

Glassiness in a Model without Energy Barriers

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We propose a microscopic model without energy barriers in order to explain some generic features observed in structural glasses. The statics can be exactly solved while the dynamics has been clarified using Monte Carlo calculations. Although the model has no thermodynamic transition, it captures some of the essential features of real glasses, i.e., extremely slow relaxation, time dependent hysteresis effects, anomalous increase of the relaxation time, and aging. This suggests that the effect of entropy barriers can be an important ingredient to account for the behavior observed in real glasses.

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The nature of the glass transition is a long debated question of much theoretical interest [1]. It is widely believed that the glass transition is mainly a dynamical process where the system can remain trapped in a metastable phase of a finite lifetime depending on the rate of the cooling process. If glasses are slowly cooled from the high-temperature region, then it is possible to reach a crystal phase of very low entropy. But if the system is fast quenched then it reaches a nonequilibrium regime characterized by the existence of very slow relaxation phenomena. Usually, the origin of these very slow relaxations is explained by the existence of a large number of metastable states separated by energy barriers [1]. The heights of the energy barriers are widely distributed and the system gets trapped in this metastable phase during its time evolution.

Recently, there have been developments towards a mean-field theory of glasses. In those cases one studies systems without quenched disorder with the aid of replica theory [2]. One finds the existence of a dynamical transition T_D where the correlation time diverges. Below that temperature the system is always off equilibrium and relaxes towards a dynamical state of higher energy. At a lower temperature replica symmetry breaks and a large number of states dominate the statics. Below the dynamical transition temperature the system remains trapped in a very complex free energy landscape with huge free energy barriers. In mean-field theory, the height of these free energy barriers increases exponentially fast with N and metastable states have an infinite lifetime. Generally speaking, free energy barriers get contributions from an energetic part and an entropic part. In real structural glasses we expect the effects of energy barriers to be substantially different from that in mean-field theory because of the existence of nucleation processes [3]. Nevertheless, the effect of entropy barriers should not be so dependent on the range of the interaction. Then we expect entropy barriers to be a relevant mechanism in mean-field as well as in short-range models.

The purpose of this work is to understand the role of entropy barriers in the behavior observed in structural glasses. By entropy barriers we mean the existence

of a very small number of directions in phase space where the energy decreases. We propose a mean-field model with pure entropy barriers and without metastable states. The phase space of this model is very simple and resembles a golf-hole landscape. It mainly consists of flat directions in energy with a very small number of channels where the energy decreases. Although the model has no thermodynamic transition, it shows a behavior reminiscent of real glasses.

The model.—Let us suppose N distinguishable identical particles that can occupy N different states. The Hamiltonian is defined by

$$H = -2 \sum_{r=1}^N \delta_{N,0}, \quad (1)$$

and the energy per site is given by the fraction of occupied states. The N_r are the number of particles that occupy the state r (r runs from 1 to N), and they satisfy the constraint

$$\sum_r N_r = N. \quad (2)$$

The model defined in Eq. (1) can be mapped into a Potts model with a large number of states N with Hamiltonian

$$H = - \sum_{r=1}^N |m_r|, \quad (3)$$

where m_r is the magnetization of state r , $m_r = N_r - 1$. Looking at the simple Hamiltonian of Eq. (1) we observe that there is a trivial ground state with energy per particle $e_{GS} = -2(1 - 1/N) = -2$ in the large N limit. In this ground state all the N particles occupy one state, its degeneracy being equal to N . At high temperatures we expect all configurations to have the same probability, and the energy per particle in this limit is $-2[(N-1)/N]^N = -2/e$. As the temperature is decreased the number of occupied states decreases while the occupied states increase their occupation numbers N_r . Let us suppose we introduce a dynamics for the model Eq. (1) (which gives the equilibrium Boltzmann distribution). The time evolution of the system as the temperature is decreased is as follows. The rate of variation of the

number of particles in one state increases due to the particles which reach the state and decreases due to the particles which leave that state. The energy decreases when one state is emptied during the dynamical process. Because the total number of particles is conserved, as the number of occupied states decreases the time the system needs to empty a further state also increases. In this off-equilibrium situation the occupation numbers N_r of the occupied states perform a random walk and the energy Eq. (1) decreases very slowly to the static value at that temperature. This model has no dynamical phase transition, but it shows the onset of very slow relaxations in the low-temperature region (below $T \approx 0.2$ close to the maximum of the specific heat). We will see that the main characteristics of this model are strong dependence of the energy of the system with the cooling rate, hysteresis effects, anomalous increase of the relaxation time, and presence of aging.

Statics of the model.—In order to solve the statics of this model we have to compute the partition function. We will suppose that we have N particles and each particle i is associated with a variable σ_i that can take N possible values according to the state the particle occupies.

The partition function is given by

$$Z = \frac{1}{N!} \sum_{\sigma_i} \exp\left(2\beta \sum_{r=1}^N \delta_{N,r,0}\right), \quad (4)$$

where the factor $N!$ in the denominator is a normalization constant in order to make the free energy extensive with N . The occupation numbers N_r satisfy the constraints $\sum_r N_r = N$ and $N_r = \sum_{i=1}^N \delta_{\sigma_i,r}$. Using the relation

$$N^N = \sum_{N_r=0}^N \frac{N!}{\prod_{r=1}^N N_r!} \quad (5)$$

(where the sum runs over the N_r that obey the constraint $\sum_r N_r = N$), Eq. (4) can be rewritten in terms of occupation numbers as

$$Z = \sum_{\{N_r=0\}} \frac{1}{\prod_{r=1}^N N_r!} \exp\left(2\beta \sum_{r=1}^N \delta_{N,r,0}\right) \delta\left(\sum_r N_r - N\right). \quad (6)$$

We use the integral representation for the delta function,

$$\delta(m) = \frac{1}{2\pi} \int_0^{2\pi} d\lambda e^{i\lambda m}, \quad (7)$$

where m is an integer. Substitution into Eq. (6) leads to

$$Z = \int_0^{2\pi} \frac{d\lambda}{2\pi} \exp N \left[-i\lambda + \ln \left(\sum_{M=0}^N \frac{\exp(i\lambda M + 2\beta \delta_{M,0})}{M!} \right) \right]. \quad (8)$$

The integral in the previous equation can be readily evaluated by the saddle point method in the large N limit. The saddle point $\lambda = iz$ gives the free energy

$\beta f = -\text{Max}_z A(z)$ with

$$A(z) = -z + \ln(e^{2\beta} - 1 + e^{e^z}). \quad (9)$$

The saddle point equation is $e^{2\beta} - 1 = (y - 1)e^y$ where $y = e^z$. The solution to this equation gives a value y^* . The free energy is given by $f = -y^*/\beta$ and the internal energy $u = -2e^{2\beta}/y^* e^{y^*}$. We have checked that the first orders in the high-temperature expansion of Eq. (4) for the energy coincide with the previous expression. The energy goes to -2 at zero temperature (see Fig. 1). The specific heat (first derivative of the energy) increases approximately like $1/T^2$ as the temperature is decreased and shows a maximum at $T \sim 0.20$. At high temperatures the entropy converges to 1 (the number of configurations at infinite temperature goes like $N^N/N!$, the dominant term for the entropy being 1). This solution is stable but gives a negative entropy below $T = 1/\beta \approx 0.345$. Because the entropy at zero temperature diverges like $\ln(T)$ (the number of configurations in this limit being $N/N!$), negative entropies are allowed in the model and there is no sign of a thermodynamic phase transition.

Dynamics of the model.—We have performed Monte Carlo (MC) dynamical calculations in this model with the Metropolis algorithm. It is simple enough to allow very fast computations for very large values of N . We did two kinds of numerical experiments. First we performed annealings starting from a random initial configuration. The temperature was slowly decreased and the energy was computed over t_0 MC sweep (a MC sweep corresponds to N trials to change the state of the—randomly chosen—particles). Also we measured the energy starting from the ground state configuration (only one state occupied) by slowly increasing the temperature. Results are shown in Fig. 1 for $N = 20000$ and for the static energy. Numerical computations for a larger number of particles ($N = 10^5$) show that finite-size effects are negligible. Below $T \approx 0.17$ we observe a strong dependence of the energy on the cooling rate and a slow relaxation of the

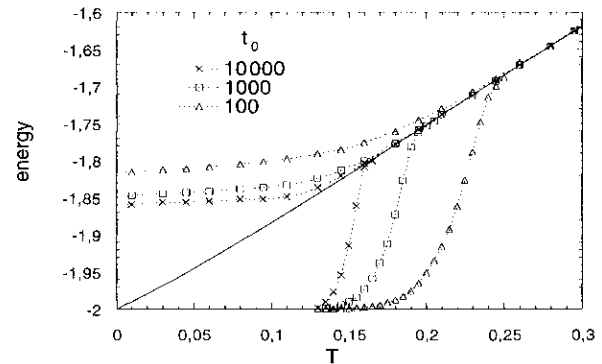


FIG. 1. Energy as a function of temperature for two different processes (cooling and heating) and three different cooling rates t_0 (defined as the number of MC sweeps per temperature step, this being 0.005). The continuous line is the static energy.

energy to its equilibrium value. Figure 1 also shows the strong dependence of the energy on the temperature change rate during the heating process. The numerical data merge to the static result at a certain temperature. This is also the temperature at which the energy departs from the static value in the cooling procedure. The dependence of this merging temperature on the time spent on the cooling rate is an estimate of the relaxation time.

We now want to show that the energy converges to its equilibrium value. We have studied the relaxation of the energy at zero temperature starting from an initial random distribution of particles. Because there are no metastable states, the system can reach the ground state. We have measured the time the system takes to reach the ground state at zero temperature as a function of the number of particles. We have computed $\langle \ln(\tau) \rangle$ for different values of N ranging from 5 to 20 (the average $\langle \dots \rangle$ means average over different random initial conditions). We find the typical time very well described by $\tau \approx 0.39 \exp(0.67N)$. This means that the system takes an exponentially large time to reach the ground state. We have not succeeded in deriving an exact expression for the decay of the energy at zero temperature in the infinite N limit. The problem, being highly nontrivial, can be approximated, taking into account the previous result for the exponentially growing time. We argue that the time dt the system needs to decrease the fraction of occupied states in a quantity $d(N_{oc}/N)$ scales like

$$dt \approx \exp(N/N_{oc}) d(N_{oc}/N). \quad (10)$$

For finite values of N this expression yields an exponentially large time for reaching the ground state. The previous expression means that for a small number of occupied states the rate of decrease of the energy is also small (there are less states with more particles per state to be emptied). Using $u = -2(1 - N_{oc}/N)$ we get for the decay of the energy

$$t = \int_{u_0}^u du \exp\left(\frac{2}{2+u}\right), \quad (11)$$

where u_0 is the initial energy at time zero. We have measured the decay of the energy as a function of time. While this expression is only approximate, it shows a remarkable agreement with the numerical data especially in the large time region over several decades of time. The relaxation of the energy, far from being of a logarithmic or algebraic type, is extremely slow as Eq. (11) shows. The fact that the energy converges to the static result at zero temperature suggests that a dynamical transition at a finite temperature is absent. In what follows we will check this point by computing the relaxation time.

The relaxation time and aging.—To fully characterize the dynamics of this model we have computed the relaxation time. We can define two types of correlation functions, one for the σ_i variables, the other one for the energy state variables. In the regime of low temperatures the system performs a random walk changing particles

from one state to another, and the appropriate correlation function is given by the state to state energy function,

$$C_e(t, t') = \frac{\sum_{r=1}^N [e_r(t') - u(t')] [e_r(t) - u(t)]}{\sum_{r=1}^N [e_r(t) - u(t)]^2}, \quad (12)$$

where $e_r(t) = \delta_{N_r(t)0}$ and $u(t)$ is the mean energy per site at time t . We have normalized it in order to have $C_e(t, t) = 1$. For times t larger than the correlation time $\tau(T)$ the $C_e(t, t')$ should depend only on the time difference $t' - t$ ($t' > t$) and decay exponentially with time $C_e(t, t') \sim \exp[-(t' - t)/\tau]$. For $t \ll \tau(T)$ the system is off equilibrium, aging effects are present, and time translation invariance is broken. We have measured the relaxation time as a function of the temperature in the low-temperature region. Calculations for this model are fast enough to allow one to compute several orders of magnitude in the relaxation time. Results are shown in Fig. 2. There is no sign of algebraic divergence at any finite temperature. While a pure Arrhenius divergence $\tau \sim \exp(A/T)$ does not fit well enough (data present a systematic curvature in Fig. 2), we find that a Vogel-Fulcher law $\tau \sim \exp[A/(T - T_0)]$ [4] describes extremely well the increase of the relaxation time. The value of $T_0 \approx 0.02$ is stable to include more points in the fit and is definitely better than the Arrhenius one. We do not attach special physical meaning to the value of T_0 besides the indication of an anomaly in the divergence of the relaxation time. This is different from the case of models where metastability is present where T_0 can be identified as a thermodynamic transition temperature [5].

The dynamical transition in this model takes place at $T = 0$, and we expect for t finite the correlation function of Eq. (12) to display aging. Introducing the waiting time t_w and redefining the times $t_w = t$, $t' = t + t_w$ in Eq. (12) we find that $C_e(t_w, t_w + t)$ is pretty well

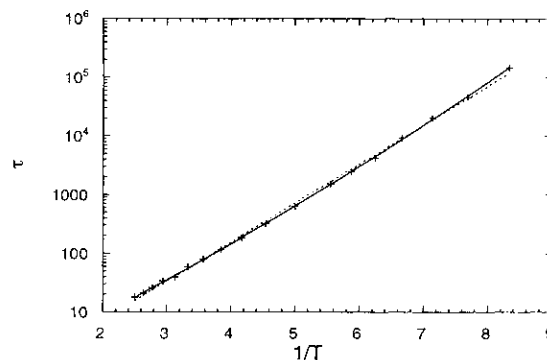


FIG. 2. Relaxation time as a function of $1/T$. The continuous line is the Vogel-Fulcher law $\tau = A \exp[B/(T - T_0)]$ with parameters $A = 0.89$, $B = 0.51$, and $T_0 = 0.02$. The dotted line is the fitted Arrhenius law $\tau = A \exp(B/T)$ with $A = 0.63$ and $B = 0.66$. Error bars for the relaxation time are of the size of the crosses.

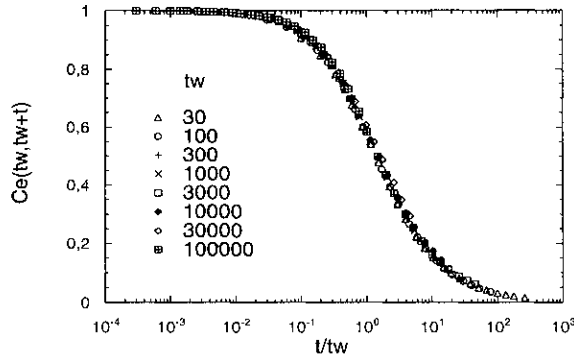


FIG. 3. $C_e(t_w, t_w + t)$ for $N = 100\,000$ as a function of t/t_w for different t_w values at zero temperature.

described by the scaling law

$$C_e(t_w, t_w + t) = f(t/t_w). \quad (13)$$

Similarly to other mean-field models [6,7], it is very plausible that this scaling behavior is exact in the large t_w limit at least at zero temperature. Results are shown in Fig. 3. Data collapse in a single curve; the scaling function f of Eq. (13) scales like $f(x) \approx 0.78x^{-0.70}$ for large values of x . If we define $u_{EA} = \lim_{t_w \rightarrow \infty} C_e(t_w, 2t_w)$ we find that this value jumps discontinuously to a finite value ≈ 0.58 at $T = 0$ being zero at any finite T in agreement with the absence of any finite T dynamical transition.

We can now summarize our results. We have introduced a simple model without energy barriers (i.e., without metastable states) and without disorder. We have exactly solved the statics while the dynamics has been clarified by numerical computations of the model. Relaxation is extremely slow at low temperatures due to the presence of high entropy barriers, i.e., the existence of small number directions in phase space where energy decreases. While the system has no thermodynamic transition, it displays the main features of real glasses, i.e., extremely slow relaxation, time dependent hysteresis effects, anomalous increase of the relaxation time, and aging. This suggests that the presence of activated energy barriers is not the only possible ingredient needed to find a Vogel-Fulcher behavior (and eventually Arrhenius behavior) for some transport quantities. The fact that the relaxation time can be nicely fitted to a Vogel-Fulcher law in this model is an indica-

tion that the existence of anomalies in the relaxation time can be affected by entropy barrier effects. The behavior observed in this model suggests that it is not easy to disentangle the effects of energy barriers from the effects of entropy barriers, at least experimentally. Real glasses do have energy barriers, and it is clear that this model cannot explain all the experimentally observed features (for instance, existence of a crystallization transition). Interestingly enough, it presents the main dynamical features observed in structural glasses. The presented model is of mean-field type because a spatial arrangement of the states is absent and it is possible to include spatial correlations. Also one can consider generalizations of this model, for instance, defining the energy as given by the number of occupied states above a certain finite level k . In this last case we expect to find similar results to those presented here.

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