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# Energy landscape and rigidity

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The effects of floppy modes in the thermodynamical properties of a system are studied. From thermodynamical arguments, we deduce that floppy modes are not at zero frequency and thus a modified Debye model is used to take into account this effect. The model predicts a deviation from the Debye law at low temperatures. Then, the connection between the topography of the energy landscape, the topology of the phase space, and the rigidity of a glass is explored. As a result, we relate the number of constraints and floppy modes to the statistics of the landscape. We apply these ideas to a simple model for which we provide an approximate expression for the number of energy basins as a function of the rigidity. This helps to understand certain features of the glass transition, like the jump in the specific heat or the reversible window observed in chalcogenide glasses.

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## I. INTRODUCTION

The physics of glass formation is a complex multiparticle problem, and in spite of its importance from the fundamental and technological points of view, many important questions remain unanswered [1]. As an example, we can cite the origin of the nonexponential relaxation laws [2] or the ability of certain materials to reach the glassy state [3]. To tackle these problems there are many different approaches [4]: phenomenological models like the Gibbs-Dimarzio model, theoretical theories like mode coupling, or the use of extensive computer simulations [5]. A very interesting question is how the glass transition temperature ($T_g$) depends on chemical composition. Chalcogenide glasses (formed with elements from the VI column doped with impurities) are very useful for understanding these effects [6]. As was discovered more than 2000 years ago, $T_g$ can be raised or lowered by adding impurities, and the fragility of the glass can be changed from strong to fragile [7]. Recently, by using stochastic matrices [8,9], the law that gives the relation between $T_g$ and the concentration of modifiers [10] has been obtained, including a constant that appears in the law for almost any chalcogenide glass [11]. Another interesting property of glasses is the behavior of their viscosity, which is usually referred to as the fragility [7]. The fragility of a glass is also related to the glass forming tendency in that melts of a strong or nonfragile liquid do not require a high speed of cooling to form glasses. On the other hand, fragile glasses are poor glass formers and require a rapid quench to form glasses. The ease of glass formation can be explained at least in a qualitative way by the rigidity theory (RT), introduced by Phillips [12] and further refined by Thorpe [13]. By considering the covalent bonding as a mechanical constraint, the ease of glass formation is related to 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 modes [14]. The resulting network is underconstrained. A transition occurs when a disordered lattice becomes rigid. Glasses that are rigid at a certain chemical composition are easier to form, and many features of this transition have been experimentally observed [6,17]. Even for simple systems like hard disks [18] and colloids [19], it seems that rigidity plays an important role. For more complex systems like proteins, rigidity has been used as a very powerful tool to understand folding and long-time scale motions [20].

A very puzzling fact of RT that has not been explored is the following. According to the idea of looking at rigidity as a vector percolation problem, at the rigidity threshold the entropy is high [21], due to strong fluctuations as happens in any phase transition. One even can define a free energy and specific heat as a function of the flexibility of the system that has a singularity at the transition [22]. However, the experimental data from modulated scanning calorimetry in chalcogenide glasses shows the opposite: at the rigidity transition the configurational entropy is less and there is a *window of reversibility* [6,23]. In particular, it has been observed that protein folding is reversible because it occurs at the rigidity transition [20], and this seems to be a crucial property for life to exist [20].

Mainly, the problem resides in the fact that although RT provides a framework to understand many features of a system, its use in a quantitative way has not been fully developed to provide a link with the thermodynamics of the system. In a previous paper we approached this problem by using a phenomenological free energy to account for many thermodynamical properties of the glass transition [24], and then we made extensive computer simulations with associative fluids to show that many concepts of the RT work in a "thermodynamical environment" [25,26]. However, the connection with thermodynamics is still not mature, since there is no general way of introducing thermodynamics in the RT.

In a different context, the energy landscape is a formalism that has been very useful for describing the molecular scale events that happen during the glass transition [27]. The landscape is a multidimensional surface generated by the system potential energy as a function of the molecular coordinates [4]. In an $N$-body system the landscape is thus determined by the potential energy function, given by $\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ where $\mathbf{r}_i$ comprise position, orientation, and vibration coordinates. For the simplest case of a particle possessing no internal degrees of freedom, the landscape is a $(3N+1)$ object. The topogra-

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phy of this landscape is fundamental for the thermodynamics of the system. At high temperatures the system does not feel the summits and valleys of $\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ because the kinetic energy contribution dominates. However, as the temperature is lowered the system is unable to surmount the highest energy barriers and therefore is forced to sample deep minima. When this happen, the kinetics of relaxation changes from exponential to stretched exponential [5]. An important observation is that, according to statistical mechanics, the entropy of the system depends on the accessible volume in the phase space. However, inside a local minimum of the potential energy, it can happen that if there are no paths that connect to other minima, the system cannot sample that part of the phase space. In such a case, ergodicity is broken and the system is no longer in thermal equilibrium. Such a glass will have a residual entropy [28]. In this article, we show that rigidity can be related to the statistics of the energy landscape, since the number of floppy modes is related to the number of different configurations of the system with nearly equal minimal energies, and thus provides an estimation for the number of minimal energy basins of the landscape. But floppy modes also provide channels in phase space that increase the entropy, which in part explains the paradox of the window of reversiblity. To show these connections, we will concentrate on the effects of rigidity on the shape of the energy landscape.

The layout of this work is the following. In Sec. II we discuss a simple way to introduce thermodynamics into RT; however, as we will see, the straightforward manner of doing this does not agree with the experimental results. Thus, we propose that the effects of floppy modes are important only at low temperatures or during glass transition. In Sec. III the connection with the energy landscape is made and a simple model is worked out. Finally, in Sec. IV we give the conclusions.

## II. RIGIDITY AND THERMODYNAMICS

In this section we explore some simple thermodynamical consequences of the RT. As explained before, the rigidity ideas of Phillips [29] and Thorpe [14] were used in order to understand the ease of glass formation. In this theory, the ability to make a glass is optimized when the number of freedom degrees, in this case $3N$, where $N$ is the number of particles, is equal to the number of mechanical constraints $(N_c)$ that are given by the bond length and angles between bonds.

The number $(3N-N_c)/3N$ gives the fraction of cyclic variables of the Hamiltonian, i.e., when one of these variables is changed, the energy of the system does not change, as for example happens with the center of mass coordinate. This fraction also corresponds to the fraction of vibrational modes with zero frequency $(f)$, called floppy modes, with respect to the total number of vibrational modes. The counting of floppy modes in a mean field, known as Maxwell counting, goes as follows [30–32]. 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 the angles are also rigid, in three dimensions (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

$$\langle r\rangle=\sum_r r x_r .$$

A rigidity transition occurs when $f=0$ and the system passes from a floppy network to a rigid one. Glasses are rigid if $f$ is a negative number, i.e., if there are more constraints than degrees of freedom, the lattice is overconstrained and the important number is how many stressed bonds are present. In 3D, the rigidity transition leads to the critical value $\langle r_c\rangle=2.4$ if all angular constraints are considered. In real systems, the Maxwell counting breaks near the rigidity transition, and the number of floppy modes is obtained from the pebble game algorithm [14].

What are the simple thermodynamical effects of floppy modes? To answer this question, first we use the simplest model for atomic vibrations in the harmonic approximation, where the interatomic potentials are replaced by springs. The corresponding Hamiltonian is

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

where $Q_j$ and $P_j$ are the $j$th normal mode coordinates in phase space, and $\omega_j$ is the corresponding eigenfrequency of each normal mode. Observe that floppy modes have zero frequency; they do not contribute to the elastic energy. Using simple statistical mechanics, we can obtain the partition function in the canonical ensemble at the classical limit (high temperatures compared with the Debye temperature),

$$Z=\int\cdots\int\prod_{j=1}^{N}dP_jdQ_je^{-H/kT}$$

$$=\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\prod_{j=1}^{3N(1-f)}\left(\frac{2\pi kT}{m\omega_j^2}\right)^{1/2},$$

where $T$ is the temperature and $k$ the Boltzmann constant. The free energy of the system is now given by

$$F=-\frac{3NkT}{2}\ln\left(\frac{2\pi mkT}{h^2}\right)-\frac{kT}{2}\sum_{j=1}^{3N(1-f)}\ln\left(\frac{2\pi kT}{m\omega_j^2}\right).$$

From this last expression, the corresponding specific heat $(C_V)$ is

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

In this simple approach, the prediction is that $C_V$ is given by the Dulong-Petit law, minus a term that depends on the number of floppy modes. The reason is clear: *floppy modes do not* *store energy* since they are cyclic variables of the Hamiltonian; the energy of the system does not change, as for example the center of mass coordinate. However, a careful examination of the experimental data shows that for chalcogenide glasses [6], like compounds of As-Ge-Se and ferroelectric materials [15], $C_V$ does not depends on $f$. Instead, they follow the Dulong-Petit law. From this simple thermodynamical argument, one is led to propose that floppy modes do not have a perfect zero frequency, i.e., in real glasses they are shifted by residual forces, like the van der Waals interaction. This argument is confirmed by neutron scattering experiments, where it has been shown that floppy modes in As-Ge-Se are blueshifted [16,17], forming a peak at around 5 meV. Thus, at high temperatures, all the $3N$ oscillators are excited. We suggest that the effects of floppy modes are important only at low temperatures since all floppy modes are frozen nearly at the same temperature. The corresponding temperature ($\Theta_f$) where these modes are frozen, can be estimated from the energy required to excite modes of 5 meV, which gives $\Theta_f \sim 60$ K. Furthermore, an Einstein-like mode in the vibrational density of states is suggested by the giant softening of the $^{119}$Sn Lamb-Mössbauer factor in $(\mathrm{Ge}_{0.99}\mathrm{Sn}_{0.01})_x\mathrm{Se}_{1-x}$ glasses [17] as $x$ steadily decreases to 0, i.e., as the glass gets more floppy. The mean square displacement at absolute zero or the first moment of the vibrational density of states is the quantum property that contains information on these floppy modes, and its variation $x$ nicely scales with the scattering strength of the 5 meV mode observed in inelastic scattering [17].

This behavior at low temperatures, where a quantum treatment is needed, can be modeled by using a simple density of states $\rho(\omega)$ that takes into account the floppy peak in the spectrum. First we use a Debye type of density of states, normalized to $3N(1-f)$. Then we add the contribution from the floppy modes, with a $\delta$ function centered around a characteristic peak at $\omega_0$. The corresponding density of states is

$$\rho(\omega) = \begin{cases} \dfrac{9N(1-f)}{\omega_D^3}\omega^2 + 3Nf\delta(\omega-\omega_0) & \text{if } \omega \leqslant \omega_D, \\ 0 & \text{if } \omega > \omega_D, \end{cases}$$

where $\omega_D$ is the Debye cutoff frequency. By using the Bose-Einstein distribution for the number of phonons in equilibrium at a certain temperature, we get that the specific heat is

$$C_V = (1-f)3NkD(x_0) + f3Nk\frac{x^2e^x}{(e^x-1)^2}$$

where $x=\Theta_{fl}/T$, $x_0=\Theta_D/T$, and $\Theta_D=\hbar\omega_D$ is the Debye temperature. $D(x_0)$ is the well known Debye function. At high temperatures, the model predicts the Dulong-Petit law as expected, while at low $T$, the following behavior is obtained:

$$C_V \approx (1-f)3Nk\frac{4\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^3 + f3Nk\left(\frac{\Theta_f}{T}\right)^2 e^{-\Theta_f/T},$$

which is a Debye law of the type $T^3$, but with a contribution that is in the form of the Einstein model. Each contribution is determined from the fraction of floppy modes for a given composition of the glass. The present model suggest that experiments at low temperatures performed on chalcogenide glasses will provide characteristic features of rigidity.

## III. ENERGY LANDSCAPE AND RIGIDITY

In the last section we discussed that floppy modes have effects mainly at low $T$. In spite of this, an examination of the experimental results shows that the number of floppy modes is also important for the thermodynamical properties at the glass transition [7]. For example, the magnitude in the jump of $C_P$, usually denoted by $\Delta C_P$, the jump in the thermal expansion, the energy for activation of viscosity, the fragility, and the entropy of a liquid melt depend on $f$. Moreover, very recently Boolchand *et al.* discovered the window of reversibility in the heat flow, associated with a phase of zero internal stress in the network [23]. Angell has pointed out the qualitative relationship between energy landscape and fragility during glass transition [27]. However, it is still not clear how to relate these features to the statistics of the landscape. Here we will show that the number of floppy modes provides a useful parameter to represent the roughness of the landscape. This roughness is evident when the glass is melted, explaining why floppy modes are important during glass transition, since they are collective motions that provide pathways across the phase space and energy landscape.

As a first and tentative step, we start again by supposing that floppy modes are at zero frequency. Around any given inherent structure, the potential has a minimum and thus can be expanded in a Taylor series, which turns out to be the expression of a harmonic potential. From the Hamiltonian presented in Eq. (1) is clear that in an inherent structure, each floppy mode provides a *channel in the landscape* since the energy does not depend upon a change in a floppy coordinate. A very simple example is shown in Fig. 1, which shows the bottom of the landscape for a system with two normal modes. In the first system [Fig. 1(a)] $f=0$, but the other has $f=1$ [Fig. 1(b)] since one of the spring constants was set to zero (of course, by excluding the center of mass coordinate). In a more general way, for a given inherent structure, the number of channels is clearly given by $f$. Each channel increases the available phase space allowed to visit. The entropy due to floppy modes is easy to calculate. In the microcanonical ensemble, the number of accessible states $[\Omega(E,V,N)]$ for a system with a volume $V$ is proportional to the area defined by the surface of constant energy $E = H(P_1,\ldots,P_N,Q_1,\ldots,Q_N)$. Since floppy modes are cyclic variables of the Hamiltonian, we can write

$$\Omega(E,V,N) = \frac{1}{h^{3N}}\int \cdots \int_{E=H(P_1,\ldots,Q_{3N(1-f)})} \times \prod_{j=1}^{3N} dP_j \prod_{k=1}^{3N(1-f)} dQ_k \left(\int_0^{V^{1/3}} dQ\right)^{3Nf},$$

and using the Boltzmann relation $S=k\ln\Omega(E,V,N)$ we get

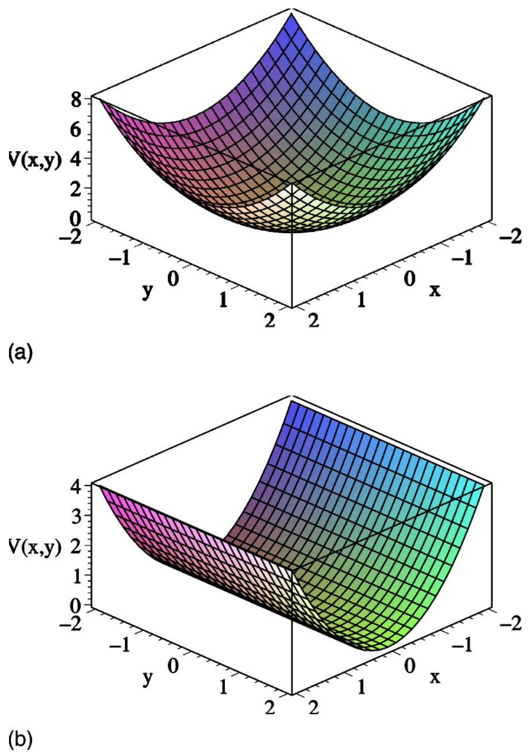

FIG. 1. Bottom of the landscape for a system (a) with no floppy modes and a potential energy in arbitrary units given by $\phi(x,y)=x^2+y^2$ and (b) with one floppy mode obtained by removing a "spring," $\phi(x,y)=x^2$. A channel is generated in the $y$ direction.

$$S=\ln\left[\frac{(2\pi m)^{3N/2}E^{3N(1-f/2)}}{h^{3N}\{[3N(1-f/2)]-1\}!}\prod_{j=1}^{3N(1-f)}\left(\frac{2}{m\omega_j^2}\right)\right]+fNk\ln V. \tag{2}$$

The entropy provided by the channels in the landscape is simply given by the last term $S_c=fNk\ln V$. At first glance, it seems that this result agrees with the experimental observations, because during glass transition, it has been observed that floppy glasses have a large entropy and as a result, they have a more fragile behavior as deduced from the Adams-Gibbs relation [7]. However, a more detailed analysis shows that if we suppose an entropy of the type given by Eq. (2), the specific heat does not follow the Dulong-Petit law. This is due to the dependence of $S$ upon $E^{3N(1-f/2)}$, which is just a result of the independence of $H$ with respect to floppy modes. As discussed in the previous section, this leads to the conclusion that floppy modes are not strictly at zero frequency. The blueshift of the floppy modes means that the *channels in phase space are not flat*: there is a small curvature in the direction of the floppy variable. This effect has the property that it restores the Dulong-Petit law and provides directions in phase space where the system can relax without big changes in energy.

In a floppy glass there is a hierarchy in the strength of the forces. The forces that restore the Dulong-Petit law are the weakest. Then it is natural to assume that the anharmonic contributions of these residual forces are also small. Under this assumption, the extra entropy due to these modes is $S\simeq fNk\ln V$ which is only activated when the glass traverses the glass transition. This entropy is just a maximal bound, since it can be less depending on the range of the floppy coordinate. We can speculate that these channels are in fact the ones that explains the fragility and ease of glass formation since is clear that it is much more difficult to trap the system in a local minimum of the landscape when many channels are present.

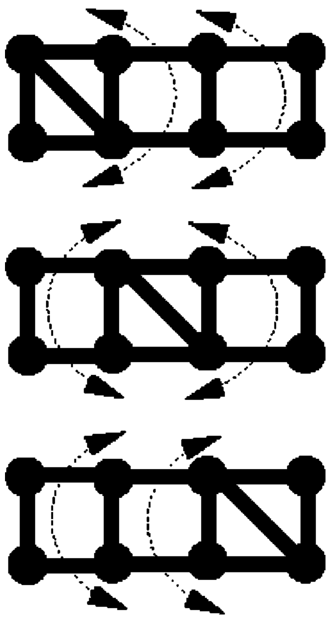

FIG. 2. A system of bars and hinges with three different configurations. The squares with the diagonal bars are rigid, while the others are flexible. The corresponding floppy modes are shown with arrows.

However, there are two important facts to consider in all the previous statements. First the number of floppy modes is a function of the energy. In fact, when the glass becomes fluid, most of the constrictions upon the bond lengths and angles are relaxed and $f$ is raised. For the extreme case of no bonding between atoms, the system behaves without constraints and all the modes are floppy $f=1$. Notice that an ideal gas is a perfect "floppy system." An improvement to Eq. (2) is to make $f$ a function of $E$; then the number of floppy modes is $3Nf(E)$. In such a case, the jump in the specific heat will also depend on $f$, as observed in the experiments. The function $f(E)$ is zero when $E\gg kT_g$ and has a value determined by the average coordination number below the glass transition, i.e., $f(E)=2-\frac{5}{6}\langle r\rangle$. The shape of this function can be estimated using a procedure that we will describe later.

The second consideration is that the number of floppy modes affects the number of minimal energy valleys (usually called inherent structures) that are available when the system has a certain energy. This effect is explained in Fig. 2, where a system of bars and hinges is considered. In the example of Fig. 2, there are no angular forces. Each bar provides a restriction to the system. There are three squares. In one of the squares there is a diagonal bar. As a result, this square cannot be deformed, since the distances between all the hinges are fixed. The other two squares are flexible as indicated by the arrows. Each of these flexible squares can be deformed independently, and the system has two floppy modes (again, without counting the center of mass translation and rotations around it). Now we move the diagonal bar to the second square and the system has the same number of floppy modes, but the structure is different, and the same thing happens if we put the diagonal in the first square. In the landscape formalism, each of these configurations is in a different "inherent structure" and corresponds to a basin with the same energy. This part of the entropy has been studied extensively in the context of rigidity transitions [21]. However, as we will see next, there is a competition between the channel and configurational entropies.

To see how these concepts are applied in a particular case, let us consider the following two-dimensional model that contains all of the previous features that we discussed. Consider a system of $N$ disks interacting with a central force where no angular forces are considered. Each disk has a hard core potential and an attractive part which has a range determined by the parameter $\lambda$. If $\sigma$ is the diameter of the disks and $r$ is the distance between the centers of two disks, the potential is written as

$$V(r)=\begin{cases}\infty, & \text{if } r<\sigma,\\ -V_1, & \text{if } \sigma\leqslant r\leqslant\lambda\sigma,\\ 0, & \text{if } r>\lambda\sigma.\end{cases}$$

The nature of the fluid and solid phases of this system has been studied in previous work [19]. Here we study only the rigidity. Within this model, a bond is formed when the distance between two disks is between $\sigma$ and $\lambda\sigma$. Each bond has an energy $-V_1$, and the energy of the system is just proportional to the number of bonds. This number is proportional to the average coordination number divided by 2 since each bond is shared by two sites. Then, the amount of energy ($E$) of the system is given by

$$E=-V_1N\frac{\langle r\rangle}{2}\simeq-2V_1N(1-f), \tag{3}$$

where it was used that for the mean field approximation in two dimensions $f\simeq[2N-(N\langle r\rangle/2)]/2N$. From the last equation, it is observed that a gas is obtained when the system is 100% flexible ($f=1$) and the state of maximal packing (the hexagonal lattice with maximal coordination $r_{\max}=6$) is overconstrained (there are $N/2$ redundant bonds in the mean field approximation). From the last equation, is clear that $f$ is a function of $E$.

As said previously, there is an entropy provided by floppy mode channels ($S_1$) and by the different configurations of floppy modes ($S_2$). According to our previous assumptions, the first contribution is $S_1\simeq fNk\ln A$ where $A$ is the area of the system. This is only valid in the flexible phase, i.e., before the freezing of the system since at that point it has been suggested that there is a rigidity transition [25]. After freezing, this contribution is zero ($S_1=0$). At high temperatures, the system is a fluid and the entropy is just the same as the one obtained from the available phase space without any interaction. A more realistic assumption although still very rough is to use that $S_1\simeq fNk\ln(A-b)$ where $b$ is proportional to the area occupied by the disks [33], $b\approx N\pi(\lambda\sigma)^2/2$.

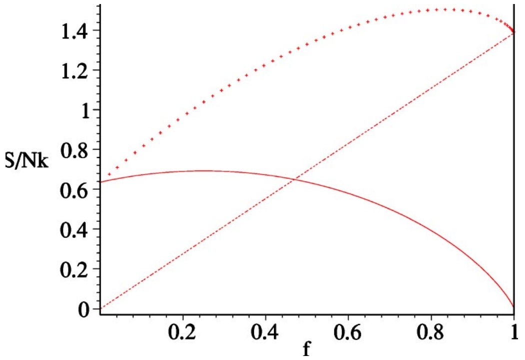

FIG. 3. Contributions to the total entropy (crosses) in units of $Nk$. The dotted line is the contribution from channels ($S_1$) with the aribitrary value $A-b=4$. The solid line is the contribution from different configurations ($S_2$).

The other contribution to the entropy comes from the number of ways in which a configuration with a given $\langle r\rangle$ can be made. Although this number is difficult to calculate, one can suppose a cell model of the fluid, and then just consider the number of ways in which absent bonds can be deleted from the lattice with maximal packing. This number of configurations $[\Omega(f,N)]$ is

$$\Omega(f,N)=\frac{(r_{\max}N/2)!}{(r_{\max}N/2-\langle r\rangle N/2)!\,(\langle r\rangle N/2)!} \tag{4}$$

where $\langle r\rangle$ is a function of $f$. The corresponding configurational entropy is $S_2=k\ln\Omega(f,N)$. A natural way to compute this entropy is to define an order parameter $m(f)$ as

$$m(f)=\frac{(r_{\max}-\langle r\rangle)-\langle r\rangle}{r_{\max}}\simeq\frac{4f-1}{3}. \tag{5}$$

In terms of this parameter, and using Stirling's approximation, the total entropy for $f\geqslant0$ now reads

$$\frac{S_1+S_2}{Nk}=\ln 2+f\ln(A-b)-\frac{[m(f)+1]}{2}\ln[1+m(f)]-\frac{[1-m(f)]}{2}\ln[1-m(f)].$$

For an overconstrained lattice, the expression for the entropy is just given by $S_2$. The expression for $f\geqslant0$ contains the effects that were discussed previously, i.e., the linear dependence of the entropy upon $f$, and the contribution from different structures with the same energy. In Fig. 3 we show a plot of the total entropy and the corresponding contributions for a given $A-b$. It is interesting to note that $S_2$ tends to grow as we diminish the number of floppy modes, since the number of configurations with the same energy grows. Notice that $S_2$ does not have a maximum exactly when $f=0$ due to the mean field approximations; the maximum is shifted to the right. From Eq. (5), this occurs near $\langle r\rangle=4$, i.e., near the two-dimensional rigidity transition. This fact seems to contradict the observation that in the rigidity transition, the experimental nonreversible heat flow is a minimum, which means that the configurational entropy is a minimum. One can expect that in the rigidity transition, a lot of fluctuations will be observed, while in the experiments it seems that the contrary is true [7]. However, the present results show that floppy modes have *two competing effects*; one is the entropy due to the different configurations, but the other is the shape of each basin, since around each minimum, floppy modes form channels that increase the entropy. Thus, as is shown in Fig. 3, when the system passes from flexible to rigid, the number of configurations increases, but the number of channels diminishes. Experimental results suggest that this last effect is more important, since the configurational entropy of a melt with a floppy glass former is higher as the number of floppy modes is increased [7,17].

Finally, the free energy for $f \geqslant 0$ can be written as

$$F(f) = -2V_1(1-f)N - T(S_1+S_2). \tag{6}$$

To compare with the energy landscape formalism, we use that the partition function is the sum of partition functions at inherent structures [34],

$$Z(T) = Z^{ha}(T)\int_0^{\infty} G(E)e^{-E/kT}dE, \tag{7}$$

where $G(E)$ is the number of energy basins with energy $E$, and $Z_i^{ha}(T)$ is the partition function for a system of harmonic oscillators [34]. Since $G(E)$ is always a growing function, and $e^{-E/kT}$ is always decreasing, the integral of Eq. (7) can be replaced by the value at the maximum $\overline{E}$,

$$\int_0^{\infty} G(E)e^{-E/kT}dE \approx G(\overline{E})e^{-\overline{E}/kT}.$$

The corresponding free energy $F$ is

$$\frac{F}{NkT} = -\ln Z(T) = -\ln Z^{ha}(T) - \ln G(\overline{E}) + \frac{\overline{E}}{kT}. \tag{8}$$

As usual, the free energy is just the contribution from the vibrations inside the basin, the entropic component due to the existence of different basins, and an energetic component which reflects the average depth of the landscape at a certain $T$. Now we turn our attention to how $G(\overline{E})$ is affected by the floppy modes. Comparing Eqs. (6) and (8), we get an estimation for $G(\overline{E})$,

$$G(\overline{E}) \approx \exp N\left[-m(\overline{E})\ln(A-b) - \frac{[m(\overline{E})+1]}{2}\ln[1+m(\overline{E})] - \frac{[1-m(\overline{E})]}{2}\ln[1-m(\overline{E})]\right] \tag{9}$$

where $m(\overline{E})$ is obtained from Eqs. (3) and (5),

$$m(\overline{E}) = 1 - 2f(\overline{E}) = \left(1 + \frac{2\overline{E}}{3V_1N}\right).$$

If the channel term is the most important, $G(\overline{E})$ can be approximated by

$$G(\overline{E}) \approx \exp\{N|m(\overline{E})|[\ln(A-b)]\},$$

which has the same general shape as that proposed by Stillinger [35]. The factor $|m(\overline{E})|[\ln(A-b)]$ in the exponential can be identified with the landscape complexity [36].

## IV. CONCLUSIONS

In this article, we have explored the effects of floppy modes in the thermodynamics of glasses. In particular, we showed that a blueshift of floppy modes can be predicted using simple thermodynamical arguments. This leads to the formulation of a simple model, which suggests effects of floppy modes at low temperatures. During the glass transition, floppy modes also play a role. Thus we explored how flexibility and rigidity determine the energy landscape. We found two competing effects that contribute to the entropy in the liquid melt; one contribution is given by channels and the other is the existence of different energy basins. By considering a simple example, we showed how to estimate both contributions, and we discussed the importance of both effects in the window of reversibility. The results of this article seem to confirm Phillip's idea that the glass forming tendency is enhanced at the rigidity transition [37], since although there is an increase in the entropy due to the different energy basins, the pathways provided by floppy modes are absent and the system is easier to trap in a certain minimum.

## ACKNOWLEDGMENTS

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