Simple solvable energy-landscape model that shows a thermodynamic phase transition and a glass transition

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When a liquid melt is cooled, a glass or phase transition can be obtained depending on the cooling rate. Yet, this behavior has not been clearly captured in energy-landscape models. Here, a model is provided in which two key ingredients are considered in the landscape, metastable states and their multiplicity. Metastable states are considered as in two level system models. However, their multiplicity and topology allows a phase transition in the thermodynamic limit for slow cooling, while a transition to the glass is obtained for fast cooling. By solving the corresponding master equation, the minimal speed of cooling required to produce the glass is obtained as a function of the distribution of metastable states.

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Humankind has been using glassy materials since the dawn of civilization. However, their process of formation still poses many questions [1–8]. Glasses do not have long range order and are formed out of thermal equilibrium, resulting in a limited use of the traditional tools of the trade in solid state and statistical mechanics. Moreover, numerical simulations are not able to provide definitive answers, since cooling speeds achieved in numerical simulations are orders of magnitude higher than in real cases [9]. One of the main issues is the nature of the glass transition [10]; for example, is it a purely dynamical effect or there is an underlying thermodynamical singularity? The answer to this question has practical implications, such as how to calculate the minimal cooling speed depending on the chemical composition in order to form a glass, or why some chemical compounds form glasses while others will never reach such a state [11]. Concerning this relationship between chemical composition and minimal cooling speed, Phillips [11] observed that for several chalcogenides (which are benchmark tool glasses obtained by doping group VI elements, such as As_xSe_{1-x} or Ge_xSe_{1-x}), this minimal speed is a function of rigidity. This initial observation was the ignition spark for the extensive investigation on rigidity of glasses [12–19], yet this basic observation has not been quantitatively obtained in glass models.

On the other hand, the energy landscape has been a useful picture to understand glass transition [10]. However, due to its complicate high dimensional topology, it is difficult to obtain closed analytical results. It is not even clear how a phase transition is related with the topology of the landscape, i.e., why a global minimum leads to singularities in the thermodynamical behavior. Clearly, there is a lack of a minimal simple solvable model of landscape that can display a phase and a glass transition depending on the cooling rate. Here we present such a model by combining the two most basic ingredients that are believed to be fundamental in the problem. Furthermore, the model allows us to get a glimpse on the connection between minimal cooling speed, energy landscapes, rigidity, and Boolchand intermediate phases [20,21]. Boolchand intermediate phases are very interesting in the sense that they represent a kind of ideal glass transition due to minimal aging, self-organized stress, and zero nonreversing

heat flow in modulated differential scanning calorimetry [22]. Thus, they are believed to have simple energy landscapes that will help to clarify many issues of the glass transition [22].

Our work is based in a previous model studied by Huse *et al.* [23] and Langer *et al.* [24–26]. This model is based in a well known fact: Glasses are trapped in metastable states, while crystals are global minimums in the landscape. Thus one can simplify the physical picture through the use of a two level system (TLS). If the glassy metastable state has energy E_1 and the crystalline global minimum an energy $E_0 = 0$, the system is trapped in the glassy state due to an energy barrier V measured from E_1, as seen in Fig. 1. However, as we will see below, this model alone does not predict a phase transition at slow cooling, which is a basic feature that any glass theory must reproduce. Here we will show that by adding the energy-landscape complexity, i.e., a distribution of metastable states, one can have a phase or a glass transition depending on the cooling speed.

Let us first briefly summarize the results by Huse *et al.* [23] and Langer *et al.* [24–26], who described the residual population of the metastable state for a TLS at zero temperature. Using the landscape presented in Fig. 1, the cooling process can be described by a master equation in which the probability $p(t)$ of finding the system in the metastable state, assuming that the system is in contact with a bath at temperature T, is [24]

$$\frac{dp(t)}{dt} = -\Gamma_{\uparrow\downarrow} p(t) + \Gamma_{\downarrow\uparrow} [1 - p(t)], \tag{1}$$

where $\Gamma_{\uparrow\downarrow}$ is the transition rate from the upper well to the lower, and the transitions from the lower to the upper take place at rate $\Gamma_{\downarrow\uparrow} = e^{-E_1/T}\Gamma_{\uparrow\downarrow}$. If quantum mechanical tunneling is neglected, $\Gamma_{\uparrow\downarrow} = \Gamma_0 e^{-V/T}$, where Γ_0 is a small frequency of oscillation at the bottom of the walls.

Equation (1) describes the relaxation towards $p_0(T)$, the population at thermal equilibrium obtained from the stationary condition, as can be seen by rewriting Eq. (1) as [24]

$$\frac{dp(t)}{dt} = \Gamma_{\uparrow\downarrow}(1 + e^{-E_1/T})[p_0(T) - p(t)], \tag{2}$$
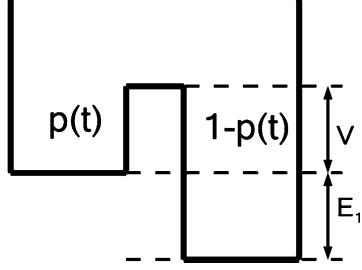
FIG. 1. The two level system energy landscape, showing the barrier height V and the asymmetry E_1 between the two levels. The population of the upper well is $p(t)$.

where $p_0(T)$ is given by

$$p_0(T) = \frac{e^{-E_1/T}}{1 + e^{-E_1/T}}. \qquad (3)$$

When the system is cooled by a given protocol $T = T(t)$, it can be proved that at zero temperature there is a probability $p(T = 0)$ for the system to be in the metastable state, which is indicative of a glassy behavior [25,27].

The model by Huse *et al.* [23] and Langer *et al.* [24–26] is very appealing and can be used to explain low temperature anomalies in glasses [28,29]. However, an important part of the physics is missing in the original model: The system does not present a phase transition at low cooling speeds. To achieve this goal, in this work we introduce a key element to the TLS landscape topology: the multiplicity of states (related with the complexity of the landscape). Again, there is a common agreement that the number of metastable states is much bigger than their crystalline counterparts. Now let us feed this information into the model. Assume that the energy E_1 has a degeneracy g_1, while the ground energy E_0 has degeneracy g_0; thus Eq. (1) needs to be modified to take into account transitions between different states that are in the low and upper wells. Call $p_{\uparrow s}(t)$ the population of one of these g_1 in the upper states, and $p_{\downarrow s}(t)$ the population of one of these g_0 in the low states. Equation (1) becomes

$$\frac{dp_{\uparrow s}(t)}{dt} = -\sum_{l \neq s}^{g_1 - 1} \Gamma_{\uparrow\uparrow}^{sl} p_{\uparrow s}(t) - \sum_m^{g_0} \Gamma_{\uparrow\downarrow}^{sm} p_{\uparrow s}(t) \qquad (4)$$

$$+ \sum_{l \neq s}^{g_1} \Gamma_{\uparrow\uparrow}^{ls} p_{\uparrow l}(t) + \sum_m^{g_0} \Gamma_{\downarrow\uparrow}^{ms} p_{\downarrow m}(t), \qquad (5)$$

where $\Gamma_{\uparrow\uparrow}^{sl}$ denotes the transition rate from state s to l, both in the upper well. The notation for the other transition rates is similar, and an equivalent expression can be written for $dp_{\downarrow s}(t)/dt$. To formulate the model, we use the simplest topology; i.e., all metastable states are connected within them with the same transition rate; i.e., $\Gamma_{\uparrow\uparrow}^{sl} \equiv \Gamma_{\uparrow\uparrow}$. A similar situation holds for the crystalline states $\Gamma_{\downarrow\downarrow}^{sl} \equiv \Gamma_{\downarrow\downarrow}$. Transitions between up and lower states have also the same probability $\Gamma_{\uparrow\downarrow}^{sl} \equiv \Gamma_{\uparrow\downarrow}$ and $\Gamma_{\downarrow\uparrow}^{sl} = \Gamma_{\downarrow\uparrow}$. Under such simple landscape topology, the previous master equation can be reduced to

$$\frac{dp(t)}{dt} = -g_0 \Gamma_{\uparrow\downarrow} p(t) + g_1 \Gamma_{\downarrow\uparrow} [1 - p(t)], \qquad (6)$$

where $p(t) = \sum_{s=1}^{g_1} p_{\uparrow s}(t)$ is the total probability of finding the system with energy E_1. Let us show how Eq. (6) can give a phase transition under thermal equilibrium conditions. In that case, $dp(t)/dt = 0$ and

$$p_0(T) = \frac{g_1 \Gamma_{\downarrow\uparrow}}{g_0 \Gamma_{\uparrow\downarrow} + g_1 \Gamma_{\downarrow\uparrow}} = \frac{(g_1/g_0)e^{-E_1/T}}{1 + (g_1/g_0)e^{-E_1/T}}. \qquad (7)$$

A phase transition can occur if $(g_1/g_0)e^{-E_1/T}$ becomes discontinuous in the thermodynamical limit. The most simple example is the following. Suppose that we have N particles, and the potential is such that the crystalline state is unique $(g_0 = 1)$, with energy $E_0 = 0$, and assume that the number of metastable states grows exponentially with N, as is the case in many glassy systems [9] where $g_1 = e^{N \ln \Omega(E_1)}$. $\Omega(E_1)$ is a measure of the landscape complexity [10]. Also, the only way to make $\langle E \rangle$ an intensive quantity with only one energy is to have $E_1 = N\epsilon$, where ϵ is an energy per particle. As an example, this behavior can be readily obtained when two particles, confined in cells, interact with neighboring cells as in nearly one dimensional models of magnetic walls [30]. For this particular case, $g_1 = 2^N$ and $g_0 = 1$. Using the previous general considerations, $p_0(T)$ can be written as

$$p_0(T) = \frac{e^{[\ln \Omega(E_1) - \epsilon/T]N}}{1 + e^{[\ln \Omega(E_1) - \epsilon/T]N}} = \frac{z^N}{1 + z^N} \qquad (8)$$

with $z = \exp[\ln \Omega(E_1) - \epsilon/T]$. In the thermodynamic limit $N \to \infty$, the function $f(z) = z^N$ develops a discontinuity at $z = 1$, and it is easy to see that there is a phase transition at temperature

$$T_c = \frac{\epsilon}{\ln \Omega(E_1)} \qquad (9)$$

with a discontinuous specific heat

$$c \equiv \epsilon \frac{dp_0(T)}{dT} = \begin{cases} 0 & \text{if } T \neq T_c, \\ \infty & \text{if } T = T_c. \end{cases}$$

Now the model is able to produce a phase transition under thermal equilibrium at a finite temperature, a feature that was not available in the original one [23–26]. This can be clearly seen in Fig. 2 for $g_1 = 2^N$ and $g_0 = 1$, where we plot Eq. (8) for different values of N using dotted lines. Notice how the phase transition is built by a progressive sharpening of the jump in $p_0(T)$ as N grows. According to Eq. (10), the specific heat is just the derivative of $p_0(T)$; thus the sharpening leads to the singularity in the thermodynamical limit.

We will show that a glassy behavior is obtained for fast enough cooling. To solve Eq. (6), one needs to specify the cooling protocol $T = T(t)$, and write the master equation in terms of a dimensionless cooling rate. Two kinds of protocols are useful [24,25]; one is the linear cooling $T = T_0 - rt$, used mainly in experiments, and the hyperbolic one $T = T_0/(1 + Rt)$, which allows a simple handling of the asymptotics involved. For the hyperbolic case, the master equation can be written as

$$\delta \frac{dp(x)}{dx} = -g_1 x^\mu + (g_0 + g_1 x^\mu)p(x), \qquad (11)$$

where $x = \exp(-V/T)$ and $\delta = RV/\Gamma_0 T_0$. The parameter $\mu = E_1/V$ measures the asymmetry of the well. The linear case also follows Eq. (11), since one can rescale the boundary
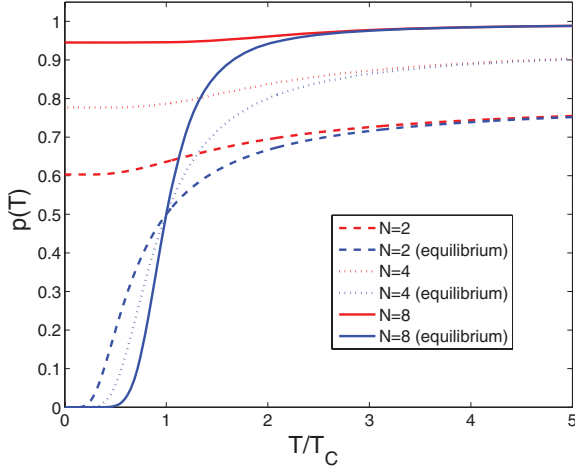
FIG. 2. (Color online) Population as a function of the temperature using a linear cooling for different number of particles $N = 2, 4$, and 8, with $V = 1.0$, $\varepsilon = 1$, $R = 1.4$ and $T_0/T_c = 72$, $g_1 = 2^N$, $g_0 = 1$ obtained by solving the master equation. The equilibrium population obtained for $\delta \rightarrow 0$ is also shown, as indicated in the inset. Notice how the phase transition is built by a progressive sharpening of the jump in $p(T)$ as N grows.

layer [25] that appears in Eq. (11), leading to the same hyperbolic equation with $\delta = r/\Gamma_0 V$. Equation (11) can be solved to give

$$p(x) = \exp\left[\frac{1}{\delta}\left(g_0 x + \frac{g_1 x^{1+\mu}}{1+\mu}\right)\right]$$
$$\times \left\{p(0) - \frac{g_1}{\delta}\int_0^x y^\mu \exp\left[-\frac{1}{\delta}\left(g_0 y + \frac{g_1 y^{1+\mu}}{1+\mu}\right)\right]\right\}.$$

As an example, Fig. 2 shows $p(x)$ for different cooling rates and system sizes, using a linear cooling and $g_1 = 2^N$, $g_0 = 1$, compared with the equilibrium distribution that develops a phase transition at T_c. Notice in Fig. 2 that $p(0)$ is the residual population at $T = 0$, indicative of a glassy behavior. Also, the slope of $dp(T)/dT$ does not tend to infinity, and the corresponding specific heat c is no longer discontinuous, as in real glass transitions.

We can obtain the analytical value of $p(0)$ by assuming that the system was at thermal equilibrium before being cooled at a temperature $T_0 \gg T_c$. In that case $x \rightarrow 1$, and the population is given by the equilibrium distribution, $p_0(x_0) = (g_1/g_0)x_0^\mu/[(g_1/g_0)x_0^\mu + 1]$, where $x_0 = \exp(-V/T_0)$. From Eq. ((11)), we obtain a general expression for $p(0)$,

$$p(0) = \frac{x_0^\mu}{x_0^\mu + (g_0/g_1)}\exp\left[-\frac{1}{\delta}\left(g_0 x_0 + \frac{g_1 x_0^{1+\mu}}{1+\mu}\right)\right]$$
$$+ \frac{g_1}{\delta}\int_0^{x_0} y^\mu \exp\left[-\frac{1}{\delta}\left(g_0 y + \frac{g_1 y^{1+\mu}}{1+\mu}\right)\right]dy.$$

Zero population is only achieved if both terms in Eq. (15) are zero, as is the case for $\delta \rightarrow 0$. Then we recover the phase transition, a fact that makes us confident in the result. To understand more deeply Eq. (13), let us study the particular case $g_1 = e^{N \ln \Omega(E_1)}$ and $g_0 = 1$, with $E_1 = N\epsilon$. The second integral contains the term $g_1 y^{1+\mu} \approx \exp\{[\ln \Omega(E_1) - \varepsilon/T]N\}$, which can be 0 or ∞ in the thermodynamic limit depending

on whether $y < x_c$ or $y \geqslant x_c$, where,

$$x_c \equiv \exp(-V/T_c) = \Omega(E_1)^{-V/\epsilon}. \quad (14)$$

If V does not scale with N, for big N Eq. (13) can be written as

$$p(0) \approx \frac{1}{1+(g_0/g_1)}\exp\left[-\frac{g_1}{\delta\mu}\right] + g_1\gamma(1+\mu, x_c/\delta)\delta^\mu. \quad (15)$$

Here γ is the lower incomplete gamma function, and $x_0 \approx 1$. The evolution of the residual population given by Eq. (15) is shown in Fig. 3 as a function of the cooling speed and system size. As a general trend, the cooling speed required to make a glass with fixed $p(0)$ increases with the system size. Also, it is possible to observe a crossover which separates different behaviors of $p(0)$. For example, in Fig. 3, if $N = 4,5,6$, and 7, $p(0)$ begins to increase for a high δ after it reaches a plateau that begins around $\delta \approx 1$. The same increase is observed for $N = 9$ and 10, although shifted to the right in such a way that it does not appear in the current plot. This crossover is due to the different growing speeds in Eq. (15). The first term of Eq. (15) goes to zero if

$$\delta \ll \frac{\Omega(E_1)^N}{N}\frac{V}{\epsilon} \equiv \delta_2(N), \quad (16a)$$

which defines a speed $\delta_2(N)$. For $\delta > \delta_2(N)$, $p(0)$ is dominated by the first term in Eq. (15). The remaining term in Eq. (15) regulates the residual population for lower speeds $\delta < \delta_2(N)$. This term produces the plateau at a saturating value of $p(0)$,

$$p(0) \approx \frac{1}{1+(N\epsilon/V)} \equiv p_s(0), \quad (17)$$

which starts at

$$\delta_1(N) \equiv \frac{1}{[\Omega^N(E_1)\gamma(1+\mu, x_c/\delta)]^{1/\mu}} \approx 1. \quad (18)$$
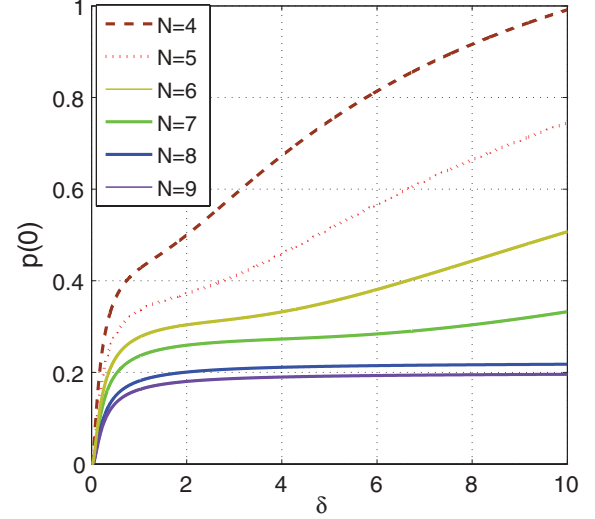

FIG. 3. (Color online) Residual population at $T = 0$ as a function of the cooling speed for different number of particles $N = 10, 15, 20, 25$, and 30, with $V = 0.5$, $\varepsilon = 1$, $R = 1.4$, $g_1 = 2^N$, $g_0 = 1$, and $T_0/T_c = 72$.

For a finite N, this implies that there are two kinds of glassy phases, one obtained for intermediate cooling rates $\delta_2(N) > \delta > \delta_1(N)$ in which $p(0)$ reaches a limiting value. The other kind is obtained for $\delta > \delta_2(N)$.

For $\delta \approx \delta_1(N)$, we obtain the critical rate to make a glass for finite systems,

$$R_1 \approx \Gamma_0 T_0 / V, \tag{19}$$

while in the thermodynamical limit, this leads to a critical R_2,

$$R_2 \approx \frac{\Omega(E_1)^N}{N} \left(\frac{T_0}{\epsilon} \right) \Gamma_0. \tag{20}$$

It is surprising that R_2 does not depend on V; this is a result of the assumption that V does not scale with N. If this is the case, the term $g_1 x_0^{1+\mu}$ in Eq. (13) can determine whether $g_0 x_0$ plays a role in the first exponential, leading to a critical speed that depends on V. Notice that the result is in agreement with the remarkable observation made by Phillips concerning chemical composition and minimal cooling speed required to make glasses [11], since R_2 depends on the number of metastable states. Rigidity provides such an indirect count of metastable and stable states [31,32]. Finally, the minimal cooling speed R_1 can be estimated for real systems, since Γ_0 is given by low frequency harmonic vibrations (usually in the terahertz region). We thus expect a critical hyperbolic cooling rate of order $R_1 \sim 10^{12}$ K/s. Assuming that δ is of the same order for linear cooling, we get $r \sim 10^{12}$ K/s, which is much higher than the usual 10^6 K/s. Such discrepancy is due to the fact that in these results, the energy barrier V does not scale with size as E_1 does; thus the probability of trapping the system in metastable states decreases with the system size, making the cooling speed much higher, as reflected in R_2. This problem can be readily fixed as explained before, although the results are not as clear as the considered case. A further comparison with real cooling speeds requires the identification of the effective parameters of the model, such as energy barriers, metastable states, and landscape complexity. It is worthwhile mentioning that there is an important body of work in these long-standing "energy landscape" types of efforts which are closely related, in which transitions between states are identified with excitations in real glasses. As an example, we can cite Angell's bond lattice model [33,34] or equivalently Stillinger's elementary excitation model [35]. In the bond model, broken bonds or smeared-out versions of interstitial defects can be taken as excitations, and thus provide a clue of the possible energy values for metastable states [33] (these kinds of models are also in agreement with a rigidity approach to the Boson peak and glass transition [36,37]). However, to our knowledge, in those models the question of a critical cooling speed has not been addressed.

In conclusion, we have introduced the topology of the energy landscape in a two level model of glass. As a result, we have a solvable model that has a thermodynamic phase transition for low cooling rates and a glass transition for fast cooling. Finally, an interesting point is how the model can be compared with realistic landscape topologies. It is known that Gaussian landscapes are able to give good fits to simulation data of realistic systems [38–41]. For example, here neither the crystal nor amorphous states have a finite heat capacity, and this is what the Gaussian approach tries to fix [41]. Again, such situation arises because our model simplifies the landscape in such a way that all metastable states and barriers between them have the same energy, resulting in similar transition rates in the master equation. This simplification allows us to solve the master equation although at the price of having zero specific heat. A more realistic case can be obtained by considering the vibrational component on each energy basin and a distribution of barriers. Yet, our critical temperature given by Eq. (9) is akin to the ideal glass transition temperature found in Gaussian landscapes (see for example Eq. (19) in Ref. [42]). Furthermore, the present model can be used as a starting point to study the effects of cooling rates in such realistic landscapes. However, it is more natural to mix the present approach with connectivity graphs, in which transition paths between metastable states and energy barriers are coded in a kind of map [43–46]. In future works, we will pursue this point using more realistic landscapes.

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