrm{c{-}Li_2SiS_3}$ [91]). At $x = 0.5$, the edge-sharing tendency remains important, the ratio of the HT and LT phases is 1:3 [91]. No characteristic signature of a lithium dithiosilicate phase is observed on the NMR spectroscopy patterns (the crystalline $\mathrm{Li_4Si_4S_{10}}$ phase), even at a concentration where this compound should be expected (at $x \simeq 0.3$, if one refers to the oxide analogous glass [31]). The same happens for the selenide glass. The structural modification imposed by the presence of $\mathrm{Li_2Se}$ is similar to the sulphide system. The basic tetrahedra $\mathrm{Q}^{(4)}$ are converted into $\mathrm{Q}^{(2)}$ tetrahedra and a $\mathrm{Li_2SiSe_3}$ phase occurs, made of almost 100% corner-sharing $\mathrm{Q}^{(2)}$ tetrahedra [91].

For these two systems, the slope equation (30) with $m = 4$ and $m' = 2$ seems best adapted and Figure 12 confirms more or less this structural scenario.

In contrast with the lithium glass, it is possible to observe a spectroscopic signature of a $\mathrm{Na_4Si_4S_{10}}$ phase in the $(1-x)\mathrm{SiS_2} - x\mathrm{Na_2S}$ glasses, confirming the presence of $\mathrm{Q}^{(3)}$ units (a $\mathrm{SiS}_{4/2}^{\ominus}\mathrm{Na}^{\oplus}$ tetrahedron), as suggested by Pradel [93]. On this basis, a reasonable structural conversion is $\mathrm{Q}^{(4)} \to \mathrm{Q}^{(3)}$ for very low x concentration (dashed line in Fig. 12). The rate of edge-sharing structures is not decreasing when x is growing and it is still equal to 0.5 at $x = 0.5$ [90]. Therefore, one should propose for these binary systems the pure edge-sharing slope equation with $m = 4$ and $m' = 3$ (shaded line in Fig. 12), which seems to agree with the experimental data of $\mathrm{Na_2S} - \mathrm{SiS_2}$ systems. However, a glass transition measurement for the concentration $x = 0.05$, or lower, is missing, but it should certainly be useful in order to give information about the local structural modification. On the basis of what has been described above, we propose for $x = 0.05$, $T_{\mathrm{g}} \simeq 616$ K in the sodium sulfide glass and $T_{\mathrm{g}} \simeq 683$ K in the lithium sulfide one.

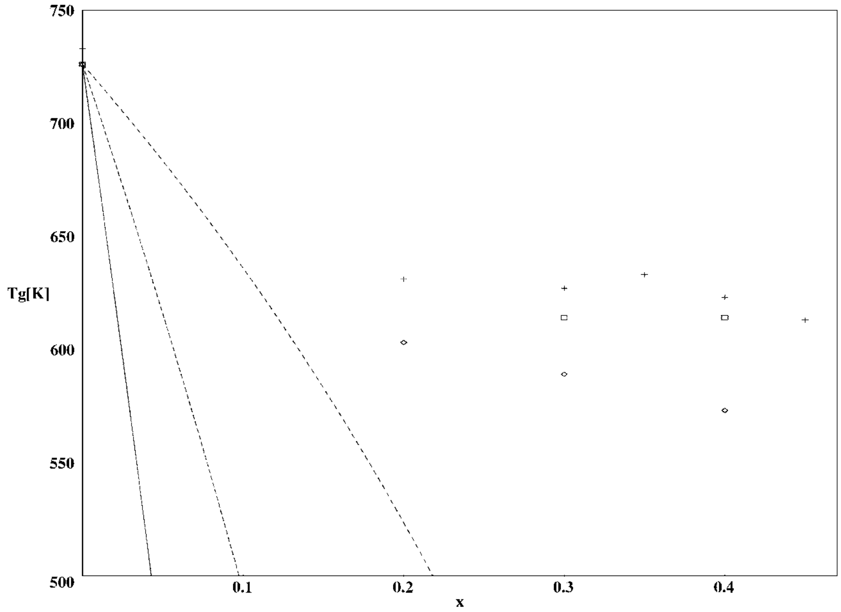

Fig. 12. Glass transition temperature (in K) of $(1-x)\mathrm{SiS}_2 - x\mathrm{M}_2\mathrm{S}$, M = Li [□] M = Na [◇] and $(1-x)\mathrm{SiSe}_2 - x\mathrm{Li}_2\mathrm{Se}$ glasses [+]. The represented lines correspond to $T_\mathrm{g} = 726(1 + \frac{2x}{(1-x)\ln(3/4)})$ (solid line, pure corner-sharing and $m' = 3$), $T_\mathrm{g} = 726(1 + \frac{2x}{(1-x)\ln(2/12)})$ (dotted line, pure edge-sharing and $m' = 2$) and $T_\mathrm{g} = 726(1 + \frac{2x}{(1-x)\ln(6/12)})$ (shaded line, pure edge-sharing and $m' = 3$). The data are taken from [88-90].

In other chalcogenide glasses, the rate of edge-sharing structures is much lower. Typical glasses displaying a non-negligible edge-sharing tendency are the $\mathrm{Sb}_2\mathrm{S}_3$ [94], $\mathrm{As}_2\mathrm{S}_3$ [95] or GeX_2 (X = S, Se) [96] binary glasses, for which numerous experimental measured glass transition temperatures are also available. In the case of a mixture of corner- and edge-sharing structures, one must use the doublet probability:

$$1 - p^{(1)} = \frac{1}{2}\left[2(p_{\mathrm{AA1}} + p_{\mathrm{AA2}}) + p_{\mathrm{AB1}} + p_{\mathrm{AB2}}\right] \quad (31)$$

where p_{AA1}, p_{AA2}, p_{AB1} and p_{AB2} are the probabilities of *doublets* which have been defined above. The slope equation is obtained as previously:

$$\left[\frac{\mathrm{d}T_\mathrm{g}}{\mathrm{d}R}\right]_{R=0} = \frac{q}{r}\frac{T_0}{\ln\left[\frac{m'}{m}\right] + \ln\left[\frac{2+\lambda(m-1)(m'-1)}{2+\lambda(m-1)^2}\right]} \quad (32)$$

where $\lambda = \mathrm{e}^{-E_\mathrm{e}/k_\mathrm{B}T_0}$ uses the energetical correcting factor E_e, if one assumes that the rate of corner- and edge-sharing structures remains roughly constant in the low-modified régime. λ can be related to the rate of edge-sharing *doublets*:

$$\eta = \frac{p_{\mathrm{AA2}}}{p_{\mathrm{AA1}} + p_{\mathrm{AA2}}} = \frac{(m-1)^2\lambda}{2+(m-1)^2\lambda}\cdot \quad (33)$$

Figure 13 shows a typical example of such intermediate systems and gives information about the rate of edge-sharing structures (dimers) in the chalcogenide binary glasses $(1-x)\mathrm{As}_2\mathrm{S}_3 - x\mathrm{Tl}_2\mathrm{S}$. In the $\mathrm{As}_2\mathrm{S}_3$ based glass, the line using the slope equation (32) with $\eta = 0.65$ has best agreement with experimental data. The rate of dimers should therefore be about 0.65 in this glass, according to Figure 13. As before, we believe that a T_g measurement for $x \leq 0.05$ should give more precise information and improve the estimation of η.

3.3.2 Influence of B-B bonds. The second slope equations

In the first consideration of section 2, the model has been constructed only with A−A and A−B *doublet* agglomeration. It corresponds to the most common situations where only a very few "*altered*" configurations should be expected when the starting structure made of almost "*regular*" configurations A is slightly modified (low x concentration). Therefore, no B−B bonds were considered. The presence of these bonds at the very beginning of the modification (*i.e.* the tendency of a system to create such bonds, even when there are very few B configurations) can of course substantially change the thermal behavior of the glass (and the final T_g) and modify the slope equations. The construction presented in the previous section corresponded to a situation where a defect (the B configuration created by a modifier) was diluted inside the whole structure, thus leading to A−B and A−A *doublets* only. This seems adapted for the description of binary oxide glasses or network glasses. If the oxide ion is replaced by a larger and more polarizable ion, such as the sulfide or the selenide ion, the local environment of a configuration, composed of electron-rich ions (S, Se) and modifier cations ($\mathrm{M}^{\oplus}$) may favour the occurrence of local B−B bonds.

With the notations introduced in Section 2, the probability of finding a pure single-bonded B *doublet* is:

$$p_{\mathrm{BB1}} = \frac{m'^2}{\mathcal{Z}_1}p^2\mathrm{e}^{-\beta E_3} \quad (34)$$

where E_3 is the B−B bond energy and the $\mathcal{Z}_1'$ the new normalizing factor:

$$\mathcal{Z}_1' = m^2(1-p)^2\mathrm{e}^{-\beta E_1} + 2mm'p(1-p)\mathrm{e}^{-\beta E_2} + m'^2p^2\mathrm{e}^{-\beta E_3}. \quad (35)$$

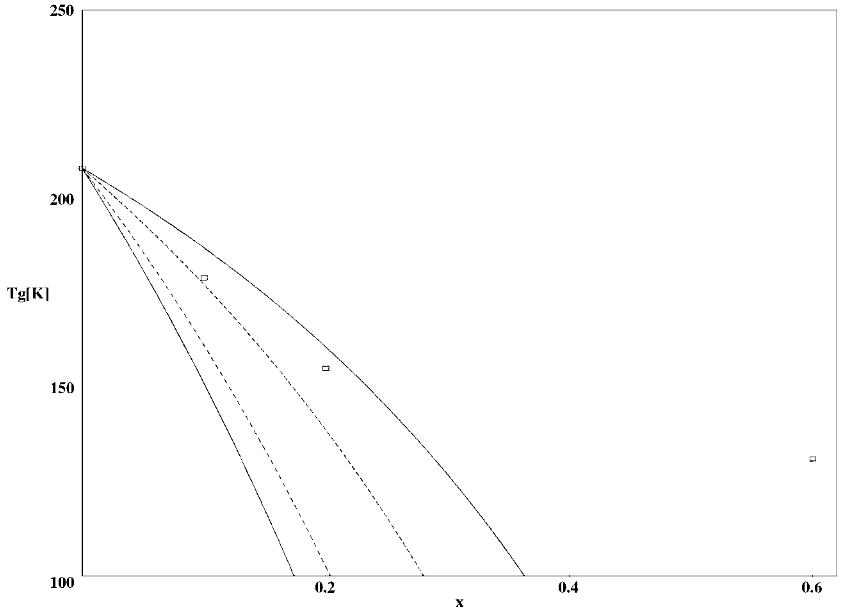

Fig. 13. Glass transition temperature of $(1-x)\mathrm{As_2S_3}-x\mathrm{Tl_2S}$ glasses. The solid lines correspond to the pure edge-and corner-sharing situations, using the slope equations (30, 17). Data are taken from [95]. Intermediate situations are plotted and correspond to ($\lambda=0.1$, $\eta=0.17$, dotted line) and ($\lambda=0.7$, $\eta=0.58$, dashed line).

$$p_{\mathrm{am}} = \frac{mm'(m-1)(m'-1)\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}}-m^2(m-1)^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}}{2mm'(m-1)(m'-1)\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}}-m^2(m-1)^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}-m'^2(m'-1)^2\mathrm{e}^{-E_3/k_{\mathrm{B}}T_{\mathrm{g}}}}. \tag{38}$$

In the pure edge-sharing situation, the probability has the following expression:

$$p_{\mathrm{BB2}} = \frac{2}{\mathcal{Z}_2'}\left[\frac{m'(m'-1)}{2}\right]^2 p^2\mathrm{e}^{-\beta E_3+\beta E_{\mathrm{e}}}. \tag{36}$$

The stationary solution of equation (6) is changed and depends on the energy E_3. Two energetical differences are now involved: E_3-E_2 and E_1-E_2.

$$p_{\mathrm{am}} = \\ =\frac{mm'\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}}-m^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}}{2mm'\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}}-m^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}-m'^2\mathrm{e}^{-E_3/k_{\mathrm{B}}T_{\mathrm{g}}}} \tag{37}$$

(see equation (38) above).

Equation (37) corresponds to the solution of (6) in a pure corner-sharing situation, whereas (38) is the solution of the pure edge-sharing situation. The glass formation occurs only if p_{am} is attractive, which happens when two conditions are satisfied, namely:

$$\frac{m'}{m} > \mathrm{e}^{\alpha} \qquad \frac{m}{m'} > \mathrm{e}^{\beta} \tag{39}$$

or, in the pure edge-sharing situation:

$$\frac{m'(m'-1)}{m(m-1)} > \mathrm{e}^{\alpha} \qquad \frac{m(m-1)}{m'(m'-1)} > \mathrm{e}^{\beta} \tag{40}$$

with $\alpha=(E_2-E_1)/k_{\mathrm{B}}T$ and $\beta=(E_2-E_3)/k_{\mathrm{B}}T$. When B$-$B *doublets* are involved, $p=1$ can be attractive when the second inequality of (39) or (40) is not satisfied. In the limit of $p_{\mathrm{am}}\rightarrow 1$ (corresponding to the pure B configuration network), it is possible to obtain an expression for E_2-E_3, similarly to (13)

$$E_2-E_3 = k_{\mathrm{B}}T_1 \, \ln\left[\frac{m}{m'}\right] \tag{41}$$

or following the situation (corner or edge-sharing):

$$E_2-E_3 = k_{\mathrm{B}}T_1 \, \ln\left[\frac{m(m-1)}{m'(m'-1)}\right] \tag{42}$$

where T_1 is the glass transition temperature of the pure B glass network (*e.g.* when $x=0.33$, the network of $(1-x)\mathrm{SiO_2}-x\mathrm{Na_2O}$ is supposed to be composed of $\mathrm{Q}^{(3)}$ structures only [31] and $T_1\simeq 445$ °C [42]). The implicit function $\Phi_2^{\mathrm{c}}(p_{\mathrm{am}},T_{\mathrm{g}})$ for the corner-sharing situation is here:

$$\begin{aligned}\Phi_2^{\mathrm{c}}(p_{\mathrm{am}},T_{\mathrm{g}}) = p_{\mathrm{am}}\Big[&2mm'\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}} \\ &-m'^2\mathrm{e}^{-E_3/k_{\mathrm{B}}T_{\mathrm{g}}}-m^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}\Big] \\ &+m^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}-mm'\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}} = 0\end{aligned} \tag{43}$$

and for the edge-sharing situation:

$$\begin{aligned}\Phi_2^{\mathrm{e}}(p_{\mathrm{am}},T_{\mathrm{g}}) = p_{\mathrm{am}}\Big[&2mm'(m-1)(m'-1)\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}} \\ &-m'^2(m'-1)^2\mathrm{e}^{-E_3/k_{\mathrm{B}}T_{\mathrm{g}}}-m^2(m-1)^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}\Big] \\ &+m^2(m-1)^2\mathrm{e}^{-E_1/k_{\mathrm{B}}T_{\mathrm{g}}}-mm'(m-1)(m'-1)\mathrm{e}^{-E_2/k_{\mathrm{B}}T_{\mathrm{g}}} \\ &=0.\end{aligned} \tag{44}$$

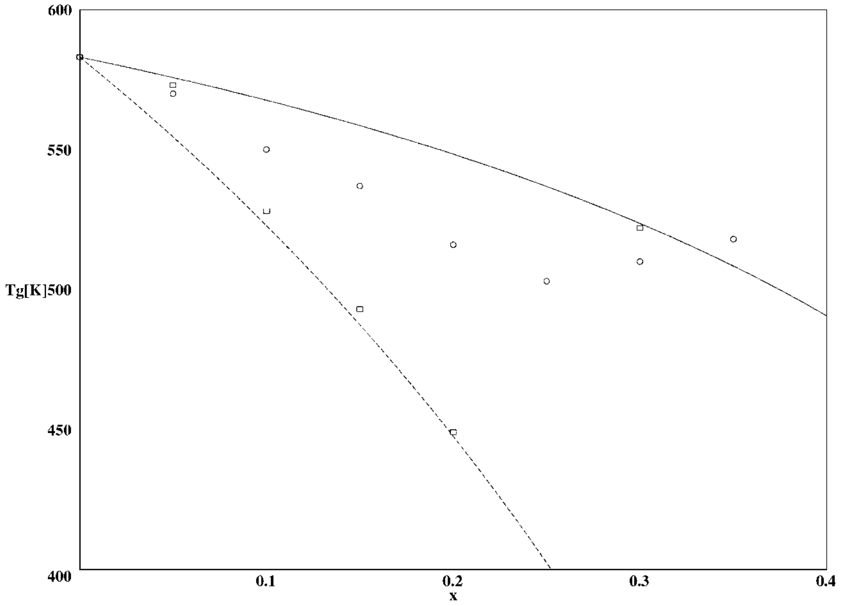

Fig. 14. Glass transition temperature (in K) of $(1-x)B_2S_3-xM_2S$ glasses with M = Na [□] and K [o]. The solid line corresponds to the slope equation (45) with $m=3$, $m'=4$, $T_0=583$ K and $T_1=449$ K (for sodium systems). Data are taken from [99]. The dotted line represents a modified slope equation using Martin's correcting factor $\alpha=7.82$ [92] for Na based glasses.

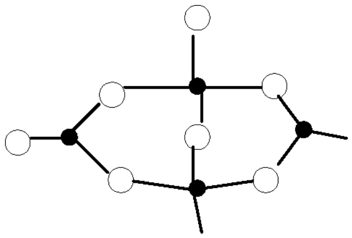

Fig. 15. The dithioborate group proposed as possible MRO structure in $B_2S_3-M_2S$ glasses [92]. This structure is made of corner-sharing B−B doublets (N4 species).

The application of (15, 16) with the two limit conditions (when $p_{\mathrm{am}}\rightarrow 1$ and $p_{\mathrm{am}}\rightarrow 0$) presented in (13) and (41), leads to the second set of slope equations:

$$\left[\frac{\mathrm{d}T_g}{\mathrm{d}R}\right]_{R=0}=\frac{q}{r}\frac{T_0}{\ln\left[\frac{m'}{m}\right]}\left[1-\left(\frac{m}{m'}\right)^{\frac{T_1-T_0}{T_0}}\right] \tag{45}$$

in the pure corner-sharing situation and with (29, 42):

$$\left[\frac{\mathrm{d}T_g}{\mathrm{d}R}\right]_{R=0}=$$
$$=\frac{q}{r}\frac{T_0}{\ln\left[\frac{m'(m'-1)}{m(m-1)}\right]}\left[1-\left(\frac{m(m-1)}{m'(m'-1)}\right)^{\frac{T_1-T_0}{T_0}}\right] \tag{46}$$

in the edge-sharing situation. In case of a mixture of corner- and edge-sharing structures, the slope equation is:

$$\left[\frac{\mathrm{d}T_g}{\mathrm{d}R}\right]_{R=0}=$$
$$=\frac{q}{r}\frac{T_0\left[1-\left(\frac{m(2+\lambda(m-1)^2)}{m'(2+\lambda(m-1)(m'-1))}\right)^{\frac{T_1-T_0}{T_0}}\right]}{\ln\left[\frac{m'}{m}\right]+\ln\left[\frac{2+\lambda(m-1)(m'-1)}{2+\lambda(m-1)^2}\right]}. \tag{47}$$

One can note that the presence of B−B bonds at the very beginning of the modification, leads to a lowering of the slope, due to the presence of the second term inside the brackets of (45) or (46). It can be also possible to obtain a negative slope at the origin $R=0$ ($x=0$), despite an increase of the coordination number $m'>m$ and *vice-versa*. This is a rather surprising result which contradicts the first slope equation and which is against the empirical rule stating that T_g is growing when the connectivity of the network is growing, and *vice-versa*. Examples of such a reverse behavior can be presented. They concern B_2S_3 and P_2S_5 based glasses.

- B_2S_3 based glasses

In the $(1-x)B_2S_3-xM_2S$ systems M = Na, K, Rb, Cs the glass transition temperature is decreasing when x is growing, although these compounds show a monotonic increase of tetrahedral boron units N4, in a manner similar to that found in the oxide glasses (Fig. 8b). The coordination number of the A configuration is $m=3$ ($BS_{3/2}$ triangle) and $m'=4$ for the B configuration (tetrahedral boron).

The connectivity of the network is increasing and the derivative should therefore be positive. According to equation (45), the unexpected negative slope can be explained by the presence of B−B bonds in the very low alkali limit,

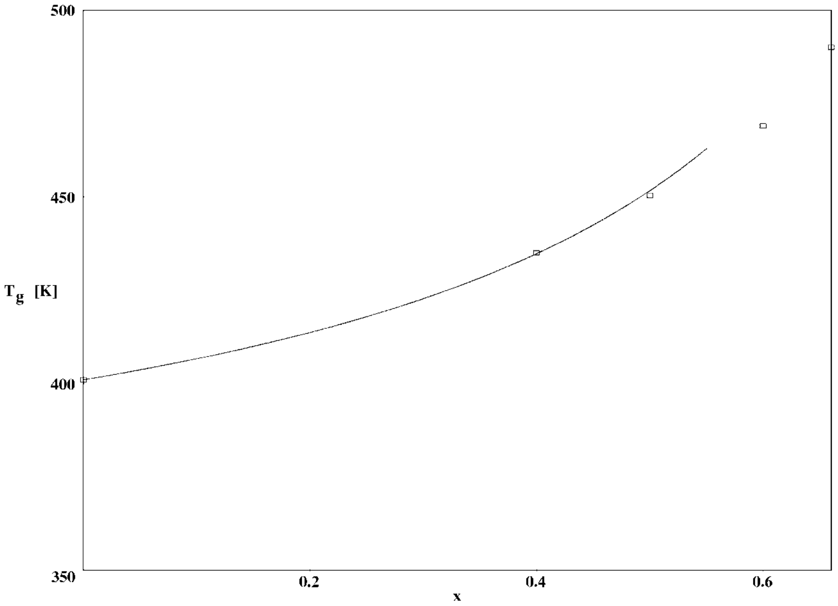

Fig. 16. Glass transition temperature (in K) of $(1-x)P_2S_5 - xLi_2S$ systems. The line represented has a slope (45) with $m = 3$, $m' = 2$, $T_0 = 128$ °C and $T_1 = 177.4$ °C. Data are reported in reference [102].

which yields a negative contribution inside the brackets of the expression (45). Indeed, the sulfide system exhibits a very sharp increase of N4 species when R is growing, much more pronounced than in B_2O_3 based systems. Martin and co-workers have studied the short-range order of these systems by ^{11}B NMR spectroscopy [98] and have shown that in the sodium glass, the rate of N4 species can be close to unity already for $x \simeq 0.2$, whereas the same rate is always lower than 0.5 in the oxide glass. According to their spectroscopic investigation N4 $\simeq 1.0$ when $x = 0.2$, *i.e.* at the measured glass transition temperature $T_1 = 176$ °C [99, 100], and $T_0 = 583$ K [101]. Inserting these values in (45) yields a negative slope and agrees with the experimental data of $B_2S_3-Na_2S$ systems in the very low modified glass, displayed in Figure 14 (solid line). For greater values of x, Martin suggests that equation (11) is modified [98] and that N4 $\simeq \frac{\alpha}{2}R$ with $\alpha = 7.82$ instead of N4 $\simeq R$ [38]. This implies that the right hand side of equation (45) has to be multiplied by 3.91. The slope equation then predicts the right $T_g(x)$ behavior up to $x \simeq 0.2$ (Fig. 14, dotted line).

The fact that N4−N4 clusters can be produced even at the very beginning, leading to a negative slope, explains why the dithioborate group, made of two corner-sharing N4 species (Fig. 15), should occur very rapidly in these systems [98], whereas it appears only for $x \simeq 0.2$ in the oxide glass [73].

- P_2S_5 based glasses

The available glass transition temperature data in these system concern only the lithium based glasses. The local structure of P_2S_5, which has the same stoichiometry than P_2O_5, is the same as that in the oxide glass (Fig. 8c). The SRO *singlet* of the network former is composed of a phosphor atom with four P−S bonds, one of them being double bonded ($Q^{(3)}$ structure). The addition of a modifier (Li_2S) leads to the creation of a $Q^{(2)}$ structure (B configuration), sharing one non-bridging sulphur atom, hence $m = 3$ and $m' = 2$ [83]. The slope at the origin ($x \simeq 0$) should therefore be negative, but this is not observed experimentally. T_g is increasing from $T_0 = 128$ °C up to 217 °C (at $x = 0.66$). For $x = 0.5$, the proposed structure is the metathiophosphate chain, made of almost 100% $Q^{(2)}$ structures [102]. The measured glass transition temperature is $T_1 = 177.4$ °C. Inserting these values (T_0, T_1, m, m') in equation (45) gives the slope at the origin, which is in very good agreement with the experimental data of Kennedy [102] (Fig. 16).

Therefore, we can conclude that the B−B *doublet* exists already at the very beginning of the modification. This means that $P_2S_5-Li_2S$ systems display the tendency to form $Q^{(2)}-Q^{(2)}$ *doublets* inside the network. This proposition has been also made by Kennedy and co-workers [102]. In order to explain the increase of T_g, these authors suggest that the modifier may create a stronger ionic bonding formed between fragments that could increase T_g (*i.e.* a B−B bonding, $Q^{(2)}$ being the fragment which displays $T_1 > T_0$).

4 Summary and conclusions

In this article, we have shown that there is strong evidence for the existence of a universal relationship between the glass transition temperature and the local structure in low-modified glass systems. Based on statistical and thermodynamical factors, the model gives the slope at the origin $\left[\frac{dT_g}{dx}\right]_{x=0}$ for binary glasses $(1-x)A_rX_q + xM_qX$ and network glasses A_xB_{1-x}. Let us recall the following important results obtained:

1. The model gives the correct value of the coordination numbers m and m' of the involved atoms or the SRO structures for a great number of systems, such as corner-sharing glasses (network and binary oxide

glasses), and edge-sharing glasses (binary chalcogenide glasses).

2. The sharp decrease of the glass transition temperature for low modifier concentration is explained by the presence of a high initial T_0 value in the expression of the slope equation. SiO_2 and GeO_2 based glasses display such a behavior.
3. The model yields an analytical expression of the constant β appearing in the modified Gibbs-Di Marzio equation. The value computed with given m and m' is in agreement with the one obtained by a least squares fit from the experimental data by different authors.
4. It explains that the decrease of T_g despite an increase of the connectivity of the glass network (and *vice-versa*) is due to the presence of local B−B *doublets*, a situation which is typical of B_2S_3 and P_2S_5 based glasses, for which the slope equations agree with experimental glass transition temperature measurements.

We believe that these encouraging results can be extended for any concentration in network and binary glasses, and will explain, mathematically, particular shapes of T_g *versus* x on the basis of structural considerations. Besides these extensions, the model can also be applied to three configurations A, B and C, in order to investigate ternary glass-forming systems. Such attempts will be presented in forthcoming articles [103].

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