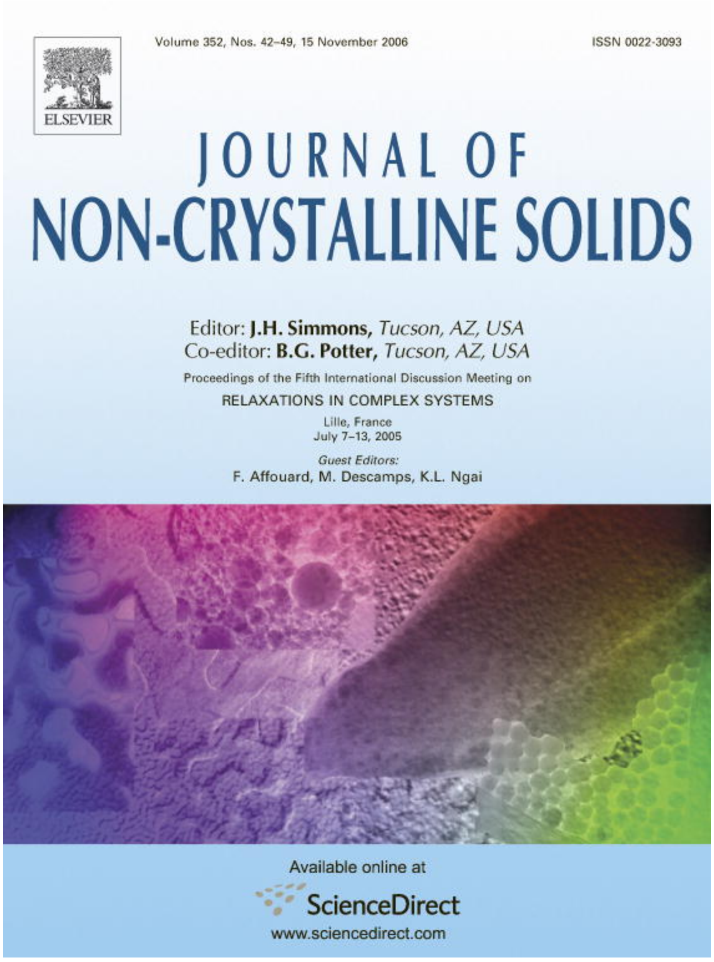

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Glass transition phenomenology and flexibility: An approach using the energy landscape formalism

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Abstract

The thermodynamic phenomenology of the glass transition in chalcogenide glasses is studied by using rigidity theory, which treats covalent bonding as mechanical constraints. Since flexible systems have a certain number of nearly zero frequency modes (called floppy modes), these modes provide channels in the energy landscape of the glass, and as a consequence, the entropy and fragility depend upon the number of constraints, even for the supercooled melt. Using this approach, the variation of the glass transition temperature with the chemical composition can be obtained from the number of floppy modes, since low frequencies enhance in a considerable way the average quadratic displacement of atomic vibrations. The result reproduces the observed experimental variation of the glass transition temperature with chemical composition.

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1. Introduction

The relaxation properties during the formation of a glass, and the nature of the process itself are important problems in modern physics [1–3]. For example, there is strong debate about the origin of the non-exponential relaxation laws near glass transition [4]. To deal with these problems, many different approaches have been devised [3,5–7], but most of the available theories have difficulties to explain even simple questions like how the glass transition temperature (T_g) depends on chemical composition, and what is the relation with the behavior of the viscosity, which is usually referred as fragility in the Angell classification of glasses [8]. The bench-mark tools used to understand such effects are chalcogenide glasses [9]. For these covalent glasses, the ease of glass formation can be successfully explained by the rigidity theory (RT) of Phillips [10] and Thorpe [11]. Therein, covalent bonding is considered as mechanical constraints, and the ease of glass formation is related with the ratio between available degrees of freedom and the number of constraints. If the number of constraints is lower than the degrees of freedom, there are zero frequency vibrational modes called floppy [12]. When the number of constraints is equal to the dimension of the configurational space, a transition to a rigid lattice occurs (called rigidity transition). Glasses with a certain chemical composition are rigid and it is observed that they are easier to form [10]. Many other features of the rigidity transition have been experimentally observed [9,13]. Even for systems like hard-disks [14] and colloids [15], rigidity plays an important role. Although RT allows to understand many features of the glass transition, its use in a quantitative way has not been fully developed to provide a link with the thermodynamics of the system [16,17]. The most dramatic piece of evidence of the relationship between rigidity and thermodynamics was provided by the experimental

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discovery of the *window of reversibility* [9,18,19], which is a self-organized phase with zero stress around the rigidity threshold that presents a thermodynamically reversible glass transition. Furthermore, this window seems to present some universal features, since for example it has been observed that protein folding is reversible because it occurs at the rigidity transition [20]. An interesting question is: why should a zero temperature vectorial percolation theory like RT be important to the thermodynamics of a glass? In previous works, we began by answering this question by showing that RT is fundamental in order to understand the energy landscape topology of a glass and others flexible systems [16]. The landscape is a multidimensional surface generated by the system potential energy as a function of the molecular coordinates [3,21,22], and in an N body system, is determined by the potential energy function, given by $V(\mathbf{r}_1, \ldots, \mathbf{r}_N)$ where $\mathbf{r}_i$ comprise all configuration coordinates. In this article we will take a further step by calculating the entropy associated with vibrational flexible modes that are not at zero frequency and then we will work out the relationship with the glass transition temperature. The layout of this work is the following: section II contains the development of the thermodynamics associated with rigidity and the relationship with the energy landscape, in section III we obtain the results of the theory, in section IV a discussion of the results is made, and finally, section V contains the conclusions.

2. Theory: rigidity and thermodynamics

The way that RT treats a glass or protein, is to consider that each bond between any of the N atoms that form the system can be viewed as an almost rigid mechanical constraint. This is very useful, specially for covalent bonds, where a hierarchy in the strength of the interatomic forces is present. If N_c is the number of constraints of a 3 dimensional system, then a fraction $(3N - N_c)/3N$ of the variables are cyclic, since the energy of the system does not depend on such variables [12]. This ratio also corresponds to the fraction of vibrational modes with zero frequency (f), called floppy modes. For example, in any system the energy does not depend on the center of mass coordinate, and as a consequence, there is always at least three vibrational modes with zero frequency.

Not all the constraints are independent, but the calculation of f involves only the independent ones [12]. Such counting can be made in an exact manner by using the pebble game algorithm [12], or with a mean-field approximation, known as the Maxwell counting. This counting goes as follows: since each of the r bonds in a site of coordination r is shared by two sites, there are $r/2$ constraints due to distance fixing between neighbors. If we assume that bond bending costs energy, the angles are also constraints, and in 3D there are $(2r - 3)$ constraints, to give,

$$f = \frac{3N - N_c}{3N} = 1 - \sum_r \frac{[r/2 + (2r-3)]x_r}{3} = 2 - \frac{5}{6}\langle r \rangle,$$

where the last term corresponds to the angular constraints, x_r is the fraction of particles with coordination r, and $\langle r \rangle$ is the average coordination number, defined as,

$$\langle r \rangle = \sum_r r x_r. \tag{1}$$

A rigidity transition occurs when $f = 0$ and the system passes from a floppy network to a rigid one. In 3D, the mean field approach predicts the transition at the critical value $\langle r_c \rangle = 2.4$ if all angular constraints are included. To understand the effects of floppy modes in the thermodynamics of a solid, we consider the atomic vibrations in the harmonic approximation. If normal modes coordinates are used, the corresponding Hamiltonian is,

$$H = \sum_{j=1}^{3N} \frac{P_j^2}{2m} + \sum_{j=1}^{3N(1-f)} \frac{1}{2} m\omega_j^2 Q_j^2, \tag{2}$$

where Q_j and P_j is the j-normal mode coordinate in phase space, and ω_j is the corresponding eigenfrequency of each mode. Notice that since floppy modes have zero frequency; they do not contribute to the elastic energy. For high temperatures, where classical statistical mechanics is valid, this poses a problem, since according to the energy equipartition each degree of freedom contributes with $kT/2$ to the internal energy. Since there are only $3N(1-f)$ non-zero frequency oscillators, the internal energy is just $U = 3NkT/2 + 3N(1-f)kT/2$. From this last expression, the corresponding specific heat (C_V) is,

$$C_V = 3Nk - \frac{3Nk}{2} f, \tag{3}$$

and thus C_V is given by the Dulong–Petit law, minus a term that depends on the number of floppy modes. An examination of the results from experimental data [9,23] shows C_V does not depend on f. Instead, glasses also follow the Dulong–Petit law, and in real glasses floppy modes are shifted by residual forces, like the Van der Waals interaction, as confirmed by neutron scattering experiments, where it has been shown that floppy modes in As–Ge–Se are blue-shifted [13,24], forming a peak around the frequency $\omega_0 \approx 5$ meV. This blue-shift restores the Dulong–Petit law, and the Hamiltonian can be written as,

$$H = \sum_{j=1}^{3N} \frac{P_j^2}{2m} + \sum_{j=1}^{3N(1-f)} \frac{1}{2} m\omega_j^2 Q_j^2 + \frac{1}{2} m\omega_0^2 \sum_{j=3N(1-f)+1}^{3Nf} Q_j^2. \tag{4}$$

The thermodynamics of this Hamiltonian can be readily obtained using statistical mechanics, however it is instructive to use the landscape paradigm to describe the qualitative behavior of the system. From the functional form of the Hamiltonian, is clear that the curvature of the potential energy in the direction of the floppy variable is determined by ω_0^2 and thus is not very pronounced along a floppy normal mode coordinate. This means that the system can move along such directions without expending too much kinetic energy, and thus floppy modes provide channels or 'mountain passes' in the landscape. This fact can be

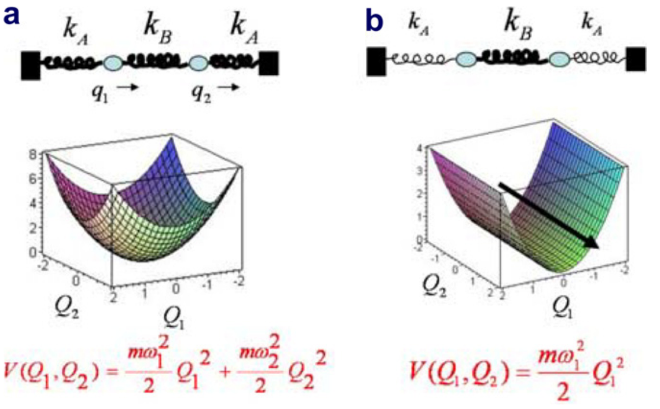

Fig. 1. Sketch of the energy landscape for a system of two masses an three springs, with strengths k_A and k_B. In (a) $k_A \approx k_B$, while in (b) a channel in the direction of the arrow appears, since $k_A \ll k_B$ and $\omega_2 \ll \omega_1$. The corresponding expressions for the potential energy are shown below the landscape.

explained in a simple fashion by using a system of two masses and three springs between walls, as shown in Fig. 1. If q_1 and q_2 are the displacements of particle 1 and 2, respectively, it is possible to write the Hamiltonian in terms of the normal mode coordinates Q_1 and Q_2, as explained in Fig. 1. The corresponding normal modes frequencies are,

$$\omega_1 = \pm\sqrt{\frac{k_A+2k_B}{m}}, \quad \omega_2 = \sqrt{\frac{k_A}{m}}. \tag{5}$$

and the surface generated by the potential energy is a paraboloid. When a hierarchy of forces is present, the ratio between the spring constants can be very small. For example, if $k_A \ll k_B$, as shown in Fig. 1(b), ω_2 is reduced as also happens with the slope of the landscape along Q_2. In the limiting case $k_A \to 0$, the system has one floppy mode at zero frequency, which corresponds to the center of mass movement of a 'diatomic molecule'.

According to the Bolztmann principle, the entropy is given by $S(E,V,N) = k\ln\Omega(E,V,N)$, where $\Omega(E,V,N)$ is the number of states for a given E,V and N, and is proportional to the allowed phase space volume visited by the system [25]. Since floppy modes provide channels, they increase the entropy. To show this in a quantitative way, let us connect with the thermodynamical properties by using the microcanonical ensamble, where the number of accessible states ($\Omega(E,V,N)$) is proportional to the area defined by the surface of constant energy $E = H(P_1,\ldots P_N, Q_1,\ldots,Q_N)$,

$$\Omega(E,V,N) = \frac{1}{h^{3N}}\int_{E=H(P_1,\ldots,Q_{3N})}\!\!\cdots\int \prod_{j=1}^{3N}\mathrm{d}P_j\prod_{k=1}^{3N}\mathrm{d}Q_k. \tag{6}$$

In the case of Eq. (4), the constant energy surface is an ellipsoid, elongated in the direction of the floppy coordinates. By calculating the area associated with this ellipsoid and using the Boltzmann principle we arrive to an expression for the entropy,

$$S(E,V,N) = k\ln\left[\left(\frac{4\pi E}{hN}\right)^{3N(1-f)}\prod_{j=1}^{3N(1-f)}\left(\frac{1}{\omega_j}\right)\right] + 3Nfk\ln\left(\frac{4\pi E}{Nh\omega_0}\right),$$

from where it follows the Dulong–Petit law since,

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk}{E}, \tag{7}$$

and the entropy in terms of the temperature,

$$S(T,V,N) = k\ln\left[\left(\frac{12\pi kT}{h}\right)^{3N(1-f)}\prod_{j=1}^{3N(1-f)}\left(\frac{1}{\omega_j}\right)\right] + 3Nfk\ln\left(\frac{12\pi kT}{Nh\omega_0}\right).$$

The last term of the previous expression is the desired channel entropy contribution, and depends linearly on the number of floppy modes. This contribution is very important due to the $1/\omega_0$ dependence that enhances the low frequency modes contribution. An important remark is that the channel term is absent at the rigidity threshold ($f = 0$).

There is a second source for entropy due to rigidity and is related with the number of different energy minima. Usually, these minima are called inherent structures [22]. In the present case, such structures are different configuration of the lattice with the same $\langle r\rangle$, and thus with almost the same elastic energy. This contribution is the one that has been studied in the context of RT as a percolation problem [26,27], where f as a function of $\langle r\rangle$ turns out to be a percolation free energy, with a divergent second derivative at the rigidity threshold [26]. It is worthwhile mentioning that this pure configurational part is unable to explain the window of reversibility, since taken in the context of percolation, around the rigidity transition there are many fluctuations, as in a phase transition, and thus it is expected that the configurational entropy will reflect this. Such important observation means that the entropy due to the channels in phase space is very likely to be much bigger than the one corresponding to percolation. A second argument that enhances this point of view is the fact that glasses are strong at the rigidity transition, because are easier to trap in a certain minima.

3. Results

In the previous section, the entropy has been obtained using an harmonic approximation, which is only valid below the glass transition temperature. This raises two important questions, the first is: do floppy modes influence the glass transition temperature? and the second: are these modes important to understand the properties of the liquid melt? From an experimental point of view, the answer is yes for both questions, but we would like to understand from theoretical principles the role of floppy modes below and above the glass transition.

A simple way to answer the first question is to use the important observation that the Lindemann criteria (1910) is valid for glasses [28,29]. This criteria (1910), was originally devised to understand crystal melting [30], and establishes that melting occurs when the mean atomic displacement $\sqrt{\langle u^2(T)\rangle}$ is around 10% of the atomic spacing a. At T_g, the Lindemann criteria applied to glasses [28] establishes that $\langle u^2(T_g)\rangle \approx \langle u^2(T_m)\rangle \approx 0.01a^2$. But the value of $\langle u^2(T)\rangle$ can be calculated from the density of vibrational states $g(\omega)$. At high temperatures,

$$\langle u^2(T)\rangle = \frac{kT}{mN}\int_0^\infty \frac{g(\omega)}{\omega^2}\mathrm{d}\omega \tag{8}$$

where k is the Boltzmann constant, T the temperature, ω the frequency and m the average mass. From this formula, is clear that low frequency modes are very important to determine T_g and T_m, due to the enhancement produced by the $1/\omega^2$ dependence inside the integral. We can model the density of states by using a combination of an Einstein like model that puts a spectral weight $3Nf$ to the floppy mode peaks at frequency ω_0. The rest of the spectral weight can be associated with a density $g_I(\omega)$, with weight $3N(1-f)$,

$$\rho(\omega) = \begin{cases} 3N(1-f)g_I(\omega) + 3Nf\delta(\omega-\omega_0), & \text{if } \omega \leqslant \omega_D \\ 0 & \text{if } \omega > \omega_D \end{cases}$$

where ω_D is a cut-off frequency. If this $\rho(\omega)$ is used to feed Eq. (8), then $\langle u^2(T)\rangle$ depends linearly upon f,

$$\langle u^2(T)\rangle = \frac{3kT}{m}\left[\left\langle\frac{1}{\omega^2}\right\rangle_R + f\left(\frac{1}{\omega_f^2} - \left\langle\frac{1}{\omega^2}\right\rangle_R\right)\right], \tag{9}$$

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

$$\left\langle\frac{1}{\omega^2}\right\rangle_R \equiv \int_0^\infty \frac{g_I(\omega)}{\omega^2}d\omega. \tag{10}$$

Using this model and the Lindemann criteria, it is easy to prove that $T_g(f)$, which is the glass transition temperature when a fraction of floppy modes is present, goes as $T_g(f) \approx T_g(f=0)/(1-\alpha f)$, where,

$$\alpha \equiv \frac{1}{\omega_0^2\langle\frac{1}{\omega^2}\rangle_R} - 1. \tag{11}$$

or using the Maxwell counting,

$$T_g(\langle r\rangle) \approx T_g(\langle r\rangle = 2.4)\Big/\left(1-\alpha(2-\frac{5}{6}\langle r\rangle)\right). \tag{12}$$

This functional form for the decreasing of T_g with $\langle r\rangle$ has been observed experimentally [8,31], and is usually called the empirically modified Gibbs–DiMarzio law. An alternative derivation of this law has also been obtained using an stochastic method [32–35], where α is a constant that depends upon the ratio of valences between the atomic species. The advantage of the method presented here is that one avoids the special assumptions that invoke the stochastic method to obtain T_g. However, the relationship between the α calculated in both ways deserves a more detailed investigation.

4. Discussion

To compare the theory presented in this work with the experimental results, here we will consider the values of T_g obtained from calorimetry experiments [8,9] for the prototype chalcogenide compound $\mathrm{Se}_{1-x-y}(\mathrm{Ge}_y\mathrm{As}_{1-y})_x$. Then we will use Eq. (12) to predict T_g, but first an estimatation for α from neutron scattering data or Lamb-Mössbauer experiments is needed. Using the neutron scattering data taken from reference [36], it is obtained that $\langle\frac{1}{\omega^2}\rangle_R = 0.01986\ \mathrm{meV}^{-2} \pm 5\%$, with a frequency $\omega_R \approx 7.0959$ meV which is equivalent to a temperature $\Theta_R \approx 76$ K. Since $\omega_f = 5$ meV $\pm 5\%$, α has the approximate value $1.014 \pm 10\%$, and $T_g(\langle r\rangle = 2.4) = 425\ \mathrm{K} \pm 5\%$. Fig. 2 shows the comparison between the experimental data (symbols) and Eq. (12). The agreement is excellent for $\langle r\rangle \leqslant 2.4$ When $\langle r\rangle > 2.4$, the isocoordination rule is no longer valid, and some other factors are needed to take into account the variation of T_g. The errors in determining α arise from the finite width of the floppy peak and the resolution of the data.

It is worthwhile mentioning that in order to derive the Gibbs–DiMarzio law, the mean field approach has only been used in the last step of Eq. (12). However, this step can be avoided if one is interested in non-mean field effects like compounds that are in the reversibility window. To do so, one can get $T_g(f)$ in terms of the density of vibrational states for a given fraction of floppy modes. In such case, the self-organization effects are encoded in the spectral distribution of modes, and thus many interesting effects in the glass transition temperature are expected to be observed.

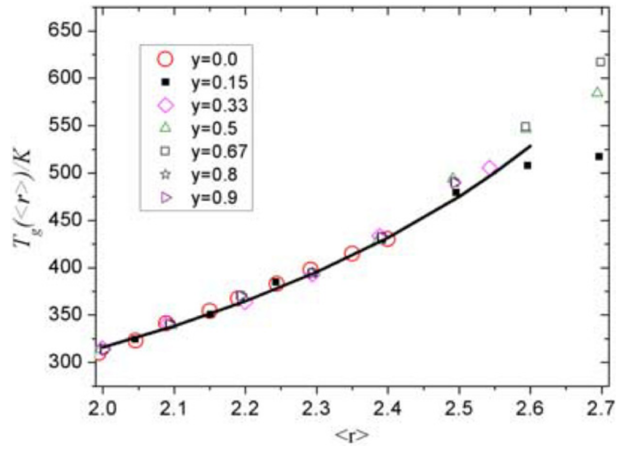

Fig. 2. T_g as a function of $\langle r\rangle$ for the compound $\mathrm{Se}_{1-x-y}(\mathrm{Ge}_y\mathrm{As}_{1-y})_x$. The symbols are taken from the experimental results given in references [8] and [9]. The solid line corresponds to Eq. (12), with $\alpha = 1.014$, and $T_g(\langle r\rangle = 2.4) = 425$ K. The sizes of the symbols are proportional to the experimental errors.

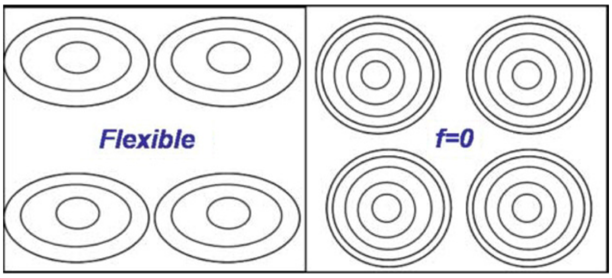

Fig. 3. Packing energy minima in the landscape when the system has floppy modes (flexible system) and non-floppy modes ($f = 0$). Both panels are views from the top in the direction of the potential energy, showing the corresponding isoenergetic level curves in the landscape. For the flexible system, there is a distorsion in the direction of the floppy coordinate, that does not allow the landscape to reach high altitudes, as seen from the different number of curve levels in the panels. This effect reduces the energy barriers.

The second question about the importance of floppy modes for the melt can be understood in terms of the channels in phase space. In Fig. 3, we show how the curvature of the potential energy around an inherent structure is essential to determine the height of the energy barriers between different minima in the landscape. For example, when the system is flexible, around each minima the surfaces of equal energy are ellipsoids elongated around the floppy coordinates, since ω_0 is small. But such elongation, if we assume that the number of minima does not contribute is an important way, means that for a certain volume in the landscape, the hills are not able to reach great heights, due to the slow steep and consequently flatter landscape. When floppy modes disappear, the curvature is bigger and the steep is much higher, resulting in bigger energy barriers between minima. Thus, is clear that a flexible system should have different relaxation properties, even when non-linear interactions become important. In fact, it is expected that floppy systems should present a fragile behavior because of this relatively flat landscape, as observed in experiments [8,22]. This simple geometrical reasoning is similar to assume that the hierarchy of forces, covalent and Van der Waals bonding, is still present for the supercooled liquid. To take into account these effects, one needs to consider non-linear terms in the Hamiltonian [37].

5. Conclusions

In this article, we have studied the effects of flexibility in the thermodynamics of a glass, by exploring the energy landscape. We found two competing effects that contribute to the entropy in the liquid melt; one contribution is given by channels in the direction of nearly cyclic variables, and the other is the existence of different energy basins. Then we discussed how the glass transition temperature depends on the flexibility due to the enhanced mean quadratic displacement produced by the important weight of low frequency modes. The present approach shows how rigidity theory and the energy landscape formalism can provide some clues about the fragility behavior of the supercooled liquid The results of this article seem to confirm the Phillip's idea that glass forming tendency is enhanced at the rigidity transition, since glasses are easier to trap in a certain minimum due to a lack of pathways in the energy landscape [38].

Acknowledgements

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