Variation of the glass transition temperature with rigidity and chemical composition

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The effects of flexibility and chemical composition in the variation of the glass transition temperature are obtained by using the Lindemann criteria, which relates melting temperature with atomic vibrations, and rigidity theory. Using this criteria and that floppy modes produce an excess of vibrational states at low frequencies which enhance in a considerable way the average quadratic displacement, we show that the consequence is a modified glass transition temperature. This approach allows us to obtain in a simple way the empirically modified Gibbs-DiMarzio law, which has been widely used in chalcogenide glasses to fit the changes in the glass transition temperature with the chemical composition. The method predicts that the constant that appears in the law depends upon the ratio of two characteristic frequencies (or temperatures). This constant is estimated for the $Se_{1-x-y}(Ge_yAs_{1-y})_x$ glass by using the experimental density of vibrational states, and the result shows a good agreement with the experimental fit from glass transition temperature variation.

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Glasses are solids that do not have long range order, usually produced by fast cooling of a liquid melt. In spite of the well-known importance of these materials, the physics of glass formation is still an open and puzzling problem,[1] since it is mainly a nonequilibrium process. Even some important technological questions are not well understood, as the origin of the nonexponential relaxation laws[2] or the ability of certain materials to reach the glassy state.[3] One approach to the problem was made by Kauzmann,[4] who pointed out that there is an underlying thermodynamical phase transition due to an entropy crisis. Kauzmann's approach was very successful, but unable to answer many questions in a quantitative way. Later on, other approaches were proposed:[5] phenomenological models like the Gibbs-DiMarzio, theories based in supercooled liquids as, for example, mode coupling and energy landscape formalism, or the use of computer simulation.[4] Most of these theories have difficulties to explain one of the most simple and interesting questions: how the glass transition temperature (T_g) depends on chemical composition. As discovered by the Phoenicians, T_g can be dramatically lowered or raised by adding few impurities. Another interesting property is the behavior of viscosity, which is usually referred to as fragility,[6] which can be changed from strong to fragile.[6] Chalcogenide glasses (formed with column VI elements doped with impurities) are very important to understand these effects. The change of T_g with the chemical composition has been observed to follow an empirically modified Gibbs-DiMarzio law:[6–9]

$$T_g(\langle r\rangle) = \frac{T_g(\langle r\rangle = 2.0)}{1-\beta(\langle r\rangle - 2.0)}, \tag{1}$$

where β is a parameter fitted from the experimental data, $\langle r\rangle$ is the average coordination number, defined as $\langle r\rangle = \Sigma_{r=0}^{Z_{\max}} r x_r$, and r is the number of covalent bonds that the designated atom can form. x_r is the occurrence of each type of atom in the glass and $Z_{\max}$ is the maximal coordination among all atomic species. For example, for a Se-As-Ge glass, $Z_{\max}=4$ which corresponds to the valence of Ge. Observe that the average coordination number approach is very useful when covalent bonds are present, since there is a hierarchy in the atomic forces, and thus homopolar bonding is negligible in $\langle r\rangle$. It is worthwhile mentioning that the original Gibbs-DiMarzio law was developed for polymers,[4] and its use for chalcogenide glasses is empirical. It can be obtained using stochastic methods,[10] but the problem is the need to define T_g in an unusual way.[10]

The rigidity theory (RT),[11,12] was an important step to understand glass formation. By considering covalent bonding as mechanical constraints, the ease of glass formation is related with the number of constraints. If this number is lower than the degrees of freedom, there are zero frequency vibrational modes called floppy.[13] The resulting network is underconstrained. A transition occurs when a disordered lattice becomes rigid. Many features of this transition have been experimentally observed.[8,14] Even for simple systems like hard-disks,[15] polymer melts,[16] and colloids,[17] rigidity plays an important role. For proteins, RT allows one to understand long-time scale motions,[18] and the window of thermodynamical reversibility,[8] explained as stress self-organization.[19] Although the success of RT, its thermodynamics has not been developed.[16] In previous papers, we approached this problem by using a phenomenological free energy[20] and computer simulations.[21] Yet, many questions remain open, as, for example, the variation of T_g with the chemical composition of a glass. However, very recently it has been shown from first principles that the energy landscape and the phase space topology of a glass depend upon the rigidity properties of the system.[22] In this Brief Report, we will take a further step by combining the structure of the phase space topology, given by the RT, and the old Lindemann criteria that relates melting with the size of atomic vibrations (which has been proved to be valid for glasses[23,24]), in order to explain the variation of T_g with chemical composition. The fundamental idea behind this approach is that flexibility increases the quadratic displacement due to low frequency modes, produced

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by directions in the phase space where there is almost no energetic cost in deforming the atomic network. Thus, nonlinear effects become more important at decreasing temperatures. Furthermore, the present approach provides a clear path to understand glass transition trends with the connectivity of the network, and it can serve to understand other flexible systems as well, like polymers or proteins.

In RT, the ability for making a glass is optimized when the number of freedom degrees, $3N$ (where N is the number of particles), is equal to the number of mechanical constraints (N_c) given by bond bending and stretching forces. The parameter $f=(3N-N_c)/3N$ gives the fraction of cyclic variables of the Hamiltonian. A variation of these coordinates do not change the energy and thus f also corresponds to the fraction of vibrational modes with zero frequency, called floppy modes.[12] The parameter f is a function of $\langle r\rangle$, and can be calculated using the pebble game algorithm,[13] but it can be estimated with a mean-field procedure,[25]

$$f=\frac{3N-N_c}{3N}=2-\frac{5}{6}\langle r\rangle. \tag{2}$$

The rigidity transition occurs when $f=0$ (at the critical value $\langle r_c z\rangle=2.4$), and the system passes from a floppy network to a rigid one. In principle, since floppy modes have zero frequency, they do not contribute to the elastic energy, and the specific heat of the glass depends on f, a result that violates the Dulong-Petit law,[20] and which is not observed in the experimental data.[8] In fact, floppy modes do not have a perfect zero frequency, i.e., in real glasses they are shifted by residual forces, like the van der Waals interaction.[12] This was confirmed in a very detailed neutron scattering[26] study, where it has been shown that floppy modes in the prototypical compound $Se_{1-x-y}(Ge_yAs_{1-y})_x$ are blueshifted, forming a peak at 5 meV. This frequency is just obtained as the maximum of the peak and remains at the same frequency for all $\langle r\rangle$ between 2.0 and 2.4. If one deconvolutes the signal and calculate the area under the peak, the spectral weight of the peak is exactly f.[26] For pure selenium, it has nearly 1/3 of all the spectral weight.[26] Observe that the role of floppy modes is to enhance the intensity of any preexisting boson peak.[27] The corresponding temperature (Θ_f) where these floppy modes are frozen, can be estimated from the energy required to excite modes of 5 meV, that gives $\Theta_f\approx 54$ K. For low temperatures, it is clear that floppy modes are important, as confirmed by the giant-softening of the 119 Sn Lamb-Mossbauer factor in $(Ge_{0.99}Sn_{0.01})_xSe_{1-x}$ glasses.[14] In principle, one can argue that floppy modes are not so important for the glass at high temperatures, since all $3Nf$ floppy oscillators are excited, leading to the Dulong-Petit law. As we will show next, this is not the case, and in fact floppy modes are essential in determining T_g. To show this, we use the Lindemann criteria (1910), which has been originally devised to understand crystal melting.[35] Such criteria establish that melting occurs when the mean atomic square displacement $\langle u^2(T)\rangle^{1/2}$ is around 1/10 of the atomic spacing a. There are experimental evidences based on neutron scattering that this criteria is applicable to glasses,[24,28,29] as is the case for Se and Se-Ge systems.[23] Computer simulations are in agreement with this observation.[30,31] A comparison between different glasses has been made for $\langle u^2(T)\rangle$ as a function of T in a review by Ngai.[32] For many glasses there is a crossover from a harmonic regimen to an anharmonic one when T_g is reached.[32] Some liquids and polymers show departures from this rule,[32] however, strong glasses and network glass formers like Se, Ge_xSe_{1-x} or B_2O_3 are among those systems where anharmonic effects are moderate below T_g. Since pure Se becomes stronger[6] with the addition of Ge or As, the criteria is even improved when cross linking agents are introduced in the network, and thus it is safe to assume this criteria in the floppy region. Notice that this change of fragility can be due to the surprising relationship between the curvature of the landscape and other properties of the energy landscape.[33]

The value of $\langle u^2(T)\rangle$ can be calculated from the density of vibrational states $g(\omega)$. For $T\leqslant T_g$, the system is in the harmonic limit, and using statistical mechanics in the classical limit,[34]

$$\langle u^2(T)\rangle=\frac{3k_BT}{m}\int_0^\infty\frac{g(\omega)}{\omega^2}d\omega, \tag{3}$$

where k_B is the Boltzmann constant, T the temperature, ω the frequency, and m the mass. Below T_g, $\langle u^2(T)\rangle$ is linear in T as observed for network glasses. At T_g, the Lindemann criteria applied to glasses[23] establish that $\langle u^2(T_g)\rangle \approx\langle u^2(T_m)\rangle\approx 0.01a^2$ where T_m is the melting temperature. This shows the fundamental importance of the excess low frequency modes observed in glasses to determine T_g, due to the enhancement produced by the term ω^{-2} in Eq. (3), which leads to an increasing $\langle u^2\rangle$. Let us make a model for the most prototypical chalcogenide glass: $Se_{1-x-y}(Ge_yAs_{1-y})_x$, since this compound allows us to obtain the same $\langle r\rangle$ with different chemical compositions. The three chemical elements of this glass have nearly the same mass; thus we can suppose that in Eq. (3) all the atomic masses are equal, although in more general cases m must be replaced by an averaged mass, since in Eq. (3) only acoustic modes have an important contribution. The most simple form for $g(\omega)$ is to use an Einstein type model, with a delta function centered around a characteristic floppy peak at ω_f, with a weight given by the number of floppy modes, plus a density of states that has the rest of the spectral weight. Such a density of states can be written as

$$g(\omega)=(1-f)g_R(\omega)+f\delta(\omega-\omega_f), \tag{4}$$

where $g_R(\omega)$ is the density of states for $f=0$. It is important to remark that in this model, $g_R(\omega)$ will be the same at all glass compositions below $\langle r\rangle=2.4$, and the relative weight on nonfloppy modes is taken into account by the factor $1-f$. Note that by using a fixed $g_I(\omega)$ for all chemical compositions, we are overestimating this contribution for flexible glasses, which will give only a small correction to the final result, since $g(\omega)/\omega^2$ goes to zero at high frequencies.[26] This assumption is also supported by the neutron scattering data,[26] which show that $g(\omega)$ follows an isocoordination rule. Using $g(\omega)$, $\langle u^2(T)\rangle$ turns out to be

$$\langle u^2(T)\rangle = \frac{3k_BT}{m}\left[\left\langle\frac{1}{\omega^2}\right\rangle_R + f\left(\frac{1}{\omega_f^2} - \left\langle\frac{1}{\omega^2}\right\rangle_R\right)\right], \quad (5)$$

where $\langle 1/\omega^2\rangle_R$ is defined as the second inverse moment at the rigidity transition,

$$\left\langle\frac{1}{\omega^2}\right\rangle_R \equiv \int_0^\infty \frac{g_R(\omega)}{\omega^2}d\omega.$$

Equation (5) predicts a linear dependence of $\langle u^2(T)\rangle$ upon f. This result and the idea of an Einstein-type mode for floppy modes are supported by the softening of the Lamb-Mossbauer factor in $(Ge_{0.99}Sn_{0.01})_xSe_{1-x}$ glasses[14] as x linearly decreases to 0, i.e., as the glass gets more floppy. The mean square displacement at absolute zero of the vibrational density of states contains the information on these floppy modes, and its variation x nicely scales with the scattering strength of the 5 meV mode observed in inelastic scattering.[14]

Now we turn our attention to combine these results with the Lindemann criteria. When $f=0$, we use Eq. (4) and the Lindemann criteria to obtain T_g at the rigidity threshold $f=0$,

$$T_g(f=0) \approx \frac{0.01ma^2}{3k_B\left\langle\frac{1}{\omega^2}\right\rangle_R}. \quad (6)$$

For the variation of T_g as a function of rigidity, we use the previous expression to rewrite Eq. (5) in terms of $T_g(f=0)$, and then we apply again the Lindemann criteria to obtain,

$$T_g(f) = \frac{T_g(f=0)}{1+\alpha f}, \quad (7)$$

where $T_g(f)$ is the glass transition temperature when a fraction f of floppy modes is present. The parameter α is defined as

$$\alpha \equiv \frac{1}{\omega_f^2\left\langle\frac{1}{\omega^2}\right\rangle_R} - 1 \equiv \left(\frac{\Theta_R}{\Theta_f}\right)^2 - 1,$$

and depends upon the ratio of two characteristic frequencies, since we define the following frequency and temperature at the rigidity transition, $\Theta_R/\hbar \equiv \omega_R \equiv \langle 1/\omega^2\rangle_R^{-1/2}$.

Equation (7) predicts that T_g should decrease as the number of floppy modes increases. Furthermore, we can transform Eq. (7) into the empirically modified Gibbs-DiMarzio Eq. (1), just by using the Maxwell mean field to express f in terms of $\langle r\rangle$ and simple algebraic manipulations,

$$T_g(\langle r\rangle) = \frac{T_g(\langle r\rangle = \langle r_c\rangle)}{1+\alpha\left(2-\frac{5}{6}\langle r\rangle\right)} \equiv \frac{T_g(\langle r\rangle = 2.0)}{1-\beta(\langle r\rangle - 2.0)}, \quad (8)$$

where the constant β is given by

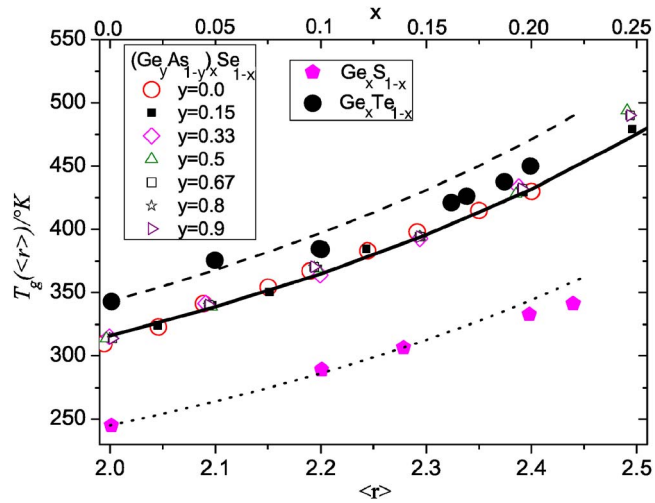

FIG. 1. (Color online) Glass transition temperature as a function of $\langle r\rangle$ for Ge_xS_{1-x}, $Se_{1-x-y}(Ge_yAs_{1-y})_x$, and Ge_xTe_{1-x} taken from Refs. 36 and 37, respectively. All the lines correspond to Eq. (8), with $\beta=0.68$, and $T_g(\langle r\rangle=2.0)=245$ K (dotted line), $\beta=0.67$, and $T_g(\langle r\rangle=2.0)=316$ K (solid line), and $\beta=0.72$, and $T_g(\langle r\rangle=2.0)=343$ K (dashed line). The upper axis shows x for Ge_xS_{1-x} and Ge_xTe_{1-x}.

$$\beta = \frac{5\alpha}{2\alpha+6},$$

and $T_g(\langle r\rangle=2.0)=T_g(\langle r\rangle=\langle r_c\rangle)/(1+\alpha/3)$. Notice that the fraction of 10% prescribed by Lindemann, only determines $T_g(\langle r\rangle=2.0)$, since the only important thing on the derivation is that glass transition occurs at a fixed quadratic displacement. If the fraction is changed, the form of the obtained law and β still are preserved. In experiments with chalcogenide glasses, β is a constant fitted from the data. Our approach shows that β depends upon the ratio of two characteristic frequencies or temperatures. It is worthwhile mentioning that the constant experimental value of β for $Se_{1-x-y}(Ge_yAs_{1-y})_x$ glass in the interval $2.0\leqslant\langle r\rangle\leqslant 2.4$ gives an extra support to the assumption made in Eq. (4). For $\langle r\rangle > 2.4$, the isocoordination rule for T_g is broken and β is no longer constant for different chemical compositions, as is also observed with T_g. Another advantage of the approach presented in this Brief Report is that β can be estimated from neutron scattering data or Lamb-Mössbauer factor. Here we will use the neutron scattering data taken from Ref. 26. We start by noting that at the rigidity transition, $f=0$ and from Eq. (5), $g_R(\omega)=g(\omega)$. Thus, $\langle 1/\omega^2\rangle_R$ can be obtained from the experimental data by calculating the second inverse moment of the normalized density of states at $\langle r\rangle=2.4$. Following this procedure, we get $\langle 1/\omega^2\rangle_R \approx 0.019\,86$ meV^{-2}, with a characteristic frequency $\omega_R \approx 7.0959$ meV, and temperature $\Theta_R \approx 76$ K. Using that $\omega_f \approx 5$ meV, α has the approximate value 1.014, and finally $\beta \approx 0.67 \pm 0.02$. The value from fitting the experimental data of the glass transition has been obtained by many groups,[6,7,9] and produces the value $\beta \approx 0.72$ which is in very good agreement with our estimation from neutron data. Using that $T_g(\langle r\rangle=2.0)=316$ K, Fig. 1 shows a plot of the experimental

data compared to Eq. (8) with the predicted β from neutron scattering. Notice that for each $\langle r \rangle$, there are many different chemical compounds. Although the agreement is good, the calculation of β can be improved by taking into account the floppy peak finite width. In Fig. 1 we also compare $T_g(\langle r \rangle)$ for Ge_xTe_{1-x} and Ge_xSi_{1-x} taken from Refs. 36 and 37, with with Eq. (8) but using the second inverse moments of $g(\omega)$ obtained from Mössbauer experiments, where $\beta \approx 0.68 \pm 0.05$ and $\beta \approx 0.72 \pm 0.03$, respectively. Observe the decreasing of T_g for pure group VI elements. The reason why Te has the highest T_g despite having the higher mass must be due to strong nonpolar interactions. Many other glasses made with elements of different masses follow the same modified Gibbs-DiMarzio law.[38] There is also an effect in the average mass against $\langle r \rangle$ in Eq. (3), but it is small compared with the effects of the floppy peak. Observe that for $\langle r \rangle \leqslant 2.4$, one can develop $[1-\beta(\langle r \rangle - 2.0)]^{-1}$ in Eq. (8) to produce a linear law $T_g(\langle r \rangle) \approx T_g(\langle r \rangle = 2.0)[1+\beta(\langle r \rangle - 2.0)]$.

In conclusion, we have shown that floppy modes, which are due to fundamental properties of the phase space and energy landscape topology,[22] are essential to determine the glass transition in flexible systems, since they enhance the square mean displacement, and thus nonlinear effects become important at lower temperatures.

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