Solvable models of glass transition

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Simple statistical agglomeration models can provide a universal link between the local structure and the glass transition temperature in network glasses. We first stress the physical features of the models and the relevancy of the hypothesis made and then show how to define the glass transition temperature. The models are applied to various types of binary, ternary and multicomponent chalcogenide glass networks and the predictions compared to experimental data.

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I. INTRODUCTION

Although much attention has been devoted to the understanding of the glass transition problem\textsuperscript{1}, a general relationship between the temperature of this transition (when measured under standard conditions, at e.g. constant heating rate), and some easily reliable quantities is still lacking\textsuperscript{2}. In this paper, we show that there are some aspects of structure or connectivity that apparently play an important part in determining the absolute magnitude of $T_g$. The construction and the prediction of this temperature from solvable agglomeration models is parameter-free and can be easily extended from binary to ternary, etc. glassy systems.

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II. AGGLOMERATION MODEL

Let us imagine a liquid that is slowly cooled and atomic motions are progressively arrested. In network glasses, the Arrhenius-like increase of viscosity upon cooling to the glass transition is intimately related to a decrease of dangling bonds as the starting network is polymerized. One typical physical process taking place in the supercooled liquid should therefore be a kind of sticking process in which clusters (or macromolecules) agglomerate together. Also, one should remark that the most important determinant of chemical and physical properties of a glass is the concentration of different types of atoms involved. Thus the simplest level of description of such agglomeration processes should use local structural configurations (LSC) defined by the concentration, corresponding to short-range order (SRO), and consequently to a random network description of the glass. We should stress here that the next level of description, using intermediate range order, is very similar to the SRO construction. The LSC’s in Ge_xSe_1−x binary can for instance be the germanium tetrahedrally coordinated to selenium atoms, or in silica based glasses the silicon tetrahedra Q^{(k)} (the subscript k refers to the number of bonding oxygens on each SiO_{4/2} tetrahedron).

Consider a typical cluster with a certain LSC distribution \( \{p_i^0\}_{i=1..N} \). As long as the viscosity is not too high, other LSC can stick on this typical cluster, creating new covalent bonds i-j with probability:

\[
p^L_{ij}(T) = \frac{W_{ij}}{Z} p^0_i p^0_j e^{-E_{ij}/k_B T} \tag{2.1}
\]

where \( W_{ij} \) is a statistical factor corresponding to the number of equivalent ways to stick a LSC i on a LSC j being part of a cluster (\( W_{ij} \) is thus related to the coordination numbers \( m_i \) and \( m_j \) of the LSC) and \( E_{ij} \) is the i-j LSC bond energy. \( Z \) normalizes the bond distribution. The creation of these new bonds produces a local variation in the probability (or concentration) distribution of the cluster and it can be encoded in the following master equation:

\[
\frac{dp_i}{dt} = \frac{1}{\tau} \left[ \frac{1}{2} \sum_{j=1}^{N} (1 + \delta_{ij}) p^L_{ij}(T) - p^0_i \right] \tag{2.2}
\]
where $\tau$ represents the mean agglomeration time and (2.2) represents a system of $(N - 1)$ non-linear differential equations. At solidification temperature $T_s$ ($T_s = T_m$ for a crystal or $T_s = T_g$ for a glass) one should reach a stationary state and $dp_i/dt = 0$, i.e. the variation of local probability distribution should be minimized.

How can we distinguish a glass from a crystal? Imagine that a local fluctuation $\epsilon_i$ appears in the vicinity of a stationary solution, satisfying a linearized version of equ. (2.2). As usual, we can distinguish three types of singular points by means of the linearization. If all the roots of the characteristic equation of the linearized system have a negative real part, the solution is a stable attractor, i.e. it will show the preferential agglomeration process, which corresponds to nucleation of the crystal. Thus there will be no possibility for a fluctuation to grow, and we identify the stable stationary solution with a crystal, and $T_s = T_m$. If all the real parts are positive, one gets an unstable stationary solution. If both are present, a saddle point solution is obtained (fig. 1). The glass corresponds to the latter characteristic, because it is neither a stable nor an unstable system, it has metastable character, and $T_s = T_g$. There is indeed still a chance for the system to escape (in other words for a fluctuation to grow) from the stationary saddle point and to fall on the stable crystalline attractor, which always happen experimentally when a glass is annealed.

One can extend such a description to binary and ternary glasses as well. First, we consider the case when $N = 2$, i.e. when there are only two different types of LSC. We denote them by $A$ and $B$ with their respective coordination numbers $m_A$ and $m_B$. The system (2.2) reduces then to a single equation with only one variable, $p^0 = x$, e.g. the probability of occurrence of the LSC B (and set equal to the concentration of B species). The solution of (2.2) yields:

$$T_g = \frac{\Delta_B}{k_B \ln \frac{m_B(2x-1)}{m_A(x-1)}} = T_0 \ln \frac{m_B}{m_A}$$

(2.3)

where $\Delta_B = E_{AB} - E_{AA}$ is introduced when computing the probabilities $p_{AA}$ and $p_{AB}$ from equ. (2.1) (we have neglected the possibility of BB bonds because we are dealing in the fol-
lowing with low modified glasses only, and below the stoichiometric composition). One can see in the second part of equation (2.3) that the relationship can be made parameter-free, by considering the limit $x \approx 0$, when $T_g \approx T_0$. The initial network (with glass transition temperature $T_0$) is made of A LSC only (e.g. the selenium network in $Ge_xSe_{1-x}$ systems) and one gets from the first part of equ. (2.3): $\Delta B = k_B T_0 \ln[m_B/m_A]$. In order to predict the glass transition temperature in a binary glass $A_{1-x}B_x$, there is just need of the coordination number of the involved LSC’s and the initial glass transition temperature $T_0$ of the A network. Finally, we can obtain a linear equation at the very beginning of structural modification:

$$\left[ \frac{dT_g}{dx} \right]_{x=0, T_g=T_0} = \frac{T_0}{\ln\left( \frac{m_B}{m_A} \right)}$$

(2.4)

The application to ternary glass networks $A_{1-x-y}B_xC_y$ is slightly different, because when $N = 3$, there are two non-linear equations to solve in terms of two probabilities $p_B^0 = x$ and $p_C^0 = y$. However, one obtains a saddle point solution from (2.2), yielding again a parameter-free relationship between $x$, $y$ and $T_g$, because the new bond energy differences $\Delta C = E_{AC} - E_{AA} = k_B T_0 \ln[m_C/m_A]$ and $E_{BC} - E_{AA} = k_B T_0 \ln[m_Cm_B/m_A^2]$ are determined again from boundary conditions (from the binary AC glass for the former, similarly to $\Delta_B$, from the binary slope equation for the latter). One interesting quantity in such systems (and in multicomponent chalcogenides) is the average coordination number, defined by $\bar{r} = m_A(1 - x - y) + m_Bx + m_Cy$ (and $m_A = 2$). From the saddle point solution of equ. (2.2), we obtain a relationship between $\bar{r}$ and $T_g$, to be compared with experiment:

$$\bar{r} = \frac{2m_Bm_C \left[ m_Bm_C \alpha \gamma(\alpha - \gamma - \alpha) + 2r_C \alpha^2(1 - \gamma) + 2r_B \gamma^2(1 - \alpha) \right]}{\left( 2r_C \alpha - 2r_B \gamma - r_B r_C \alpha \gamma \right)^2 + 8r_B r_C \alpha \gamma}$$

(2.5)

where $\alpha = (2/m_C)^{(T_0/T_g)}$ and $\gamma = (2/m_B)^{(T_0/T_g)}$. The slope in the limit $\bar{r} = 2$ (i.e. $x=y=0$) has also a simple expression:

$$\left[ \frac{dT_g}{d\bar{r}} \right]_{\bar{r}=2, T_g=T_0} = \frac{T_0}{(m_B - 2) \ln\left( \frac{m_B}{2} \right) + (m_C - 2) \ln\left( \frac{m_C}{2} \right)}$$

(2.6)
III. COMPARISON WITH EXPERIMENTAL DATA

The obtained relationships (2.4) and (2.5) can be compared to the experimentally measured glass transition temperatures in binary, ternary and multicomponent chalcogenide glass systems.

Given the initial glass transition temperature $T_0$ of vitreous sulphur ($245 \, K$), selenium ($316 \, K$) and tellurium ($343 \, K$ extrapolated from the data in [7]), we have plotted the equations (2.4) and (2.5) for chalcogenides including elements of Group IV and V. We can see that equation (2.4) predicts the $T_g(x)$ trend at low concentration for all the binary systems IV-VI and V-VI systems displayed (fig. 2). From obvious structural considerations, we can insert in equ. (2.4) the value $m_B = 4$ (Group IV) or $m_B = 5$ (Group V), $r_A = 2$ and $T_0$, to be compared with the plotted experimental measurements on glass transition temperatures. The prediction gives also an indirect evidence of the stiffness transition (occurring at $\bar{r} = 2.4$ following the theory of Phillips and Thorpe [9]). For $\bar{r} > 2.4$ ($x > 0.2$ in IV-VI glasses), the network loses its random character and chemical ordering occurs, due to the chemical stability composition at $x=0.333$. Thus the description in terms of a random network of $A−A$ and $A−B$ bonds should fail at this concentration. This is clearly seen for the $Ge_xSe_{1−x}$ data, which start to deviate from the equation (2.4) at $x = 0.18$, and even more at $x = 0.24$, consistently with Mössbauer spectroscopy [10]. The sulfide system behaves very similarly, as seen on fig. 2 (and still $r_B = 4$), although the structure of the initial glass ($x=0$) is rather different (chains and $S_8$ rings). The addition of germanium leads to a random network composed of $GeS_{4/2}$ linkages between S chains and rings. Note that there is no deviation for the Ge-Te compound at $x=0.2$. This can be related to the fact that $c−GeTe_2$ does not exist (in contrast with the existence of $c−SiSe_2$, $c−GeSe_2$, etc.) and probably that chemical ordering probably does not occur at the same concentration. As a consequence, the network of $Ge_xTe_{1−x}$ can be thought as random.

Agreement of the prediction with experimental measurements is also obtained in V-VI network glasses. For all the systems displayed in figure 2, the slope equation (2.4) gives the
correct trend in the variation of the glass transition temperature with network modification. Deviation of the stochastic prediction of (2.4) is here also supposed to occur at $\bar{r} = 2.4$, corresponding to $x = 0.4$ in the As-Se system. There is some evidence that the Bismuth atom could be five-fold coordinated in binary Bi-Se glasses. If this is the case, the stiffness transition may occur $x \simeq 0.13$ (corresponding to $\bar{r} = 2.4$ and may be observable in the $T_g$ data, as well as the deviation of the stochastic prediction of equ. (2.4)). We can observe the same kind of agreement in ternary chalcogenides, where the glass transition temperature is given as a function of the average coordination number by equ. (2.5) or (2.6). The figure 3 shows that in very different systems (germanium chalcohalide glasses, thus $m_B = 4$, $m_C = 1$, and telluride glasses) the network is random for $\bar{r} < 2.4$ and the description in terms of A-A, A-B, A-C and B-C bonds only is accurate. The same deviation is observable at $\bar{r} = 2.4$ which can again be interpreted by the occurrence of chemical ordering due to the stiffness transition (e.g. occurrence of a $Sb_2Te_3$ phase in the Ge-Sb-Te system). However, we should point out that experimental measurements in the low modified region of telluride systems (lower plot fig. 3) should be realized in order to definitely confirm the prediction. Other systems exhibit the same universal trends in the glass transition temperature variation and the construction can be extended to quaternary and multicomponent chalcogenide systems in a simple fashion.5

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FIG. 1. The right-hand side of one of the equation (2.2) for $N = 3$ in a simple polygon model. The system out of equilibrium can fall on the attractive $p_3 = 1$ stationary solution (crystallization, and $T_s = T_m$) and never on $p_2 = 1$ or $p_1 = 1$. In some situations, the liquid can stay in the metastable state characterized by the saddle point solution at $(p_1 = 0.6, p_2 = 0.2, p_3 = 0.2)$ and $T_s = T_g$. Note that the plot has to be truncated in order to have $p_1 + p_2 + p_3 = 1$. 

FIG. 2. Binary IV-VI (upper plot) and V-VI (lower plot) chalcogenide glasses (e.g. $Ge_xSe_{1-x}$).

The lines represent the slope equation (2.4) with $m_A = 2$ and $m_B = 4$ for the IV-VI glasses, and $m_B = 5$ for V-VI glasses. Data have been displaced by 200 K and 100 K for a clearer presentation. The vertical shaded line corresponds to the critical average coordination number $\bar{r}_c = 2.4$, predicted by Phillips and Thorpe.
FIG. 3. Glass transition temperature in ternary chalcogenides as a function of average coordination number $\bar{r}$. Upper plot: chalcohalide glasses. Lower plot: ternary tellurides. The curves represent equ. (2.5) with $m_A = 2$ and $m_B$ and $m_C$ inserted following the Group of the Periodic Table. Data have been displaced for simplicity and are taken from [11].