REVISIÓN REVISTA MEXICANA DE FÍSICA **56** (2) 97–105 ABRIL 2010

The problem of glass formation and the low frequency vibrational modes anomalies

G.G. Naumis and J.R. Romero-Arias
Instituto de Física, Dpto. de Física-Química, Universidad Nacional Autónoma de Mexico,
Apartado Postal 20-364, México 01000, D.F., México.

Recibido el 11 de noviembre de 2009; aceptado el 16 de febrero de 2010

In this article, we give a short review of the theoretical problems concerning the formation of disordered materials (known as glasses). Then we show how this problem is related to the anomalies in the low frequency vibrational modes observed in glasses. Rigidity theory and the energy landscape topology picture is used to decode how this relationship is built for network glasses. Finally, the problem of the speed of cooling and the ability to reach thermal equilibrium in glasses is explored using a simple model with non-linear interactions. The results are also interesting in soft-matter and protein folding.

Keywords: Glass transition; glasses; low frequency modes.

En este trabajo se presenta una revisión de los problemas concernientes a la formación de materiales con estructuras desordenadas, llamados vidrios, y su relación con el exceso de modos vibracionales de baja frecuencia. La teoría de la rigidez y la topología del paisaje de energías se usan para entender como surge dicha relación. Finalmente, el problema de la velocidad mínima de enfriamento y la habilidad de formar vidrios se estudia en el mismo contexto, pero usando un modelo de interacción no lineal. Los resultados son interesantes tanto para materia suave como para el problema del doblamiento de proteínas.

Descriptores: Transición vítrea; vidrios; modos de baja frecuencia.

PACS: 64.70.P-; 64.70.Q-; 63.50.Lm

1. Introduction

Ever since the beginnings of civilization, humankind has used glassy materials. For example, the Teotihuacan civilization in Mesoamerica was based on the control of the obsidian mines [1]. Obsidian is a glassy material used to make tools and weapons. Its importance to such societies has been compared to the value of steel to modern civilization [1]. More recently, the 2009 Nobel prize was shared by Charles Kao "for groundbreaking achievements concerning the transmission of light in fibers for optical communication". The resulting increase in bandwidth leads to a new era: the information age. In spite of this, the process of glass formation, known as glass transition, is not well understood. According to the Nobel laureate Phillip Anderson, glass transition and high temperature superconductivity are the most fundamental unsolved problems of solid state physics [2] (recently there seems to be compelling evidence that both problems are related [3]). In this article, we shall make a short review of the theoretical problems concerning glass transition, to show how an important and forgotten feature of glasses, the excess of low frequency vibrational modes (LFVM), is fundamental to understanding the problem.

In regard to the atomic configuration, solid state materials are divided into ordered and disordered structures. Glasses have a disordered atomic structure. They are obtained from liquids by fast cooling [4]. Under this classification, the word (glasses) is used to denote a wide spectrum of materials, which are classified as in Table I.

The oxides, chalcogenides and amorphous semiconductors form a family known as network glasses, since their structure is similar to a network with topological disorder. Also, there are soft analogous of glasses. Colloids, foams, granular media and other systems with small elastic modulus have disordered structures similar to those present in glasses [5,6]. In fact, the glass transition seems to be related to the jamming transition. Jamming occurs when the particles are trapped inside cages made from their neighbors, and the particles are not able to flow anymore, as happens in a traffic jam. It is believed that the jamming and glass transitions are interrelated in some kind of universal phase diagram [5]. Also, proteins and glasses share many physical properties, such as peculiar relaxation processes [7].

TABLE I.

Glass	Compounds	Some applications
Polymers	Chains of organic molecules	Plastics
Oxides	Contain O, like SiO_2	Window glass, optical fibers
Chalcogenides	Contain S,Se,Te like $GeSe_2$	Rewritable DVD+RW, optical fibers
Metallic	Metals like Zn, Cu, Fe,...	Mobile phones
Amorphous semiconductors	$Si_{0.9}H_{0.1}$	Solar Cells

However, it is surprising that we are not able to understand the process of formation of all these materials. The reason is the following. If we cool a melt slowly, a first order phase transition occurs to an ordered structure (a crystal). This transition is revealed as a discontinuity of the volume (V) against temperature (T). By cooling fast enough, the melt is supercooled, the phase transition is avoided, and there is a smooth change to a solid at a temperature known as glass transition temperature (T_g). During the process, the viscosity (η) changes by at least 20 orders of magnitude [4]. This span of decades is unique in physics, and explains the widespread use of glasses since one can mold the material in a continuous way. The glass transition occurs when $\eta = 10^{13}$ Poise. The viscosity is mainly the inverse of the time that takes the atoms to relax (τ). In the liquid $\tau \approx 10^{-12}s$, while in the glass $\tau \approx 10^{10}$ years, more or less the estimated age of the universe. Surprisingly, during these huge changes in η and τ, almost nothing happens with the atomic structure. Why is this process not well understood? The reasons are,

- there is NO thermal equilibrium, since the process depends on time,
- there is NO long range order.

The first reason means that one cannot use the usual thermodynamics, and the second avoids the use of the traditional tricks of the solid state physics and statistical mechanics, such as using order parameters or expansion in Fourier series. Furthermore, molecular dynamics simulations are not able to provide definitive answers, since the cooling speeds in numerical simulations are orders of magnitude higher than in the real cases.

What are the unsolved questions?

- How to calculate the minimal cooling speed in order to form a glass
- Why some chemical compounds form glasses while others will never reach such a state [4].
- The origin of the non-exponential relaxation laws [8]. Typical correlations or response functions cannot be represented by a single exponential. They are represented by stretched exponentials. For example, the intermediate scattering function $F(k,t)$ can be represented for long times by [4],

  $$F(k,t) = A(k)\exp-\left(\frac{t}{\tau(k,T)}\right)^{\beta_s}$$

  where $\beta_s < 1$ and the relaxation time $\tau(k,T)$ scales with the temperature like the viscosity.
- The thermodynamical nature of the glass transition, *i.e.*, is it a phase transition or close to a thermodynamical singularity?
- How to calculate T_g or the jumps in some of the thermodynamical parameters like the specific heat of thermal expansivity.
- How to calculate the aging properties of glasses, *i.e.*, the properties of the glasses change with time and history of formation.

All these questions are interrelated [9-13]. To make a glass, it must be cooled fast enough to avoid crystallization, but there is a minimal cooling speed for doing this, so relaxation is related to the glass-forming ability. An important feature is how viscosity behaves near the glass transition. This property is known as fragility [14-16]. For network glasses, fragility is related to the glass-forming tendency, since a non-fragile glass former (known as a strong glass former) does not require a very fast cooling speed in order to be produced. The viscosity behavior can be changed from strong to fragile by chemical doping [16]. Thus, the minimal cooling speed (as well as the aging properties) depends on the chemical composition. It is worthwhile mentioning, that this relationship is not generally true, since for example $CaNO_3$-KNO_3 is the most fragile of all glasses yet is an excellent glass former.

There are many theories available in the field, but most of them are not able to explain all the associated phenomenology. From a theoretical point of view, the main effort has been aimed at solving the thermodynamical nature of the glass transition. There are two main schools of thought.

- There is an underlying phase transition due to a change in the configurational entropy. This leads to entropic theories, like the Adams-Gibbs [14]. The driving force of such theories is the observation made by Kauzmann in 1948 about a crisis that appears when the entropy of a supercooled liquid is extrapolated toward low temperatures [14]. At a certain temperature, known as the Kauzmann temperature (T_K), the extrapolated entropy begins to be lower than the crystal entropy. Such a "paradox" is avoided by the glass transition, since the entropy has a sharp change due to an underlying phase transition.

- The transition is purely dynamical. There is no singularity, except that the dynamics is so slow that the system behaves as a solid [15]. The most famous theory of this kind is the mode coupling approach, based in a non-linear feedback mechanism [14]. This mechanism is obtained by separating slow and fast modes in the molecular hydrodynamics.

Both schools have successes and failures. The failures are predictions that have not been corroborated, such as divergences in the viscosity, special temperatures, etc.. Maybe more frustrating is the fact that neither school allows us to make practical predictions for real glasses. Furthermore, it is very well known that all glasses present an excess of low frequency vibrational modes (LFVMs) when compared with crystals. The most famous excess is the boson peak [17]. There are others, such as the floppy mode contribution, due to the flexible/rigid character of the atomic network [18-20]. Most of the theories concerning the glass transition fail to place special importance to the excess of LFVMs. This situation is surprising because as shown by Peierls in 1935, the thermal stability of a crystal depends upon LFVMs [17]. In fact, it is a subtle matter that concerns dimensionality and LFVMs due to their high population [17]. The condition required for mechanical stability is that the displacement field of two atoms separated by a distance R must not tend to infinity as $R \to \infty$. Let atom i with equilibrium position $\mathbf{r}_i$ have a displacement $\mathbf{u}(\mathbf{r}_i)$. This stability can be measured as

$$\left\langle \|\mathbf{u}(\mathbf{r}_i) - \mathbf{u}(\mathbf{r}_j)\|^2 \right\rangle = \left\langle \|\mathbf{u}(\mathbf{r}_i) - \mathbf{u}(\mathbf{r}_i + \mathbf{R})\|^2 \right\rangle, \qquad (1)$$

where $\mathbf{R}$ is the vector $\mathbf{R} = \mathbf{r}_j - \mathbf{r}_i$ that joins atoms i with j, and the bracket $\langle\rangle$ denotes thermal average at temperature T. Assuming a harmonic Hamiltonian for a crystal, and by writing $\mathbf{u}(\mathbf{r}_i)$ and $\mathbf{u}(\mathbf{r}_j)$ in normal coordinates, we get [17],

$$\left\langle \|\mathbf{u}(\mathbf{r}_i) - \mathbf{u}(\mathbf{r}_j)\|^2 \right\rangle = \frac{2\hbar}{mN} \sum_{\mathbf{q}\in \mathbf{1B.Z.}} \frac{1 - \cos(\mathbf{q}\cdot\mathbf{R})}{\omega(\mathbf{q})} \qquad (2)$$

$$\times \frac{1}{[\exp(\hbar\omega(\mathbf{q})/k_B T) - 1]}. \qquad (3)$$

where $\omega(\mathbf{q})$ is the frequency of a state with wave vector $\mathbf{q}$, and the sum is over the first Brillouin zone. Eq. (2) shows the fundamental role of LFVM in the stability since a Bose-Einstein factor appears. The denominator can make the sum divergent for acoustic modes when $\omega(\mathbf{q}) \to 0$. For crystals in D dimensions, the density of vibrational states $\rho(\omega)$ in the low frequency region goes like ω^{D-1}. In 1 D, Eq. (2) goes like R, and in 2 D like $\ln R$. In 1 D and 2 D, crystals are unstable against thermal fluctuations since $\left\langle \|\mathbf{u}(\mathbf{r}_i) - \mathbf{u}(\mathbf{r}_i + \mathbf{R})\|^2 \right\rangle \to \infty$ when $R \to \infty$. Crystals in 3 D are stable [17] since the density of vibrational states $\rho(\omega)$ goes like ω^2 and the divergence for low frequencies can be integrated. The lesson is clear: the stability of a solid is contained in the density of states. Similar arguments work for glasses [21] and thus it is surprising to see the lack of attention to this important point.

Here we will show the fundamental importance of LFVMs in the formation of network glasses, specially by focusing our attention on rigidity theory (RT) and the energy landscape. Both ideas provide a useful framework for understanding many features observed in the glass transition. The main importance of RT is that it provides a unique opportunity for tuning the number of LFVMs by chemical doping, and for observing the resulting consequences in the properties of the glass transition [22-24].

2. Energy landscape picture

Although there are many different theories concerning the glass transition, there is a common agreement to visualize the events that takes place during glass transition using the energy landscape picture [25]. The landscape is a surface generated by the potential energy as a function of the molecular coordinates [15]. In an N body system, the landscape is determined by the potential energy, given by $\Phi(Q_1, ..., Q_{3N})$ where Q_j is a generalized configurational coordinate for the simplest case of particles possessing no internal degrees of freedom. The landscape is a $(3N+1)$ object (see Fig. 1). A system with kinetic energy K and potential energy Φ has total energy $E = K + \Phi$. K is always positive and thus only configurations for which $K = \Phi - E \geq 0$ are allowed, as it happens in a roller coaster. At high temperatures, the system does not feel the summits and valleys of $\Phi(Q_1, ..., Q_{3N})$ because the kinetic energy contribution dominates ($k_B T \gg \Phi$). As the temperature is lowered, the system is unable to climb the high energy barriers and therefore is forced to sample deep minima ($k_B T \approx \Phi$). According to statistical mechanics, the entropy depends on the accessible volume in the phase space. Inside a local minimum of the potential energy, it can happen that there is not a mountain pass to reach another minima. The system cannot sample other available parts of the phase space (see Fig. 1). Ergodicity is broken and the system is no longer in thermal equilibrium. Such a glass will have a residual entropy [26]. When this happen, the kinetics of long time relaxation changes from exponential to stretched exponential [14], as shown in Fig. 1.

This change between different relaxation laws has its origins in the fact that the dynamics can be divided into two time scales (see Fig. 1). Over short times, the system is trapped

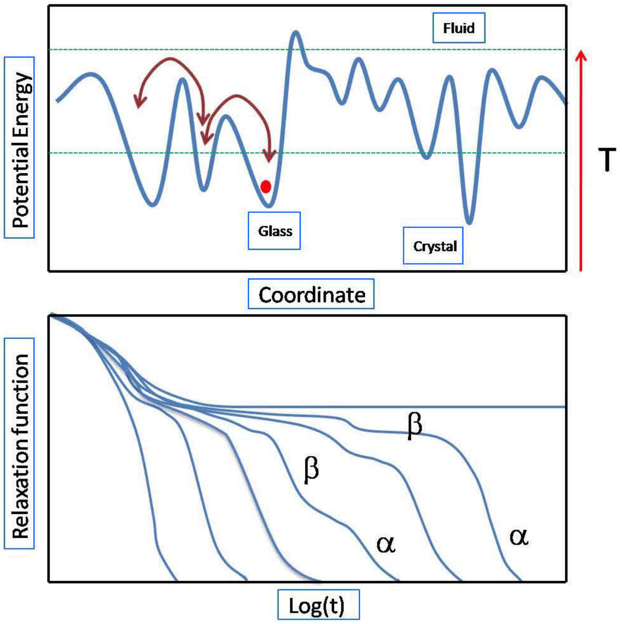

FIGURE 1. Energy landscape picture defined by the potential energy. At a given temperature, the system can visit the configurations between the dotted line and the solid curve. A glass is trapped in a metastable state performing harmonic oscillations. Jumps between neighboring basins, indicated by arrows, are related to the β relaxations shown in the lower panel. Jumps to other megabasins produce the long time α relaxation.

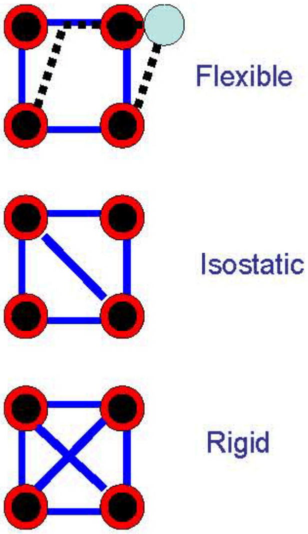

FIGURE 2. A 2D version of rigidity. Four hinges joined by 4, 5 and 6 bars. The first is flexible with one floppy mode. Such floppy mode is removed using a bar, and the system becomes isostatic. Any other bar leads to an overconstrained system.

in a metastable minimum performing harmonic oscillations. Fast relaxation events (called β relaxation) are related to transitions to neighboring basins [27], while slow relaxation events, which are collective motions that involve tens of atoms (α relaxation) are related to transitions between different megabasins (a megabasin contains inside many basins with similar energies [27]). Both of them occur via saddle points of the landscape. These collective motions require enough energy to jump the surrounding energy barriers and depend on rare thermodynamical fluctuations. The topology of the landscape has a self-similar, multifractal structure [28]. As we shall see, the importance of the LFVM anomalies in the formation of glasses can be understood by looking at their impact upon the energy landscape.

3. Rigidity theory: the key to understand low frequency vibrational modes anomalies

In this section, we discuss how RT provides key ideas for understanding LFVMs and the glass transition. RT considers each bond between any of the N atoms as a mechanical constraint. This is a very useful idea for covalent bonds. It was introduced in this area by Phillips [18] and Thorpe [19] to understand the ease of glass formation [18,29-32]. RT was originally developed to study mechanical systems, to solve questions like how many bars are needed to make a rigid bridge or building. If the system has fewer bars than a minimal threshold, the system is flexible (see Fig. 2). Otherwise it is rigid. If the number of bars is the minimal number required to be rigid, the lattice is isostatic (see Fig. 2). So the question is, with N hinges, what is the minimal number of bars required to make the system rigid?

If N_c is the number of constraints of a 3 dimensional system, then a fraction $(3N - N_c)/3N$ of the $3N$ configurational coordinates are cyclic, since the energy of the system does not depend on such variables [29]. Thus, f is also the fraction of vibrational modes with zero frequency (f), called floppy modes.

The counting of constraints can be done using a pebble game [29], or under a mean-field approximation known as the Maxwell counting. The mean-field goes as follows: each of the r bonds in a site is shared by two sites, and 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, then,

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

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

$$\langle r\rangle = \sum_r r x_r . \tag{4}$$

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. It is well known that the chemical composition corresponding to $\langle r_c\rangle = 2.4$ is special, since it corresponds to the best glass formers with small rates of aging [30-32].

In fact, floppy modes are not the only anomalies explained using RT. There are a great deal of evidence that the boson peak is also a consequence of the lack of atomic contacts [33]. This assertion has even been proved for the case of jammed systems [33], in which LFVM anomalies arise as a consequence of the isostatic nature of random packings [34,35], *i.e.*, the corresponding network is neither overconstrained nor flexible. As a matter of fact, even in the case of hard-spheres, the idea of a mechanical constraint can be used considering an effective potential [33] or a dynamical contact [36-40].

4. Thermodynamics of rigidity and the energy landscape

It is clear that LFVM anomalies have a great impact upon the low temperature properties of glasses. Such behavior is very well known [17]. However, here we are interested in a more subtle question: are these anomalies important for glass formation? Let us consider first a simple model of two masses and three springs, as shown in Fig. 3. 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. The corresponding normal modes frequencies are

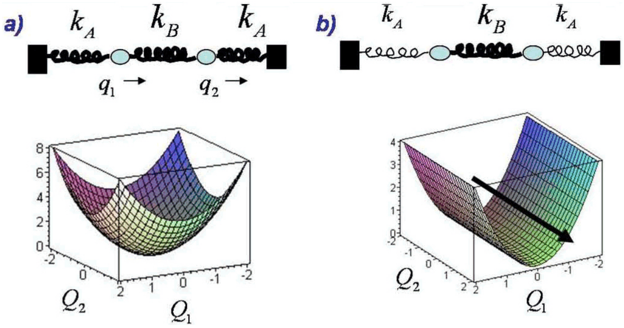

FIGURE 3. Energy landscape for a system of two masses and three springs, with strengths k_A and k_B. In a), $k_A \approx k_B$, while in b), a channel in the direction of the arrow appears, since $k_A \ll k_B$ and $\omega_2 \ll \omega_1$.

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

and the surface generated by the potential energy is the paraboloid (shown in Fig. 3),

$$\Phi(Q_1, ..., Q_{3N}) = \sum_{j=1}^{3N(1-f)} \frac{1}{2} m\omega_j^2 Q_j^2$$

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. 3b), ω_2 is reduced as also happens with the slope of the landscape along Q_2. In the limiting case $k_A \rightarrow 0$, the system has one floppy mode at zero frequency, which corresponds to the center of mass coordinate of a "diatomic molecule". A channel is open in the floppy mode coordinate direction. According to the Bolztmann principle, the entropy is given by $S(E,V,N) = k_B \ln \Omega(E,V,N)$, where $\Omega(E,V,N)$ is the number of states for a given E, V and N. $S(E,V,N)$ is proportional to the allowed phase space volume visited by the system [41]. Since floppy modes provide channels, they increase the entropy. In Fig. 3b), this idea is indicated by an arrow. For this particular example, the extra entropy is given by the center of mass, which can visit all the space between the walls. A real glass in a metastable state performs harmonic oscillations for short time scales, but due to residual Van der Waal forces, floppy modes are not at zero frequency [42], instead they are blue-shifted to a frequency [43,44] $\omega_0 \approx 5$ meV. The potential energy can be written as,

$$\Phi(Q_1, ..., Q_{3N}) = \sum_{j=1}^{3N(1-f)} \frac{1}{2} m\omega_j^2 Q_j^2 \tag{6}$$

$$+ \frac{3Nf}{2} m\omega_0^2 \sum_{j=3N(1-f)+1}^{3Nf} Q_j^2. \tag{7}$$

The corresponding energy landscape is a paraboloid with different curvatures, depending on each normal mode frequency. The curvature in the direction of the floppy modes is determined by ω_0, and thus is not very pronounced in this direction, as explained in the previous simple example. This means that the system can move easily along such directions since the energy barriers are less pronounced. Thus, one can think that floppy modes lead to low "mountain passes" in the landscape, although not every low-vibration needs to be connected to a pass. Of course, one needs to be very careful since this simple picture seems contradictory at first sight. It is clear that a pure harmonic potential with all frequencies different from zero is not able to reproduce a mountain pass, because per se it can only have the shape of a paraboloid. To have a mountain pass, the potential must have other high order non-linear terms to shape a corridor or saddle point. However, here we are assuming that there is a hierarchy of force strengths: covalent and the ever-present Van der Waals bonding. The non-linear terms in the expansion of the potential must reflect this fact, and thus the hierarchy is also preserved when we consider deviations from a pure paraboloid landscape. As a consequence, a small curvature of the paraboloid for floppy modes also leads to small non-linear terms in the same direction in the landscape, as confirmed by a normal modes analysis based on the local quadratic approximation of the energy, which captures a system dynamics quite well [45,46]. In other words, this approach is based on the assumption of a direct connection between low-frequency vibrations and low-energy passes, and is in line with relating the short elastic times scale behavior with the long time relaxation properties of the glass. The success of such an approach has been confirmed in several empirical relationships, as has been extensively reviewed in Ref. 47.

Using statistical mechanics, it is easy to find the entropy in terms of the temperature [42]:

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

The last term of the previous expression is a "channel" entropy contribution, produced by translations along floppy coordinates. It depends linearly on the number of floppy modes, and has a huge contribution due to the $1/\omega_0$ factor for small ω_0. This expression has been corroborated by studying the specific jump during glass transition [48] and the viscosity behavior for 700 different glasses [49,50].

There is a second source for entropy due to rigidity, and is related to the different energy minima configurations [42]. These minima are basins of the energy landscape [51], and have been studied in the context of RT as a vectorial percolation problem [52,53]. However, the entropy due to the channels in phase space is very likely to be much greater than the one corresponding to percolation [42].

5. Flexibility and the glass transition temperature

Now we raise the important question, do LFVM modes influence the glass transition temperature? There are arguments against this. If a glass relaxes in the direction of a floppy mode coordinate, after a certain time it can reach a new basin in which the floppy coordinates are different. Also, floppy modes are important for fast relaxation processes, since the long-time scale relaxation (α) does not retainany memory of the almost instantaneous configuration of a floppy mode. However, the energy minima of the landscape are very similar [28]. Even in protein folding, this observation holds, and a detailed analysis of the landscape leads to the conclusion that the similarity of the minima is behind the remarkable phenomena of relaxation along soft coordinates [46]. For protein G, slow modes display a very mild dependence on the trajectory duration in the landscape. This property originates from a striking self-similarity of the free-energy landscape embodied by the consistency of the principal directions of the local minima [46], where the system dwells for several nanoseconds, and of the virtual jumps connecting them. Incidentally, proteins also have a boson peak [7].

Now we will show how LFVMs can determine T_g, using some results from density functional theory for disordered systems. According to this theory, the idea is to look for transition states between basins, using the ansatz that atoms travel the least motion path between adjacent minima [53]. This ansatz is again in the same framework of the idea of relating short times scales with long time relaxation [47]. The viscosity $\eta(T)$ is given by [53],

$$\ln \eta(T) \approx \ln \eta_0 + \frac{3r_0^2}{4\left\langle u^2(T)\right\rangle}, \tag{8}$$

where η_0 is the typical value of the viscosity in the liquid phase, r_0^2 is a constant for a given system and $\left\langle u^2(T)\right\rangle$ is the mean quadratic displacement of the atoms. The mean quadratic displacement should be taken as measured by Mossbäuer scattering, since $\left\langle u^2(T)\right\rangle$ will diverge for long time scales. For typical interatomic potentials, $0.3\sigma<r_0<0.5\sigma$ (where σ is the size of the particles [53]). Since T_g can be defined as the temperature at which $\eta \approx 10^{13}$ Poise, from Eq. (8) and using $r_0 \approx 0.3\sigma$ we get,

$$\frac{\left\langle u^2(T_g)\right\rangle}{r_0^2} \approx \frac{3}{4(13-y)\ln 10} \approx \frac{0.03}{13-y}, \tag{9}$$

where y is an exponent defined as $\eta_0 = 10^y$. For typical fluids [53], $y \approx 3$. Thus,

$$\frac{\left\langle u^2(T_g)\right\rangle}{\sigma^2} \approx 0.0125, \tag{10}$$

and $\sqrt{\left\langle u^2(T_g)\right\rangle} \approx 0.11\sigma$. Since σ is of the order of the interatomic distance, it turns out that we just obtained for glasses the well-known Lindemann, *i.e.*, for crystals melting occurs when the mean atomic displacement $\sqrt{\left\langle u^2(T)\right\rangle}$ is around 10% of the atomic spacing a [54]. In fact, this criterion is valid for many glasses [55,56]. At this point, the fundamental role of low frequency modes to determine T_g and T_m is clear, since we can separate the problem in two time scales. For short timescales, a glass is in a metastable state. Thus, we can suppose that the glass can be represented as a harmonic Hamiltonian in thermal equilibrium. Under this approximation, it is easy to prove that

$$\left\langle u^2(T)\right\rangle \approx \frac{3k_BT}{\langle m\rangle}\int_0^\infty \frac{\rho(\omega)}{\omega^2}d\omega. \tag{11}$$

Any excess of LFVM is enhanced by the $1/\omega^2$ inside the integral in Eq. (11). LFVMs lead to an increased $\left\langle\left\langle u^2(T)\right\rangle\right\rangle$ of the glass when compared with the crystal. Thus, the glass transition happens at a lower temperature than melting. Furthermore, using Eq. (11) and that $\sqrt{\left\langle u^2(T_g)\right\rangle} \approx 0.11\sigma$, T_g is given by

$$T_g \approx 0.01\left[\frac{3\rho^{2/3}k_B}{\langle m\rangle}\int_0^\infty \frac{\rho(\omega)}{\omega^2}d\omega.\right]^{-1} \tag{12}$$

We can combine the previous analysis with RT to estimate the glass transition as a function of chemical doping [57,58]. To do so, let us make a simple model for $\rho(\omega)$ by using a combination of an Einstein model that puts a spectral weight $3Nf$ to the floppy mode peaks at frequency ω_0. The rest of the spectral weight $3N(1-f)$ is carried by a density $\rho_R(\omega)$,

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

where ω_D is a cut-off frequency. If this $\rho(\omega)$ is used to feed Eq.(11), and Eq. (12),

$$T_g(\langle r\rangle) \approx T_g(\langle r\rangle = 2.0)/\left(1-\gamma(\langle r\rangle - 2)\right), \tag{13}$$

with γ a constant determined by $\rho_R(\omega)$ (the density of states when $f=0$) and ω_0,

$$\gamma \equiv \left[\omega_0^2\int_0^\infty \frac{\rho_R(\omega)}{\omega^2}d\omega\right]^{-1} - 1. \tag{14}$$

This functional form deduced here for the decreasing of T_g with $\langle r\rangle$ has been observed experimentally by many groups [16,59], and is called the empirically modified Gibbs-DiMarzio law (see Fig. 4).

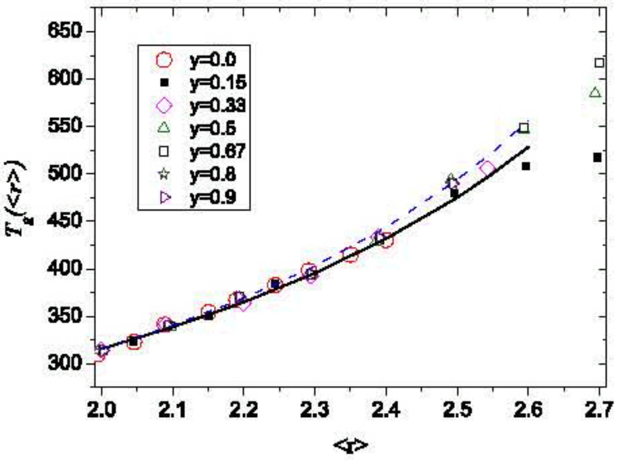

FIGURE 4. T_g as a function of $\langle r\rangle$ for the compound $Se_{1-x-y}(Ge_yAs_{1-y})_x$. The symbols are taken from the experimental results given in references [16] and [30]. The solid line corresponds to Eq. (13), with $\gamma = 0.67$, and $T_g(\langle r\rangle = 2.4) = 425K$.

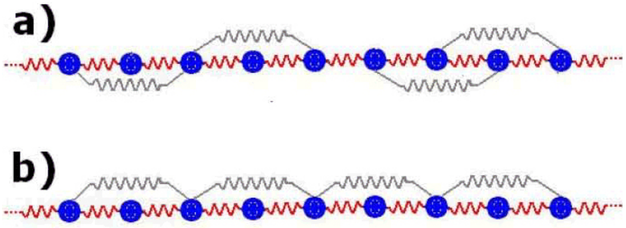

FIGURE 5. Lattices in which extra constraints are added by using second neighbors springs. In (a) the springs are placed at random, while in (b) the arrangement is periodic. Model (a) is an example of an overconstrained glass, while (b) corresponds to a overconstrained crystal.

6. Thermal relaxation

Even if low frequency modes play a role in the ease of glass formation through the minimal cooling speed for glass formation [18,60], it is not clear what is behind this remarkable observation [42]. However, one can expect that a system which relaxes fast will have a tendency for crystallization. For example, it has been experimentally observed that in metallic glasses, T_g is related to the chemical composition through the thermal conductivity [61]. In fact, thermal conduction is responsible for transferring the excess of internal energy to an external bath, where it is finally dissipated. When heat is not removed fast enough, the system will not reach thermal equilibrium. Thus, thermal relaxation and thermal conductivity are closely related. Although there are experimental observations on this matter [18,60,61], from the theoretical point of view the problem is almost virgin territory. Here we provide a small review of our recent work on this subject. One of the firsts attempts to study thermal relaxation in harmonic systems was made by Fermi-Pasta-Ulam (FPU). They were interested in the paradox that a solid described by harmonic oscillations can never reach thermal equilibrium since there is no way of sharing energy between normal modes. Their model was a chain of equal masses with non-linear springs [62,63]. The non-linearity was supposed to relax the system and restore the equipartition of energy. The resulting equations were solved using the famous ENIAC computer, performing an act considered to represent the birth of numerical experiments. The answer was much more complex than expected and still there are many unsolved question concerning this simple model [64]. After years of research, in the last few years it has become more or less clear that relaxation is dominated mainly by LFVMs [65-68], due to their quasiresonant nature [65,68,69]. As a result, they share energy in an efficient way [68] when compared with high-frequency modes.

A suitable model to study the role of LFVMs and bond constraints is to change the number of LFVMs in the FPU model. Then we will be able to see how such a system relaxes after a rapid quench. The FPU model is made of equal masses (m) joined by equal spring constants. In the case of a linear chain, removing bonds does not lead to a flexible lattice, since the lattice is separated in pieces. The only possibility is to add constraints to reduce the number of LFVMs. To achieve this goal, we add new springs that connect second neighbors (we denote these new springs as SNS), as shown in Fig. 5a and 5b. The concentration of such springs is given by c, and is defined as the numbers of second neighbor springs divided by N. These new springs can be placed at random (Fig. 5a), or in a periodic way (Fig 5b). The corresponding Hamiltonian can be written as

$$H=\sum_{j=1}^{N}\left[\frac{p_j^2}{2m}+\frac{k}{2}(u_{j+1}-u_j)^2+\frac{k'}{4}(u_{j+1}-u_j)^4\right] \qquad (15)$$

$$+\sum_{j=1}^{N}\Theta_{j+2,j}\left[\frac{k_2}{2}(u_{j+2}-u_j)^2+\frac{k_2'}{4}(u_{j+2}-u_j)^4\right], \qquad (16)$$

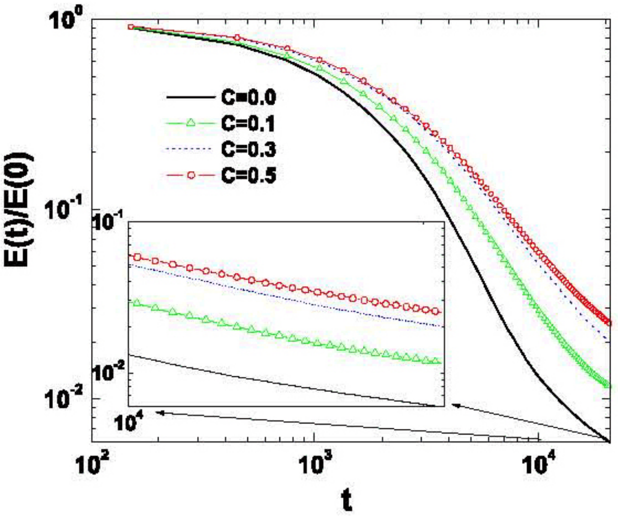

FIGURE 6. Energy relaxation as a function of time for concentrations from $c = 0$ to 0.5 using a non-linear Hamiltonian with parameters $k = k_2 = 0.5$ and $k' = k_2' = 0.5$. The inset shows a zoom of the relaxation tail. For all chains, $N = 100$, $dt = 0.01$. An average over 40 disorder realizations was made.

where $\Theta_{j+2,j}$ is a random variable that takes the value 0 or 1, with probability c and $1-c$ respectively. u_j is the displacement of the mass m at site j, and N is the number of sites. k is the harmonic spring constant, and k' is the strength of the non-linear interaction. In what follows, we set $m = 1.0$.

To study the dynamics of the relaxation, first the systems need to be thermalized by using a bath [70]. To achieve thermalization, we can use a Langevin dynamics, in which a stochastic force [$\eta(t)$] and a damping (γ_0) are added to the equation of motion,

$$\frac{d^2u_j}{dt^2} = -\frac{\partial H}{\partial u_j} - \gamma_0 \frac{du_j}{dt} + \eta_i(t).$$

As usual, the force has a Gaussian distribution, with zero mean $\langle \eta_i(t) \rangle = 0$ and correlation given by

$$\langle \eta_i(t)\eta_i(t') \rangle = 2\gamma_0 k_B T \delta(t-t') \tag{17}$$

where γ_0 is the damping amplitude.

These equations can be solved by using a fourth-order Runge-Kutta algorithm, with parameters such that $\gamma_0 < 8\pi^2 k/N^2$ and $0.0 \leq T \leq 1.0$. Here k_B is set to 1.0, so T has always energy units.

The relaxation of the thermalized models from an initial temperature T to zero temperature can been studied following two steps [70]: the thermal bath is retired and then a damping term is added at both ends of the chains. The resulting equations of motion are

$$\frac{d^2u_j}{dt^2} = -\frac{\partial H}{\partial u_j} - \sum_{j=1}^{N} \Gamma_{jl} \frac{du_j}{dt}, \tag{18}$$

where Γ_{jl} is the dissipation at the ends of the chain,

$$\Gamma_{jl} = \gamma_E \delta_{jl} \left[\delta_{j,1} + \delta_{j,N} \right], \tag{19}$$

γ_E is the damping constant and δ_{jl} is a Kronecker delta. For all chains we took $\gamma_E = \gamma_0$. Notice that in the previous equation, the system relaxes to zero energy and not to the original equilibrium energy at temperature T, since our equations of motion do not contain a stochastic force. The reason is that here we are interested in how fast the system relaxes when we change its energy, as happens in a rapid quench. In the present case, a quench is realized from a temperature $T \neq 0$ to $T = 0$. Thus, we are measuring how the heat is removed by thermal conduction and dissipated at the chain ends.

In Fig. 6, we plot the energy relaxation using non-linear Hamiltonians for different concentrations of SNS. Each energy relaxation was made for $N = 100$, starting from thermalized baths at $T = 0.5$. An average over 40 realizations of disorder was made in all cases.

There are many interesting features in the relaxation. The first is that the time required for relaxation increases as c goes from 0.0 to 0.5. We can conclude that for long times, relaxation is always slower when the number of LFVMs is reduced. The relaxation of high frequency modes requires a transference of energy to LFVMs [67]. Such a phenomenon is akin to turbulence [68], in which energy is injected at large scales, and transferred via a cascade of self-similar eddies to a small scale, where energy is finally dissipated. In the present case, the reduction of LFVMs means that not as many modes are available to dissipate energy and energy relaxation becomes slower. Observe that we can generalize our results to supercooled liquids since at small time scales the liquid behaves as a solid. This opens the study of the relationship between the ease of glass formation and LFVM.

7. Conclusions

In this article we presented the main features of one of the most fundamental problems in solid state physics: the formation of glasses. Although there are many theories on this subject, none of them take into account the important role played by low frequency mode anomalies which are very well-known in glasses. Here we presented a mini review of the arguments that any successful theory must explain such features and their relation with the glass transition phenomenology. Still there are many questions to be solved, especially on the supercooled "side" of the glass transition, where a lot of experimental and theoretical efforts are needed.

Acknowledgments

We thank DGAPA-UNAM projects IN-117806. and CONACyT 50368 for financial support and C. Moukarzel for pointing out to us the rigidity properties of the second neighbor spring chain. Calculations were carried at the KanBalam and Baklitz supercomputers of DGSCA-UNAM.

---

1. I. Bernal, *Historia General de México* (El Colegio de México, México, 2000).
2. P.W. Anderson, *Science* **267** (1995) 1615.
3. J.C. Phillips, *PNAS* **106** (2009) 15534.
4. J. Jackle, *Rep. Pro. Phys.* **49** (1986) 171.
5. A.J. Liu and S.R. Nagel, *Nature* **396** (1998) 21.
6. A. Huerta, G.G. Naumis, D.T. Wasan, D. Henderson, and A. Trokhymchuk, *J. of Chem. Phys.* **120** (2004) 1506.
7. S. Ciliberti,P. De Los Rios, and F. Piazza, *Phys. Rev. Lett.* **96** (2006) 198103.
8. J.C. Phillips, *Rep. Prog. Phys.* **59** (1996) 1133.
9. G.G. Naumis and R. Kerner, *J. of Non-Cryst. Solids* **231** (1998) 111.

10. R. Kerner, *Physica B* **215** (1995) 267.
11. R. Kerner and G.G. Naumis, *J. of Phys: Condens. Matter* **12** (2000) 1641.
12. M. Micoulaut and G.G. Naumis, *Europhys Lett.* **47** (1999) 568.
13. G.G. Naumis, R.A. Barrio, R. Kerner, and M. Micoulaut, *Rev. Mex. de Fís.* **44** (1998) 80.
14. P.G. Debenedetti, *Metastable Liquids* (Princeton Unv. Press, 1996).
15. P.G. Debenedetti and F.H. Stillinger, *Nature* **410** (2000) 259.
16. M. Tatsumisago, B.L. Halfpap, J.L. Green, S.M. Lindsay, and C.A. Angell, *Phys. Rev. Lett.* **64** (1990) 1549.
17. K. Binder and W. Kob, Glassy materials and disordered solids (World Scientific, Singapoure, 2005).
18. J.C. Phillips, *J. Non–Cryst. Solids* **34** (1979) 153.
19. M.F. Thorpe, *J. Non-Cryst. Solids* **57** (1983) 355.
20. J.C. Phillips, in Rigidity Theory and Applications, ed. by M. Thorpe and P.M: Duxbury (Kluwer Academic/Plenum Publishers, New York, 1999).
21. G.G. Naumis an H. Flores-Ruiz, *Phys. Rev. B* **78** (2008) 094203.
22. P. Lucas, E.A. King, A.D. Horner, and S.K. Sundaram, *J. of Non-Cryst. Solids* **352** (2006) 2067.
23. P. Lucas, *J. of Phys.: Cond. Mat.* **18** (2006) 5629.
24. P. Boolchand *et al.*, **5** (2002) 713.
25. A. Angell, *Nature* **393** (1998) 521.
26. M. Goldstein, *J. of Chem. Phys.* **64** (1976) 11.
27. G. Fabricius and D.A. Stariolo, *Physica A* **331** (2004) 90.
28. G.G. Naumis, *Phys. Rev. E* **71** (2005) 056132.
29. H. He and M.F. Thorpe, *Phys. Rev. Lett.* **54** (1985) 2107.
30. D. Selvanathan, W.J. Bresser, and P. Boolchand, *Phys. Rev. B* **61** (2000) 15061.
31. P. Boolchand, *Vibrational Excitations in glasses: rigidity transition and Lamb-Mössbauer Factors*, in: Insulating and semiconducting glasses, ed. by P. Boolchand (World Scientific, Singapore, 2000).
32. Y. Wang *et al. Phys. Rev. Lett.* **87** (2001) 185503.
33. M. Wyart, *Ann. Phys. Fr.* **30** (2005) 1.
34. C.F. Moukarzel, *Phys. Rev. Lett.* **81** (1998) 1634.
35. C.F. Moukarzel, *Phys. Rev. E* **68** (2003) 056104.
36. A. Huerta and G.G. Naumis, *Phys. Lett. A* **299** (2002) 660.
37. A. Huerta and G.G. Naumis, *Phys. Rev. B* **66** (2002) 184204.
38. A. Huerta and G.G. Naumis, *J. of Non-Cryst. Solids* **329** (2003) 100.
39. A. Huerta and G.G. Naumis, *Phys. Rev. Lett.* **90** (2003) 145701.
40. A. Kraemer and G.G. Naumis, *J. of Chem. Phys.* **128** (2008) 134516.
41. T.L. Hill, *An introduction to statistical thermodynamics* (Dover, New York, 1986).
42. G.G. Naumis, *Phys. Rev. E* **71** (2005) 026114.
43. P. Boolchand *et al.*, *Solids State Ionics* **39** (1990) 81.
44. W.A. Kamitakahara *et al.*, *Phys. Rev. B* **44** (1991) 94.
45. M.M. Tirion, *Phys. Rev. Lett.* **77** 1905 (1996).
46. F. Pontiggia, G. Colombo, C. Micheletti, and H. Orland, *Phys Rev Lett.* **98** (2007) 048102.
47. J.C. Dyre, T. Christensen, and N. B. Olsen, *J. Non-Cryst. Solids* **351** (2006) 4635.
48. G.G. Naumis, *Phys. Rev. B* **61** (2000) R9205.
49. P.K. Gupta and J.K. Mauro, *J. of Chem. Physics* **130**, (2009) 094503.
50. J.C. Mauro, Y. Yue, A. J. Ellison, P.K. Gupta, and D.C. Allan, *PNAS* **106** (2009) 19780.
51. F.H. Stillinger, *Phys. Rev. E* **59** (1999) 48.
52. P. Duxbury, D. Jacobs, M. Thorpe, and C. Moukarzel, *Phys. Rev. E* **55** (1999) 2084.
53. R.W. Hall and P.G. Wolynes, *J. Chem. Phys.* **86** (1987) 2943.
54. D. Tabor, *Gases, liquids and solids* (Cambridge University Press, Cambridge, 1996).
55. W.A. Phillips, U. Buchenau, N. Nücker, A.J. Dianoux, and W. Petry, *Phys. Rev. Lett.* **63** (1989) 2381.
56. U. Buchenau and R. Zorn, *Europhys. Lett.* **18** (1992) 523.
57. G.G. Naumis, *Phys. Rev. B* **73** (2006) 172202.
58. G.G. Naumis, *J. of Non-Cryst.* Solids **352** (2006) 4685.
59. A.N. Sreeram, D.R. Swiler, and A.K. Varshneya, *J. Non-Cryst. Solids* **127** (1991) 287.
60. J.C. Phillips, in: Rigidity Theory and Applications, ed. J.C. Phillips and P.M: Duxbury, Kluwer Academic/Plenum Publishers (New York, 1999) p. 279.
61. D.V. Louzguine-Luzgin, T. Saito, J. Saida, and A. Inoue, *Journal Materials Research* **23** (2008) 515.
62. E. Fermi, J. Pasta, and S. Ulam, Los Alamos report L.A.1940, Enrico Fermi, Collected Papers II (1955) (Univ. Chicago Press, Chicago 1965).
63. M. Toda, *Theory of Non-Linear Lattices* (Springer-Verlag, Berlin, 1988).
64. D.K. Campbell, S. Flach, and Y.S. Kivshar, *Physics Today* **43** (2004).
65. J. Ford, *J. Math. Phys.* **2** (1961) 387.
66. R. Reigada, A. Sarmiento, and K. Linderberg, *Phys. Rev. E* **64** (2001) 066113.
67. R. Reigada, A. Sarmiento, and K. Linderberg, *Phys. Rev. E* **64**, 066608 (2001).
68. A. Ponno, in: *Chaotic Dynamics and Transport in Classical and Quantum Systems*, Proceedings of the NATO Advanced Study Institute on International Summer School on Chaotic Dynamics and Transport in Classical and Quantum Systems Cargèse, Corsica 18-30 August 2003, Vol. 182 (Springer Netherlands, Amsterdam, 2005) p. 431.
69. I. Cerón, G.G. Naumis, F. Salazar, and C. Wang *Phys. Lett. A* **337** (2005) 141.
70. R. Reigada, A. Sarmiento, and K. Lindenberg, *Phys. Rev. E* **66** (2002) 046607.