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Low-frequency vibrational mode anomalies and glass transition: Thermal stability, phonon scattering, and pressure effects

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The relationship between the excess of low-frequency vibrational modes observed in glasses and the stability against thermal fluctuations is explored. Such study is performed by calculating the correlation of atomic displacements inside the glass. As a result, it is proved that thermal stability requires that modes present in the boson or floppy peak (due to the flexibility or rigidity of the glass atomic network) should be localized or strongly scattered. The glass transition is thus determined by the size of the quadratic mean displacement. Also, the 2/3 relationship between melting and glass transition temperature is shown to have its origins in the differences between the mean-free path of phonons due to scattering. The size of this scattering is estimated using the Boson peak frequency and sound velocity. Finally, the change in the glass transition temperature with pressure is obtained from the displacement of low-frequency modes.

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I. INTRODUCTION

The formation of glasses, which are solids that do not have long-range order, remains a puzzling problem due to its nonequilibrium character.[1–4] For example, even if our civilization has been making window glass for more than two thousands years, until a few years ago its chemical composition was basically an empirical recipe. A theoretical explanation came from studying with care a fundamental fact discovered by the Phoenicians:[5,6] The glass transition temperature (T_g), defined as the temperature at which relaxation time exceeds experimental time scale, can be dramatically lowered or raised by adding impurities.[7,8] In almost all glasses there are anomalies in the density of low-frequency vibrational modes (LFVMs).[9,10] The most famous one is the Boson peak,[10] but there are others, such as the floppy mode peak,[11] due to the flexible/rigid character of the atomic network.[12–17] It is surprising that although vibrational anomalies are present in all glasses, most of the theories concerning glass transition do not give a special importance to such observation.[18] This lack of attention is even more surprising when one realizes that LFVMs are fundamental to the thermodynamical stability of solids. In 1935 Peierls[19] proved that crystals in one and two dimensions are unstable against thermal fluctuations, while three-dimensional crystals are stable. The derivation made by Peierls showed that the interplay between the density of LFVM, dimensionality, and the localization nature of the normal modes is fundamental in the stability due to the high population of LFVM at low temperatures. Although glasses are in a metastable state,[20] it is clear that they are stable from a laboratory time scale point of view. This leads to the natural question of what we can learn from the excess of LFVM in glasses and thermal stability. Following this line, in a previous paper we showed that T_g depends upon the rigidity of the lattice through the quadratic mean displacement,[21] which is determined by LFVM. Thus, there is a relationship between such modes and glass transition, as pointed out by others using experiments[22] and simulations.[23] In this paper we propose to continue with such exploration. As we shall prove, the states in the anomalies need to avoid propagation of thermal fluctuations and as a result there must be phonon localization or scattering. The structure of this paper is as follows: In Sec. II we calculate the displacement correlation of a glass at thermal equilibrium. In Sec. III we show that there is a relationship between mode localization and thermal anomalies, while Sec. IV is devoted to the study of the glass transition temperature and phonon scattering. Such results are used in Sec. V to calculate the effects of pressure; and, finally, in Sec. VI the conclusions are given.

II. DISPLACEMENT CORRELATIONS IN A GLASS

A. Correlation function of atomic displacements

We start by observing that once a glass is formed, it must be mechanically stable, at least in a laboratory time scale,[20] and thus resistant to thermal phonon field fluctuations for temperatures T below T_g. The condition required for such stability means that the correlation of the displacement field of two atoms separated by a distance R must not tend to infinity as $R \to \infty$. Let atom i at an equilibrium position $\mathbf{r}_i$ have a displacement $\mathbf{u}(\mathbf{r}_i)$. The correlation between two atoms can be measured as

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

where $\mathbf{R}_{ij}=\mathbf{r}_j-\mathbf{r}_i$ is the vector that joins atom i with j, and the bracket $\langle\,\rangle$ denotes thermal average at temperature T. In order to calculate the previous quantity, we will argue that nonlinear effects are negligible for a range of temperatures such that $T<T_g$ and $T \gg T_a$, where T_a is a temperature in

which the very low-temperature anomalies observed in glasses are not present. Usually it is observed that $T_a \leqslant 10$ °K and below this temperature there are anomalies due to anharmonic effects, for example, the linear dependence on T of the specific heat.[24] There are many different experimental and theoretical arguments to support the use of a harmonic Hamiltonian for the glass in the regime $T_a \ll T < T_g$. For instance, the nature of bonding in a glass is similar to the one observed in the corresponding crystal. The atoms in a crystal are basically oscillating around equilibrium positions. In a glass we expect a similar situation. In terms of the energy landscape picture, the system is arrested in one metabasin and thus it can only sample states around an inherent structure,[20] which means basically harmonic oscillations. This is in agreement with the well-known experimental fact that the specific heat (C_p) of glasses differs only slightly from the Dulong-Petit law[25–27] near T_g.

Yet, there is another path to prove the harmonic character of the Hamiltonian below T_g. This path is related with the main topic of the present paper. The basic idea is that the mean atomic square displacement $\langle\|\mathbf{u}(\mathbf{r}_j)\|^2\rangle$ is linear in T when the Hamiltonian that describes atom vibrations is harmonic. By proving this we will make our first encounter with a fundamental fact, which is ignored in most of the discussions about glasses: the role of the excess of modes in the low-frequency region. Following this line of thought, first we will calculate $\langle\|\mathbf{u}(\mathbf{r}_j)\|^2\rangle$ for a glass *assuming* a harmonic Hamiltonian. Although some expressions are available in the literature for monatomic systems,[28] here we revisit the problem to account for the case of glasses made from different atomic species, such as in binary and ternary glasses.

B. Correlation using the harmonic potential

In this section, we will study the atomic harmonic vibrations in the glass phase assuming mass variance. If each atom has mass m_j, the Hamiltonian of such glass made from N atoms can be written as[29]

$$H=\sum_{j=1}^{N}\left[\mathbf{p}_j'^{2}+\frac{1}{2}\sum_{l=1}^{N} y(\mathbf{r}_j)\mathbf{D}'(\mathbf{r}_j,\mathbf{r}_l)\mathbf{y}(\mathbf{r}_l)\right]. \qquad (2)$$

The renormalized displacement $y(\mathbf{r}_j)$ is defined as $y(\mathbf{r}_j)=\sqrt{m_j}\mathbf{u}(\mathbf{r}_j)$. The corresponding momentum is $\mathbf{p}_j'=-i\hbar\nabla_{y(\mathbf{r}_j)}$ and $\mathbf{D}'(\mathbf{r}_j,\mathbf{r}_l)=\mathbf{D}(\mathbf{r}_j,\mathbf{r}_l)/\sqrt{m_l m_j}$, where $\mathbf{D}(\mathbf{r}_j,\mathbf{r}_l)$ is the dynamical matrix written in the real-space basis.[29] Equation (2) can be solved by finding a diagonal base for $\mathbf{D}'(\mathbf{r}_j,\mathbf{r}_l)$. If $\omega(s)$ is the eigenvalue of the s eigenvector denoted by $\mathbf{e}_s(\mathbf{r}_j)$ and $a_s^{\dagger}$ (a_s) is the corresponding creation (annihilation) operator, the Hamiltonian can be transformed into[29] $H=\sum_{s=1}^{3N}(a_s^{\dagger}a_s+\frac{1}{2})\hbar\omega(s)$. Notice that we avoid the obvious choice of using the label k for the states, in order to highlight that we do not know if the modes are extended or localized. The only information is that modes oscillate in time with frequency $\omega(s)$. The quadratic displacement at temperature T can be calculated by taking a thermal average over the number of phonons and a configurational average over all atoms. In the classical limit, when $k_BT \gg \hbar\omega(s)$, such displacement is given by[28]

$$\langle\langle u^2(T)\rangle\rangle \equiv \frac{1}{N}\sum_{j=1}^{N}\langle\|\hat{\mathbf{u}}(\mathbf{r}_j)\|^2\rangle \approx \frac{k_BT}{N}\sum_{j=1}^{N}\sum_{s=1}^{3N}\frac{\|\mathbf{e}_s(\mathbf{r}_j)\|^2}{m_j\omega^2(s)}. \qquad (3)$$

A further simplification can be obtained by writing the mass on a given atom (m_j) as an average part $\langle m\rangle$ minus a fluctuation δm_j. Then, using the identity $(1-x)^{-1}=1+x+x^2+\ldots$ with $x=\delta m_j/\langle m\rangle$ we have

$$\langle\langle u^2(T)\rangle\rangle \approx \frac{k_BT}{N\langle m\rangle}\sum_{s=1}^{3N}\frac{1}{\omega^2(s)}\left[\sum_{j=1}^{N}\sum_{l=0}^{\infty}\left(\frac{\delta m_j}{\langle m\rangle}\right)^{l}\frac{\|\mathbf{e}_s(\mathbf{r}_j)\|^2}{\omega^2(s)}\right], \qquad (4)$$

where l is an integer. The term with $l=0$ in Eq. (4) is an average term, while the others contain the correlation between mass fluctuations and normal modes. Only a bound can be provided for such term. If the correlations between fluctuations of masses and modes are neglected, we can replace $(\delta m_j)^2$ by the standard deviation of the mass distribution σ_m^2. Using that the vectors $\mathbf{e}_s(\mathbf{r}_j)$ are normalized $\sum_{j=1}^{N}\|\mathbf{e}_s(\mathbf{r}_j)\|^2=1$, the first three terms in Eq. (4) are

$$\langle\langle u^2(T)\rangle\rangle \approx \frac{k_BT}{\langle m\rangle N}\left(1+\frac{\sigma_m^2}{\langle m\rangle^2}\right)\left[\sum_{s=1}^{3N}\frac{1}{\omega^2(s)}\right]. \qquad (5)$$

Notice that in general, $\omega(s)$ is shifted due to the mass variance. This shift goes as $\langle m\rangle^{-1}$, so in fact $\langle\langle u^2(T)\rangle\rangle$ is proportional to the inverse of the average elastic constant of the glass. To verify the approximations made with the masses, we have performed numerical simulations in disordered one-dimensional (1D) lattices. The results are presented in the Appendix and show a good agreement with the exact calculations.

The sum over all states in Eq. (5) can be made using the density of vibrational states $\rho(\omega)$ to get

$$\langle\langle u^2(T)\rangle\rangle \approx \frac{k_BT}{\langle m\rangle}\left(1+\frac{\sigma_m^2}{\langle m\rangle^2}\right)\langle\omega^{-2}\rangle_{\rho}, \qquad (6)$$

where the second inverse moment of the frequency is defined as

$$\langle\omega^{-2}\rangle_{\rho}=\frac{1}{N}\int_0^{\infty}\frac{\rho(\omega)}{\omega^2}d\omega. \qquad (7)$$

Equation (6) proves that $\langle\langle u^2(T)\rangle\rangle$ goes as T, as was said previously for harmonic Hamiltonians. A comparison between different glasses has been made by Ngai[30] for $\langle\langle u^2(T)\rangle\rangle$ as a function of T showing that below T_g, $\langle\langle u^2(T)\rangle\rangle$ is linear in T. Thus we can conclude that the harmonic model is good below T_g. The slope of $\langle\langle u^2(T)\rangle\rangle$ versus T is given basically by $\langle\omega^{-2}\rangle_{\rho}$. This fact tells a lot about the relationship between an excess of modes and the nature of the density of states (DOS) since low-frequency modes have a great impact in the integral due to the $1/\omega^2$ factor.

C. Correlation and phonon localization

Now we return to the original goal of finding the phonon spatial correlation given by Eq. (1). The last term in Eq. (1) can be calculated under the harmonic approximation. In the classical limit we get

$$\langle \mathbf{u}(\mathbf{r}_i)\cdot\mathbf{u}(\mathbf{r}_i+\mathbf{R}_{ij})\rangle \approx \sum_{s,s'=1}^{3N}\frac{k_BT}{\sqrt{m_im_j}\,\omega(s)\omega(s')}\times\mathbf{e}_s(\mathbf{r}_i)\mathbf{e}^*_{s'}(\mathbf{r}_i+\mathbf{R}_{ij}). \quad (8)$$

A configurational average can be obtained after a sum over all pairs of atoms,

$$\langle\langle \mathbf{u}(\mathbf{r})\cdot\mathbf{u}(\mathbf{r}+\mathbf{R})\rangle\rangle \approx \frac{2}{N^2}\sum_{i,j=1}^{N}\langle \mathbf{u}(\mathbf{r}_i)\cdot\mathbf{u}(\mathbf{r}_i+\mathbf{R}_{ij})\rangle. \quad (9)$$

Let us estimate Eq. (9). First the mass can be treated again as an average plus a fluctuation part. Then we ignore correlations between mass variation and local modes for LFVM. Also, for a normal mode $\mathbf{e}^*_s(\mathbf{r}_j+\mathbf{R}_{ij})$ the dependence upon $\mathbf{R}_{ij}$ can be factored out. Using this observation, we propose the use of a modulation factor $\Lambda_s(R)$ such that $\mathbf{e}_{s'}(\mathbf{r}_i+\mathbf{R}_{ij}) \approx \Lambda_{s'}(R)\mathbf{e}_{s'}(\mathbf{r}_i)\delta(R-\|\mathbf{R}_{ij}\|)$, where R is a distance and $\delta(x)$ is the Kronecker delta function. Assuming isotropy in the glass, we can perform the sum over j in Eq. (9) by considering all contributions from atoms at distance R. The result is the following:

$$\langle\langle \mathbf{u}(\mathbf{r})\cdot\mathbf{u}(\mathbf{r}+\mathbf{R})\rangle\rangle \approx \frac{k_BT}{\langle m\rangle}\left(1+\frac{\sigma_m^2}{\langle m\rangle^2}\right)\sum_{s=1}^{3N}\frac{\Lambda_s(R)}{\omega^2(s)}. \quad (10)$$

Equation (5) as well as Eq. (10) are fundamental to the stability of the glass. In Sec. III, we will explore such consequences.

III. STABILITY AGAINST THERMAL FLUCTUATIONS AND PHONON PROPAGATION

In this section we relate the excess of modes in the low-frequency region to the localization or scattering in order to assure thermal stabilization. We return to the original calculation of the correlation given by Eq. (1). Combining Eqs. (5), (6), and (10),

$$\langle\|\mathbf{u}(\mathbf{r}_i)-\mathbf{u}(\mathbf{r}_j)\|^2\rangle = \langle\langle u^2(T)\rangle\rangle + \frac{k_BT}{N\langle m\rangle}\left(1+\frac{\sigma_m^2}{\langle m\rangle^2}\right)\left[\sum_{s=1}^{3N}\frac{\Lambda_s(R)}{\omega^2(s)}\right]. \quad (11)$$

The sum over states can be performed using the density of states. However, at a given energy, normal modes can have different localization properties. Here we can use the fact that in glasses, a boson or a floppy peak is observed while a background of modes that follows Debye spectra is also present. Suppose that a fraction f of the $3N$ modes is contained in a peak centered at a frequency ω_0, while the rest corresponds to the background modes. We assume that all the modes in the Boson or floppy peak have the same localization properties. The density of states can be separated into a background $\rho_b(\omega)$ and a peak contribution, which we model as a Delta function $\delta(\omega-\omega_0)$, such that

$$\rho(\omega) \approx \rho_b(\omega) + 3Nf\delta(\omega-\omega_0). \quad (12)$$

For $\rho_b(\omega)$ one can use a Debye model with a cut-off frequency ω_D that contains $3N(1-f)$ modes since we are only interested in very low-frequency modes. In that sense, the model is a weighted mix between an Einstein model and a Debye one.[29]

The sum in Eq. (5) can be made using the proposed DOS to obtain

$$\langle\|\mathbf{u}(\mathbf{r}_i)-\mathbf{u}(\mathbf{r}_j)\|^2\rangle \approx \langle\langle u^2(T)\rangle\rangle + \frac{k_BT}{\langle m\rangle}\left(1+\frac{\sigma_m^2}{\langle m\rangle^2}\right)\left[\frac{1}{N}\int_0^\infty\frac{\rho_b(\omega)\Lambda_{s(\omega)}(R)d\omega}{\omega^2} + \frac{3f}{\omega_0^2}\Lambda_{s(\omega_0)}(R)\right], \quad (13)$$

where the dependence of $\Lambda_s(R)$ in ω is made explicit by writing s as a function of ω. The states in the background are extended plane-wave acoustical modes, and thus $\Lambda_{s(\omega)} \approx \cos[2\pi s(\omega)R/a]$ where a is the mean lattice parameter. For acoustic modes, $\omega(s)\approx v_\infty sa$ where v_∞ is the average sound velocity. Now we take the limit $R\to\infty$. The integral term goes to zero, while the first term does not depend upon R. In order to have a stable glass, the last term must not depend on R. Thus, the limit $R\to\infty$ produces a condition for the function $\Lambda_{s(\omega_0)}(R)$,

$$\lim_{R\to\infty}\Lambda_{s(\omega_0)}(R)=0. \quad (14)$$

Such equation can be satisfied by two basic mechanisms: localization or scattering. In any case, there must be at least one characteristic length associated with such modes. This is in agreement with some recent work made by other groups, which pointed out by using very different arguments the existence of a characteristic length scale in glasses related to LFVM.[31,32] Notice that here appears a first natural length scale (L), since $\Lambda_{s(\omega_0)}(R)$ is adimensional. From Eq. (13) we obtain

$$L \sim \sqrt{\frac{3fk_BT}{\langle m\rangle\omega_0^2}}. \quad (15)$$

This length basically quantifies the ratio of the thermal energy contained in the boson or floppy peak with the elastic potential energy of the corresponding modes. For a typical glasslike Se, $f=1/3$, $\omega_0\approx 7.6\times 10^{12}$ Hz, and $L\simeq 2$ Å, which is comparable with a bond length. Notice that L already provides criteria for stability since, as we shall see in Sec. IV, T_g occurs when $\sqrt{\langle\langle u^2(T)\rangle\rangle} \approx 0.01a$, where a is the bond length, namely, a few Å.

IV. GLASS TRANSITION AND LOW-FREQUENCY MODES

Here we will develop the relationship between glass transition and low-frequency modes. We start by pointing out that stability cannot be achieved when $\sqrt{\langle\langle u^2(T)\rangle\rangle}$ is of the same order of magnitude of the lattice spacing because nonlinear effects or bond breaking destabilizes the lattice. A hint about the nature of the stability comes from the fact that $\langle\omega^{-2}\rangle_g > \langle\omega^{-2}\rangle_c$, due to the excess of LFVM of the glass, from where it follows that $\langle\langle u^2(T)\rangle\rangle_g \sim \langle\omega^{-2}\rangle_g > \langle\omega^{-2}\rangle_c \sim \langle\langle u^2(T)\rangle\rangle_c$, where the subindex g denotes the glass and c the crystal. Thus, in a glass $\langle\langle u^2(T)\rangle\rangle$ is always bigger than in the crystal.

In fact, crystal melting occurs when $\langle u^2(T)\rangle^{1/2}$ is around 1/10 of the atomic spacing a: A rule known as the Lindemann criteria. There are experimental evidences based on neutron scattering that this criteria is applicable at T_g for glasses,[33–36] as is the case for Se and Se-Ge systems.[37] It is important to remark that this T_g nearly coincides with the temperature in which relaxation time exceeds experimental time scale. As a result, here we will take such temperatures as equal. Computer simulations are in agreement with this observation;[38,39] and, in a previous article,[21] we have showed that in fact the number of floppy modes and the Lindemann criteria can be used to predict variations of T_g. Such development provided the first theoretical derivation of the modified empirical Gibbs-DiMarzio law[21] used by experimentalists. Let us use the previous discussion to derive a general relationship between melting and glass transition temperature.

Assuming that the glass transition and melting occur when $\langle\langle u^2(T)\rangle\rangle$ reaches a fraction r of the lattice spacing, from Eq. (6) we obtain at T_g that

$$r^2a^2 \approx \frac{k_B T_g}{\langle m\rangle N}\int_0^\infty \frac{\rho_g(\omega)}{\omega^2}d\omega = \frac{k_B T_g}{\langle m\rangle}\langle\omega^{-2}\rangle_g. \qquad (16)$$

Equation (16) leads to an important expression for T_g ,

$$T_g \approx \frac{\langle m\rangle r^2 a^2}{k_B}\langle\omega^{-2}\rangle_g^{-1}. \qquad (17)$$

Equation (17) has been tested against numerous experiments in a previous work.[21] Notice that according to Eq. (6), T_g changes with chemical composition due to a different average mass $\langle m\rangle$ and vibrational spectrum.[40] Now we can compare with the melting temperature (T_m), since a similar equation holds for it,

$$T_m \approx \frac{0.01\langle m\rangle a^2}{k_B}\langle\omega^{-2}\rangle_c^{-1}. \qquad (18)$$

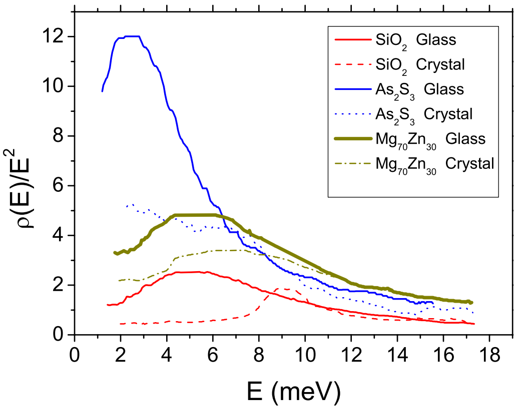

FIG. 1. (Color online) $\rho(E)/E^2$ for different glasses and their corresponding crystals. The data set was taken from Refs. 37 and 41.

Combining Eq. (17) with Eq. (18) we get

$$T_g \approx (\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g)T_m. \qquad (19)$$

It is very well known that for almost all glasses[9] $T_g/T_m \approx 2/3$. We can infer using Eq. (18) that

$$\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g \approx \frac{2}{3}. \qquad (20)$$

Equation (20) indicates an almost universal relationship between the excess of modes of the glass compared with the crystal. In Fig. 1 we plot the excess of vibrational states $\rho(E)/E^2$ (where $E=\hbar\omega$) for several glasses compared with their corresponding crystals. The values of $\langle\omega^{-2}\rangle$ for each system are presented in Fig. 2. Table I summarizes the results for some representative glasses. In Fig. 3 we plot the ratio $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$ versus T_g/T_m for the data presented in Table I. From Fig. 3 it is clear that $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$ has the same order of magnitude as T_g/T_m. Furthermore, the case of $Mg_{70}Zn_{30}$ is atypical in the sense that T_g/T_m is nearly one, a fact reflected in the high value of $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$. For comparison, we included the results for a monocomponent Lennard-Jones glass taken from Ref. 24. Clearly, the ratio $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$ is very small, reflecting the unstable character of such glass, which

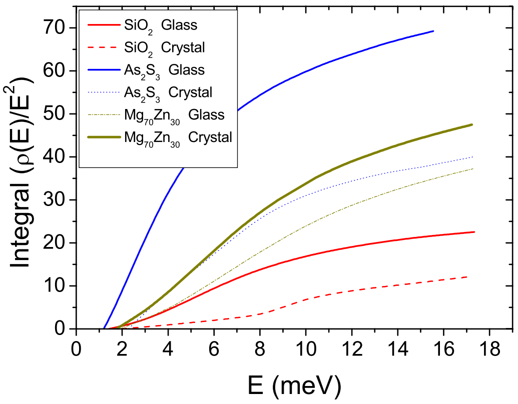

FIG. 2. (Color online) The integral $\int_0^E \rho(E)/E^2$ for the glasses and crystals that appear in Fig. 1. The data set was also taken from Refs. 37 and 41.

TABLE I. A comparison between the ratio T_g/T_m and $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$ for several glasses.

System	$\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$	T_g/T_m	Ref.
As_2Se_3	0.57	0.83	41
$Mg_{70}Zn_{30}$	0.78	0.96	41
Se	0.50	0.63	37
SiO_2	0.52	0.72	41
Lennard-Jones	0.15	*	24

is known to be a very bad glass former[24] maybe because of its very low $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$ ratio.

The origin of the 2/3 rule can be traced to the stability limit of the system against thermal fluctuations. However, the remaining question is why such rule appears in the vibrational spectrum. A possible path to solve this problem consists in studying the relationship between $\rho(\omega)$ and the elastic response function[42] $D(k,\omega)$,

$$\rho(\omega) \propto -\omega \,\mathrm{Im}\left\{\int_0^{k_D} d^3k D(k,\omega)\right\}, \tag{21}$$

where k is the wave vector and k_D is a Debye-type cutoff. For acoustic vibrations in the hydrodynamical limit, $D(k,\omega)$ can be written as

$$\mathrm{Im}\, D(k,\omega) \approx -\omega F''(k)/\{[\omega^2 - v_\infty^2 k^2 + \omega F'(k)]^2 + [\omega F''(\omega)]^2\}. \tag{22}$$

Here v_∞ is the sound velocity and $F(k)$ is a function, which characterizes the damping of fluctuations. $F''(k)$ and $F'(k)$ are the imaginary and real parts of $F(k)$. $F''(k)$ is related with the mean-free path of the vibration $L(k)$ by $F''(k) \approx 2v_\infty/L(k)$. For a crystal, $F(k)\rightarrow 0$ and $\mathrm{Im}\,\omega D(k,\omega)$ turns out to be a delta function $\delta(\omega^2 - v_\infty^2 k^2)$ and the usual $\rho(\omega) \propto \omega^2$ Debye dependence is recovered. According to the results of Ref. 42, the excess of modes at low ω is a consequence of the decreasing mean-free path, which goes as

$$L(k) = (G/k^4 + L_0), \tag{23}$$

where G and L_0 are constants. The k^4 dependence is due to Rayleigh scattering as has been determined from thermal conductivity[43] and inelastic x-ray scattering.[44] Also, the results are not very much dependent on $F'(k)$ so it can be set to zero.[42]

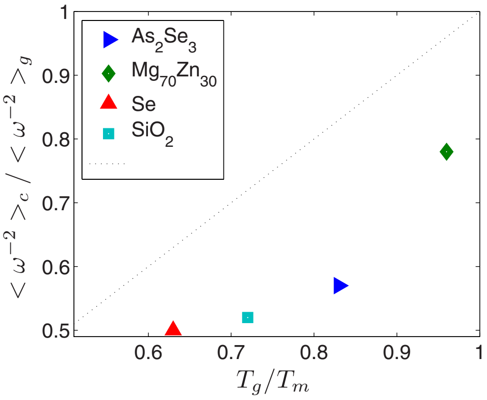

FIG. 3. (Color online) Comparison between the ratio of the second inverse moments $\langle\omega^{-2}\rangle_c/\langle\omega^{-2}\rangle_g$ versus T_g/T_m. The dotted line is a guide to indicate the identity.

However, in Ref. 42 it was not observed that $F''(k)$ must have a crossover since to normalize $\rho(\omega)$, $F''(k)$ needs to decay at least as k^2 when $k\rightarrow 0$ to avoid a singularity. Acoustic modes are expected for $k\rightarrow 0$. The most reasonable consistent assumption is that $F''(k)=k^2$. Thus, there must be a transition at a critical k_c from a k^4 to a k^2 law. This theoretical argument is in agreement with the experimental observations.[44] It is important to remark that the crossover occurs at a frequency that corresponds to the boson peak maximum[44] $F''(k_c)\approx\omega_0$, where $\omega_0 \approx v_\infty k_c$. For glasses we can summarize the behavior of $F(k)$ as follows:

$$F''(k) \approx \begin{cases} \omega_0[(k_c/k)^2]^{-1} & k < k_c \\ 2v_\infty[G/k^4 + L_0]^{-1} & k \geq k_c \end{cases} . \tag{24}$$

A relationship between the parameters can be obtained from $F(k)$ by asking the same free path at the crossover, i.e., $\omega_0 \approx 2v_\infty[G/k_c^4 + L_0]^{-1}$, from where it follows

$$G \approx \left(\frac{\omega_0}{v_\infty}\right)^3\left[2 - \left(\frac{\omega_0 L_0}{v_\infty}\right)\right]. \tag{25}$$

Equation (25) shows that the size of the Rayleigh scattering is related with the Boson peak frequency. Moreover, G needs to be a positive quantity. This observation provides a bound for L_0,

$$L_0 < 2v_\infty/\omega_0. \tag{26}$$

For glasses, $\omega_0 \approx 10^{12}$ Hz and v_∞ takes values between 10^3 and 10^4, which produces a typic length L_0 between 20 and 200 Å. For v-SiO$_2$, $\omega_0 \approx 3\times 10^{12}$ Hz, $v_\infty \approx 8430$ m/s, and $L_0 \approx 60$ Å. This confirms the discussion made in Sec. II: Stability requires a length scale for the distance of phonon damping, which enters in Eq. (14). Notice how L and L_0 will enter in the glass transition temperature via the position of the Boson peak. In fact, L_0 also contributes to determine L since the fraction of modes f in the anomaly is given by Eq. (21).

To understand the effects of G and L_0, let us obtain $\langle u^{-2}\rangle$ from $\langle\langle\omega^2\rangle\rangle$ using Eqs. (21) and (22)),

$$\langle\omega^{-2}\rangle = \frac{4\pi}{C}\int_0^{k_D}\int_0^{\omega_D} dk d\omega k^2 F''(k)/\{[\omega^2 - v_\infty^2 k^2]^2 + [\omega F''(k)]^2\}, \tag{27}$$

where C is the normalization constant of $\rho(\omega)$,

$$C = -\mathrm{Im}\left\{\int_0^{\omega_D}\int_0^{k_D} d\omega d^3k \omega D(k,\omega)\right\}. \tag{28}$$

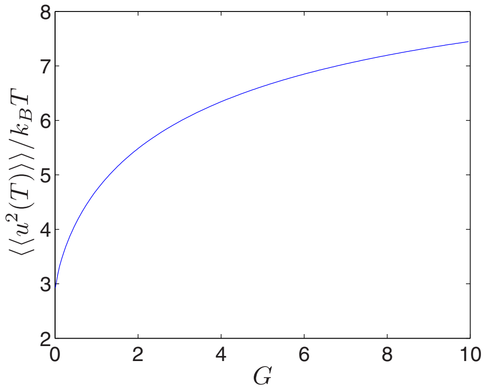

FIG. 4. (Color online) A plot of the mean quadratic displacement as a function of G for $\lambda_0=1$ and $k_c=10^{-2}/L_0$ using arbitrary units as in Ref. 42.

As an example, in Fig. 4 we present a plot of $\langle\langle u^2(T)\rangle\rangle/k_BT$ for different values of G using $L_0=1$ and $k_c=10^{-2}/L_0$. Notice that here we use adimensional units as in Ref. 42. Figure 4 shows how Rayleigh scattering, which enters through G, leads to an increased quadratic displacement.

In a similar way, we can fix G and vary L_0 as shown in Fig. 5. This plot reveals how $\langle\langle u^2(T)\rangle\rangle/k_BT$ decreases with L_0. This means that stability is enhanced as the mean-free path grows. Notice that such behavior is a delicate balance between two mechanisms. On one hand, to enhance the mean-free path, phonon scattering must decrease. The free path decreases as disorder is decreased as what happens in a crystal. On the other hand, $\rho(\omega)$ tends to reduce anomalies in the low-frequency region because damping is reduced.

Finally, since $\langle\omega^{-2}\rangle_c \approx \frac{2}{3}\langle\omega^{-2}\rangle_g$, it follows from Eq. (27) that there must be a kind of universal relationship between $L(k)$ for a glass and a crystal. In fact, it is known that the phonon free path for most glasses is around 150 phonon wavelength, which is an empirical observation that supports the hypothesis.[45] Thus, phonon scattering provides a mechanism for thermal stabilization via the required anomalies in the density of states and also explains the plateau between 1° and 30 °K in the thermal conductivity of glasses.[45]

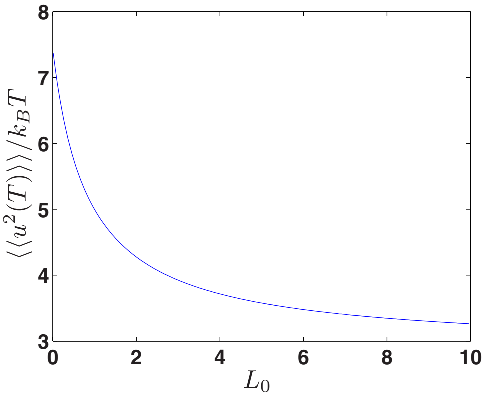

FIG. 5. (Color online) A plot of the mean quadratic displacement as a function of L_0 for $G=1$ and $k_c=10^{-2}/L_0$ using arbitrary units as in Ref. 42.

V. EFFECTS OF PRESSURE ON THE GLASS TRANSITION TEMPERATURE

Finally, we would like to sketch out how T_g changes with the applied pressure (P) using the approach developed in this work. The usual path, involving several approximations, is to prove the following relation:[9]

$$\frac{dT_g}{dP} \approx T_g v_g \frac{\Delta\alpha_p}{\Delta c_p}, \tag{29}$$

which is known to be accurate only within a 30% for a wide variety of substances. Here v_g is the volume per particle and $\Delta\alpha_p$ (Δc_p) is the jump of the thermal-expansion coefficient (specific heat) during glass transition. We propose a different path to obtain such change. By taking the derivative of Eq. (17) with respect to the pressure, we obtain

$$\frac{dT_g}{dP} \approx -T_g\left[3\kappa_T + \frac{d}{dP}\ln\int_0^\infty \frac{\rho_g(\omega)}{\omega^2}d\omega\right], \tag{30}$$

where κ_T is the compressibility. For liquids and solids κ_T is very small and can be neglected.[46] Thus,

$$\frac{dT_g}{dP} \approx -T_g\left(\frac{d}{dP}\ln\langle\omega^{-2}\rangle_\rho\right). \tag{31}$$

In many systems, the effect of pressure upon $\rho(\omega)$ is to shift the boson peak toward higher frequencies[40,47] since the coordination of the lattice increases with pressure. As a result, T_g is changed through the density of states. It is worthwhile mentioning that the Lindemann fraction r can vary with the pressure depending on the system; although, we neglected such influence because it is smaller than the peak shift. A complete discussion about how r changes with pressure can be found in Ref. 48.

As a token, Eq. (30) provides a simple connection between $\Delta\alpha_P$, Δc_p and the density of states. A comparison between Eqs. (29) and (30) leads to a simple prediction,

$$\frac{\Delta\alpha_p}{\Delta c_p} \approx -\frac{1}{v_g}\frac{d}{dP}\ln\langle\omega^{-2}\rangle_g. \tag{32}$$

VI. CONCLUSIONS

In conclusion, we have shown that low-frequency vibrational anomalies present in glasses are fundamental to provide stabilization against thermal fluctuations. Such collective effect is not any more effective near glass transition. From pure thermodynamical arguments, we have shown that modes present in boson or floppy peaks are localized or strongly scattered and, as a result, there must be a length scale associated. In fact, we obtained two characteristic scales: $L \sim \sqrt{3fk_BT/\langle m\rangle\omega_0^2}$ and $L_0 \sim 2v_\infty/\omega_0$. The first one is of order of the bond lengths and provides a good approximation to the glass transition temperature. It is basically the ratio between the thermal and elastic energy contributions of the boson peak. The second one corresponds to distances in the medium-range order resulting from phonon damping. It is given by the average sound velocity divided by the boson or floppy peak frequency.

The present approach still requires a fine tuning of the hypothesis involved. For example, some crystals (such as cristobalite SiO_2) show a Boson peak at the same frequency as in SiO_2 glass. This is usually associated with significant dynamic disorder. In other words, the system does not become unstable but disorders dynamically. As a result, there are other contributions to T_g.

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APPENDIX: ONE-DIMENSIONAL EXAMPLE

To test the approximations made with the masses and as a simple example, we have performed numerical simulations in a disordered 1D lattice, in which two types of atoms with different masses (m_A and m_B) were present with concentrations x and $1-x$ using a first-neighbor harmonic Hamiltonian. Notice that although in 1D $\langle\langle u^2(T)\rangle\rangle$ is divergent for an infinite number of atoms N, its value can be calculated for a finite chain. In Fig. 6, the solid line represents the evolution of $\langle\langle u^2(T)\rangle\rangle$ as a function of the average mass $\langle m\rangle = xm_A + (1-x)m_B$ for a fixed mass ratio m_A/m_B using a random distribution of masses in a chain with $N=100$ sites. The calculation was made using formula (3). These results were obtained by a diagonalization of the Hamiltonian, which provides the eigenvectors $\mathbf{e}_s(\mathbf{r}_j)$ and eigenfrequencies $\omega(s)$. In the same figure, the dotted line is the result obtained by the method of treating the mass as an average plus a fluctuating part, as given by Eq. (5). One can observe that the approximation is good, especially for small amounts of disorder. The role of the correlations is clear in the figure since the proposed approximation is not symmetric around $x=1/2$, while the complete result is symmetric, indicating a correlation between oscillation and mass.

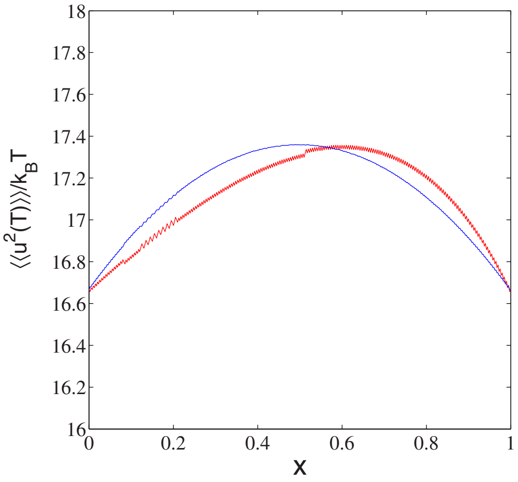

FIG. 6. (Color online) Normalized average mean quadratic as a function of the concentration of impurities with mass m_A in a one-dimensional disordered chain for a fixed ratio between the masses $m_A/m_B=2$. The elastic constants are one, and the system has $N=100$ atoms. The solid line corresponds to the exact calculation using the Eq. (3), while the dotted line corresponds to the averaged mass approximation using Eq. (5).

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