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Minimal cooling speed for glass transition in a simple solvable energy landscape model

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HIGHLIGHTS

- A simple solvable energy model landscape is presented.
- This model captures a glass transition or crystallization.
- The minimal cooling rate to obtain a glass is related to the thermal history.
- The glass transition temperature has a logarithmic dependence on cooling rate.

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ABSTRACT

The minimal cooling speed required to form a glass is obtained for a simple solvable energy landscape model. The model, made from a two-level system modified to include the topology of the energy landscape, is able to capture either a glass transition or a crystallization depending on the cooling rate. In this setup, the minimal cooling speed to achieve glass formation is then found to be related with the crystallization relaxation time, energy barrier and with the thermal history. In particular, we obtain that the thermal history encodes small fluctuations around the equilibrium population which are exponentially amplified near the glass transition, which mathematically corresponds to the boundary layer of the master equation. The change in the glass transition temperature is also found as a function of the cooling rate. Finally, to verify our analytical results, a kinetic Monte Carlo simulation was implemented.

1. Introduction

The importance of glassy materials in our societies is indisputable. It is an essential component of numerous products that we use on daily basis, most often without noticing it. Even though the glass formation process has been extensively studied using different approaches, it remains an open and puzzling problem, and this far our best understanding of the process is barely limited at the phenomenological level [1–12]. The reason behind this situation is that glass formation is mainly a non-equilibrium process [13].

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From a fundamental and technological point of view, the most important variable for glass formation is the cooling speed [10,14]. Indeed, the industrial use of metallic glasses has been hampered for a while due to the high cooling speed required in order to form glasses [15–17]. However, by chemical modification, the cooling process of metallic glasses has been improved a lot [18], and very recently it was possible to form a monocomponent metallic glass, achieved by hyperquenching [19]. Regarding the relationship between chemical composition and minimal cooling speed, Phillips [20] observed that for several chalcogenides, this minimal speed is a function of the rigidity. His initial observation was the starting point for an extensive investigation on the rigidity of glasses, yet this observation has not been quantitatively obtained in glass models although it is related with the energy landscape topology when the rigidity is taken into account [21–24].

As the cooling rate effects on glass formation are poorly understood, one would expect that in any sensible model of glass transition, the phase transition to the crystal should be included for low cooling rates. However, this point has been overlooked in several theories of glass formation, even though phase change materials have a paramount importance for information storage technologies. For example, recently it has been possible to access the full temperature range of the crystallization process, including the full supercooled liquid regime, for the chalcogenide-based materials used to store information in rewritable DVDs [25]. On the other hand, the energy landscape has been a useful picture to understand glass transition [9] but, due to its complicate high dimensional topology, it is difficult to understand how cooling rates are related with the topological sampling.

Simple models of glass transition have been introduced trying to capture the physical properties of this phenomenon (see for instance [26,27]). In particular, in a previous paper, a minimal simple solvable model of landscape that can display either a crystalline phase or a glass transition depending on the cooling rate was presented by one of us [28]. Such model, a refinement of a two-level system (TLS) model previously studied [29–33], included the most basic ingredients for a glass formation process: metastable states and the landscape topology [28]. As a result, the model was able to produce either a true phase transition or a glass transition in the thermodynamic limit [28]. Nonetheless, there were important questions that were not tackled in our previous publication. In particular, it was not clear how to define a critical cooling speed that separates the transition either to a glass or to a crystal, and how this critical speed depends upon the physical characteristics of the system like relaxation times, energy barriers and the thermal history. In this study, we answer these open questions by obtaining analytical expressions to all these quantities. To verify these analytic calculations, a kinetic Monte Carlo is performed showing an excellent agreement.

This article is organized as follows: Section 2 is devoted to recall the model and its features, as well as to obtain the system's behavior and an analytical expression of the glassy state when a given cooling protocol is applied [28]. In Section 3, we derive the characteristic relaxation time of our system. In Section 4 we obtain the relation between the metastable state, the cooling rate, the characteristic relaxation time and the thermal history of our system; here we also obtain the expression which relates the glass transition temperature with the energy barrier and the cooling rate. In Section 5 we compare our results with kinetic Monte Carlo simulation. Finally, in Section 6 we summarize and discuss our findings.

2. Revisiting a solvable energy landscape model: glass transition and crystallization

The model is defined as follows: topologically there are many basins in the energy landscape, each corresponding to a possible state of the system [28]. However, there are only two energetic levels (see Fig. 1). One of these levels has energy $E_0 = 0$, while the other has energy $E_1 = N\epsilon_1$, where N corresponds to the number of particles in the system and ϵ_1 gives the energy scale. Within the model, the crystalline state is the one with zero energy, while there are g_1 glassy states with energy E_1. It turns out that $g_1 = \exp(N \ln \Omega)$, where Ω is just the complexity of the energy-landscape [9], taken as $\Omega = 2$ for simplicity. Finally, the model assumes that the energy barriers that separates each of the g_1 states among them are the same, while the barriers that separate each of the glassy states from the crystal are also equal and given by V (see Fig. 1).

When the system is in equilibrium at a certain temperature T, the canonical partition function[1] reads:

$$Z(T, N) = 1 + g_1 e^{-E_1/T}, \tag{1}$$

and the equilibrium probability $p_0(T)$ of the system having energy E_1 is given by the usual ensemble average:

$$p_0(T) = \frac{g_1 e^{-E_1/T}}{1 + g_1 e^{-E_1/T}}. \tag{2}$$

As shown in Ref. [28], for this equilibrium population the system experiences a phase transition associated with crystallization when the temperature crosses the critical value $T_c = \epsilon_1/\log(2)$.

To study the system out of equilibrium, one observes that due to the simple landscape topology, all transition probabilities per time between metastable states are the same. The transition probability per time from each metastable state to the ground state is also equal for all metastable states [28]. In this setup, the probability $p(t)$ of finding the system with energy E_1 at time t obeys the following master equation:

$$\dot{p}(t) = -\Gamma_{10} p(t) + \Gamma_{01} g_1 (1 - p(t)), \tag{3}$$

[1] From now on Boltzmann's constant $k_B = 1$.