

Structural Glass Transition and the Entropy of the Metastable States

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The metastable states of a glass are localized and counted by adding a weak pinning field that explicitly breaks the ergodicity. The entropy of the metastable states, that is, the logarithm of their number, is extensive in a range of temperatures $T_s < T < T_c$ only. It is argued that T_s and T_c are the ideal calorimetric and kinetic transition temperatures, respectively. An explicit computation of the metastable states entropy for a $(\vec{\phi}^2)^2$ model is given.

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During the last decade, a great deal of work has been devoted to the understanding of the glass transition. Basically, two different approaches have been employed to tackle this problem. On the one hand, the density functional theory (DFT) [1] is an equilibrium approach where the static density field obtained through the minimization of a free-energy functional becomes inhomogeneous below the structural glass transition temperature. Experimentally, however, the glass transition temperature T_g depends on the cooling rate [2]. Therefore, it does not seem to be related to a well-defined equilibrium transition as predicted by DFT. On the other hand, the mode coupling theory (MCT) [3], using a self-consistent treatment of the microscopic dynamical correlation and response functions in the liquid phase, predicts that the onset of the glassy state is due to a kinetic transition at a temperature T_c higher than T_g . The quasibraking of ergodicity at T_c coincides with the appearance of nonvanishing density fluctuations, the system becoming partially frozen in metastable states with very large relaxation times. Though MCT strengthens the intuitive feeling that the presence of metastable states in the free-energy landscape is responsible for the dynamical arrest arising at the glass transition, the precise relationship between the dynamic and static descriptions of glasses is still to be established. This Letter is an attempt to clarify this important issue.

As was shown some years ago, the connection between the dynamic and the static approaches can be made more transparent in the special case of mean-field spin glasses [4,5]. It has indeed been found that the models exhibiting a discontinuous replica symmetry breaking [6] at the static transition temperature T_s present a dynamic transition at a higher temperature T_c below which equilibrium is never reached [4,5,7,8]. In addition, the temperature T_c whose significance is *a priori* purely dynamical may be related to the equilibrium free energy using the Thouless-Anderson-Palmer (TAP) approach [7,9]. In the TAP formalism, one writes the set of equations that the mean-field local magnetizations $M(x)$ must satisfy. The correct replica symmetric (RS) free-energy density is given by the homogeneous "liquidlike" solution $M(x) = M$ for high temperatures T down to T_s . Surprisingly enough,

in an intermediate range $T_s < T < T_c$, the *same* RS free-energy density is also achieved by the weighted sum of an exponential number of space-dependent solutions $M(x)$ with a higher free energy [4]. At T_c , a rather subtle transition takes place: there appear an exponential number of spin-glass-like metastable states in the free-energy landscape leading to a complete dynamical freezing of the system while at the same time the free energy itself does not show any singularity since the equilibrium state remains nonglassy. To what extent these results may be applied to structural glasses is a crucial question [4,5,10].

In this Letter, we shall present an alternative and purely thermodynamical method to investigate the metastable states in the equilibrium free-energy landscape in any glassy system. More precisely, we shall define the entropy S_{hs} as the logarithm of the number of these "hidden" metastable states and present a general scheme to compute this quantity. In the case of mean-field models, the results of the TAP approach are recovered: S_{hs} is extensive in the range of temperatures $T_s < T < T_c$ only. Since our approach is *a priori* valid beyond the mean-field level, we shall argue that the same holds in finite dimension and that these two temperatures then correspond to the ideal calorimetric and kinetic temperatures, respectively. An example of the calculation of the metastable states entropy S_{hs} and the glassy correlation functions inside these states will be given for a $(\vec{\phi}^2)^2$ model.

Let us start with a theory of a field $\phi(x)$ defined by a Hamiltonian $H[\phi]$. For simplicity, we shall use scalar notation though x spans a D -dimensional space and $\phi(x)$ can be an N -component field. The equilibrium Gibbs free energy at the temperature $T = 1/\beta$ is given by

$$F_\phi(\beta) = -\frac{1}{\beta} \log \int d\phi(x) \exp\{-\beta H[\phi]\}. \quad (1)$$

For the usual ferromagnet below the Curie temperature, the physical decomposition of the Gibbs free energy into two states of opposite magnetizations may be obtained by imposing a small (but finite) external field aligned along the up or down directions. In the case of disordered systems or glasses, there is, however, no *a priori* privileged direction towards which the field $\phi(x)$ will point once

stuck in a metastable state. We can nevertheless choose a possible direction, given by another field $\sigma(x)$, and compute the free energy of our system when it is weakly pinned by this external quenched field

$$F_\phi[\sigma, g, \beta] = -\frac{1}{\beta} \log \int d\phi(x) \exp\left\{-\beta H[\phi] - \frac{g}{2} \int dx [\sigma(x) - \phi(x)]^2\right\}, \quad (2)$$

where $g > 0$ denotes the strength of the coupling. This free energy (2) will be small when the external perturbing field $\sigma(x)$ lies in a direction corresponding to the bottom of a well of the unperturbed free energy (1). Therefore we should be able to obtain useful information about the free-energy landscape by scanning the entire space of the configurations $\sigma(x)$ to locate all the states in which the system can freeze after spontaneous ergodicity breaking ($g \rightarrow 0$) [11]. According to this intuitive idea, we now consider the field $\sigma(x)$ as a thermalized variable with the "Hamiltonian" $F_\phi[\sigma, g, \beta]$. The free energy of the field σ at inverse temperature βm where m is a positive free parameter therefore reads

$$F_\sigma(m, \beta) = \lim_{g \rightarrow 0^+} \left(-\frac{1}{\beta m} \log \int d\sigma(x) \exp\{-\beta m F_\phi[\sigma, g, \beta]\} \right). \quad (3)$$

When the ratio m between the two temperatures is an integer, one can easily integrate $\sigma(x)$ in Eq. (3) after having introduced m copies $\phi^\rho(x)$ ($\rho = 1, \dots, m$) of the original field to obtain the relation

$$F_\sigma(m, \beta) = \lim_{g \rightarrow 0^+} \left(-\frac{1}{\beta m} \log \int \prod_{\rho=1}^m d\phi^\rho(x) \exp\left\{-\beta \sum_{\rho} H[\phi^\rho] - \frac{g}{2m} \sum_{\rho < \lambda} \int dx [\phi^\rho(x) - \phi^\lambda(x)]^2\right\} \right) \quad (4)$$

up to an irrelevant additive constant. The meaning of relation (4) is clear. We have to study the statics of m interacting systems, with an attractive coupling between themselves. An alternative formulation of the intuitive idea expressed above is then that several coupled systems evolving in the same free-energy landscape will have a tendency to "condense" in the same metastable states since their relative distances in such states are smaller than in the liquid state. However, the original free-energy landscape of a single system is recovered only in the limit $m \rightarrow 1$, that is, when the pinning field σ is annealed at the same temperature as ϕ : $F_\phi(\beta) = F_\sigma(m = 1, \beta)$ from (4). The basic idea of this Letter is to decompose $F_\sigma(m = 1, \beta)$ into its energetic and entropic contributions to obtain

$$S_{hs}(\beta) = \beta [F_{hs}(\beta) - F_\phi(\beta)], \quad (5)$$

where $S_{hs}(\beta) = \beta \partial F_\sigma / \partial m|_{m=1}$ and $F_{hs}(\beta) = \partial(mF_\sigma) / \partial m|_{m=1}$ are, respectively, the entropy and the "internal energy" of the field σ . The subscript "hs" stands for hidden states. We stress that $S_{hs}(\beta)$ and $\beta^2 \partial F_\phi / \partial \beta$, which is the entropy of the field ϕ , are two distinct quantities with different physical meanings.

To get some insights into the significance of Eq. (5), we shall now turn to the particular case of disordered mean-field systems and show how it rigorously gives back the analytical results derived within the TAP and dynamical approaches [4,7,9,10,12]. We shall then analyze the physical meaning of identity (5) for the general case of glassy systems.

The free energy $F_\phi(\beta)$ of a mean-field disordered system is a self-averaging quantity which may be computed using the replica trick [6] to end up with $F_\phi(\beta) = \lim_{n \rightarrow 0} \text{Ext}_{\{q^{ab}\}} \mathcal{F}_\phi(\{q^{ab}\})$. $q^{ab} = \int dx \phi^a(x) \phi^b(x)$ are the overlaps between the n replicas. Above the static transition temperature T_s , the physical saddle point of \mathcal{F}_ϕ is RS $q^{a \neq b} = q$. If we now compute the free energy (3) of

the field σ by introducing n replicas and averaging over the quenched disorder, we obtain from Eq. (4) the same free-energy functional \mathcal{F}_ϕ where the number of replicas $\phi^{a\rho}(x)$ now equals $n \times m$ and with an additional term $(g/2m) \sum_{\rho, \lambda=1}^m q^{a\rho, a\lambda}$. This interaction term explicitly breaks the symmetry of permutations of the $n \times m$ replicas [13] into n groups of m indistinguishable replicas. Consequently, even above T_s , the simplest ansatz one can resort to contains at least one step of replica symmetry breaking (RSB), which reads

$$F_\sigma(m, \beta) = \text{Ext}_{q_0, q_1} \mathcal{F}_\phi(q_0, q_1, m, \beta), \quad (6)$$

when $g \rightarrow 0^+$. As a result of the introduction of the field σ , we have obtained the usual one-step expression of the free energy but without any optimization over the free parameter m , which we can choose at our convenience (see [14] for a related case where σ acquires a simple geometrical interpretation). Let us now send $m \rightarrow 1$ while $T > T_s$. The saddle-point equation over q_0 becomes identical to the RS equation for q . Thus $q_0 = q$ and we find $F_\sigma(m = 1, \beta) = F_\phi(\beta) = \text{Ext}_q \mathcal{F}_\phi(q, \beta)$ as expected. Defining $\mathcal{V}(q_1) \equiv \beta \partial \mathcal{F}_\phi / \partial m (q_0 = q, q_1, m = 1, \beta)$, the optimization condition over the second overlap implies that q_1 must be a stable local minimum of \mathcal{V} . The entropy of σ is then $S_{hs} = \mathcal{V}(q_1)$. It turns out that \mathcal{V} defined above is equal to the potential recently introduced in mean-field glasses [10,15] to compute the temperature T_c at which the relaxational dynamics exhibits a drastic slow down [4,7] as mentioned in the introduction. The typical behavior of the entropy $S_{hs}(\beta)$ is as follows. At high temperature, there is only the RS solution $q_1 = q$, $S_{hs} = 0$. At a given T_c , there appears a nontrivial saddle point q_1 [which shifts the free energy (6) by an extensive amount [13] and must then be preferred], and the entropy S_{hs} shows a first order jump. It has been recently verified in the particular case of the random orthogonal model [12] that the entropy S_{hs} defined

here coincides with the logarithm of the number of TAP solutions [16], which is sometimes called complexity or configurational entropy [4,17]. When T decreases, S_{hs} goes down and vanishes at T_s . The identity $S_{hs}(T < T_s) = 0$ is mathematically equivalent to the usual optimization condition of \mathcal{F}_ϕ with respect to m below the RSB transition temperature. Therefore, this optimization condition, whose meaning has always been far less clear than the optimization with respect to the overlaps q_0 and q_1 [6], may be interpreted as the absence of an exponential number of contributing states below T_s .

The significance of formula (5) may now be discussed for glasses in general. At high temperature, the pinning due to σ is not sufficient to break ergodicity: $F_{hs}(\beta) = F_\phi(\beta)$ and $S_{hs}(\beta) = 0$. Physically, there exists only one state. When the temperature goes down, there may appear some barriers that separate an exponential number of metastable states of free energies higher than the true $F_\phi(\beta)$. As long as the number of these states does not compensate for their small weights, they are not "seen" by the Gibbs partition function. At some temperature T_c , their number $e^{S_{hs}}$ becomes large enough to make up for the difference of free energies and the identity (5) expresses this compensation mechanism. In a system with finite range interactions, the ergodicity breaking taking place at T_c is not complete. The partial freezing inside the metastable states makes the dynamics very slow but does not forbid some microscopic changes (the so-called activated processes) [3], allowing the system to relax towards the liquid equilibrium state by visiting more and more states and diminishing its free energy [4,10]. Thus, no sharp transition occurs at T_c , and it is reasonable to think that T_c should coincide with the ideal kinetic transition temperature predicted by MCT since it detects the first occurrence of glassy states having a nonvanishing weight in the partition function. Below T_c , $F_\phi(\beta)$ comes from the superposition of many states with high free energies. The number $e^{S_{hs}}$ of these hidden states decreases since their free energy F_{hs} gets closer and closer to the true value F_ϕ . At a given temperature T_s , these states cease to be metastable since their free energy F_{hs} equals F_ϕ , implying from (5) that the entropy S_{hs} is not extensive anymore [17]. The true thermodynamical transition therefore takes place at T_s , which should correspond to the ideal calorimetric glass transition temperature [18]. Below T_s , formula (5) cannot hold any longer since it would predict a negative configurational entropy of metastable states having a lower free energy than F_ϕ . Physically, one expects that freezing into a small (nonexponential) number of states will still occur and that $S_{hs}(T < T_s) = 0$. As a consequence, the effective temperature of the states, that is, of the field σ , becomes different from the temperature of the field ϕ : their ratio m is determined through the condition that the hidden states' entropy vanishes. More precisely, the freezing implies that the σ 's act more and more as a quenched disorder for the field ϕ , that is, their temperature becomes higher than T and m lower than one [19]. Furthermore,

let us notice that if S_{hs} is already nonextensive at T_c , then T_c and T_s must coincide. This is what happens for systems with a continuous RSB transition [6] where the intermediate phase $T_s < T < T_c$ is skipped. Such systems seem therefore to exhibit a less generic behavior [4,5].

Formula (4) is a convenient starting point to compute S_{hs} in the case of systems without quenched disorder [11]. We begin with m uncoupled copies $\phi^\rho(x)$ of the model. The matrix of the correlation functions of the global system is then *a priori* diagonal: $\langle \phi^\rho(x) \phi^\lambda(y) \rangle = \delta^{\rho\lambda} G(x-y)$. For simplicity we shall assume that in the liquid phase the average value of the field $\langle \phi(x) \rangle$ is equal to zero. The onset of the glassy phase will be characterized by the appearance of many metastable states α , each of them having a weight \mathcal{P}_α , in which the expectation value $\langle \phi(x) \rangle_\alpha$ does not vanish anymore, and therefore by the emergence of nonzero off-diagonal propagators $G_{hs}(x-y) = \sum_\alpha \mathcal{P}_\alpha \langle \phi(x) \rangle_\alpha \langle \phi(y) \rangle_\alpha = \langle \phi^\rho(x) \phi^\lambda(y) \rangle$ ($\rho \neq \lambda$) in the limit $m \rightarrow 1$ [20]. As discussed above, the diagonal correlation function $G(x-y) = \sum_\alpha \mathcal{P}_\alpha \langle \phi(x) \phi(y) \rangle_\alpha$ is simply obtained from the calculation of $F_\phi(\beta)$ for a single system ($m = 1$). The computation of $F_\sigma(m \neq 1, \beta)$ is technically more delicate since a perturbative calculation in the presence of a weak coupling g between the copies will not generate (in the limit $g \rightarrow 0$) an effective correlation $G_{hs}(x-y) \neq 0$ and will not detect the first order glass transition. We shall now present a simple self-consistent calculation that permits us to obtain S_{hs} and $G_{hs}(x-y)$.

The example we shall consider is a $O(N)$ model with a quartic interaction: $H[\vec{\phi}] = \frac{1}{2} \int dx dy \vec{\phi}(x) (-\Delta + \nu) \vec{\phi}(y) + (1/4N) \int dx [\vec{\phi}(x)^2]^2$. We do not expect this model to exhibit a glass transition for large N , but the small N case may have an important physical interest; e.g., polymers that are related to $N \rightarrow 0$ [21] are known to have a glassy behavior at low temperatures. The free energy F_σ may be computed using a self-consistent screening approximation [22]. This $1/N$ expansion is exact to order $1/N$ and contains a partial resummation of an infinite class of diagrams and is thus well defined in the whole range $0 < N < \infty$. One obtains $F_\sigma(m, N, \nu)$ as an extremum over the set of all propagators $G(k)$ and $G_{hs}(k)$ [20,23]. When $m \rightarrow 1$, the diagonal propagators are solutions of the implicit equations

$$\frac{1}{G(k)} = k^2 + \nu + \int dq G(q) + \frac{2}{N} \int dq \frac{G(k-q)}{1 + \Pi(q)}, \quad (7)$$

where $\Pi(k) \equiv \int dq G(k-q)G(q)$. Equation (7) is identical to Bray's original result as expected [22]. The entropy of the metastable states then reads

$$S_{hs}(N) = \text{Ext}_{G_{hs}(k)} \int dk \left[s \left(\frac{G_{hs}(k)}{G(k)} \right) - \frac{1}{N} s \left(\frac{\Pi_{hs}(k)}{1 + \Pi(k)} \right) \right], \quad (8)$$

where $\Pi_{hs}(k) \equiv \int dq G_{hs}(k-q)G_{hs}(q)$ and $s(x) \equiv -x - \log(1-x)$. The numerical resolution of the

saddle-point equations stemming from Eqs. (7) and (8) in dimension $D = 3$ (on small lattices) seem to show that a nonzero set of propagators G_{hs} may appear when N becomes lower than a given N_c that depends on the bare mass ν . Despite different choices of ν , we have always found $N_c < 1$. A more careful analysis of the equations would, however, be necessary. In dimension $D = 0$, the equations for G and G_{hs} may be solved exactly, and we find that there exists a first order transition at some small enough critical value of N . One can show that N_c is always lower than 1. If, for instance, we choose the bare mass $\nu = -0.2$, S_{hs} is equal to zero when $N > N_c \approx 0.65$ and jumps discontinuously to 0.31 at the transition with $G_{hs}/G \approx 0.91$. The entropy then decreases smoothly when N gets smaller and vanishes at $N_s \approx 0.54$ where $G_{hs}/G \approx 0.96$. We notice that the ratios N_c/N_s and G_{hs}/G are remarkably similar to the values of T_c/T_s and q_1 , which may be found in mean-field disordered models [7,8,12]. Though one must consider this result with caution due to the approximations made in its derivation, it seems that the free-energy landscape of the $(\phi^2)^2$ model in zero dimension may be complicated at small N ($N < 1$), even above the ferromagnetic transition temperature. This is strongly reminiscent of the random field Ising model that is recovered here if $N = 1$ and g keeps a finite value [23].

A deeper understanding of the mechanism of the quasi-ergodicity breaking occurring in the range $T_s < T < T_c$ is still to be found in finite dimensional systems [18]. We hope that the description of the complicated free-energy landscape sketched in this Letter [24] will be of some help to understand the dynamical processes taking place in structural glasses [4,10].

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