The Structural Glass Transition and the Entropy of the Metastable States

Rémi Monasson [1,2]

[1] *INFN and Dipartimento di Fisica, P.le Aldo Moro 2, I-00185 Roma, Italy*

[2] *Laboratoire de Physique Théorique de l'ENS* *, *24 rue Lhomond, F-75231 Paris cedex 05, France*

Abstract

The metastable states of a glass are counted by adding a weak pinning field which explicitly breaks the ergodicity. Their entropy, that is the logarithm of their number, is extensive in a range of temperatures $T_G < T < T_C$ only, where T_G and T_C correspond to the ideal calorimetric and kinetic glass transition temperatures respectively. An explicit self-consistent computation of the metastable states entropy for a non disordered model is given.
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*Unité propre du CNRS, associée à l'ecole Normale Supérieure et à l'Université de Paris Sud

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 T_G. On the other hand, the mode coupling theory (MCT) [2] is an off-equilibrium theory which self-consistently treats the microscopic dynamical correlation and response functions in the liquid phase. The onset of the glassy state is then due to a kinetic transition at a temperature T_C higher than T_G. The breaking of ergodicity at T_C coincides with the appearance of non vanishing density fluctuations in the long time limit, the system becoming partially frozen in metastables states with very large relaxation times.

The connection between the dynamic and the static approaches can been made more transparent and rigorous in the special case of mean-field spin glasses [3,4]. It has indeed been found that the models exhibiting a discontinuous replica symmetry breaking [5] at the static transition temperature T_S present a dynamic transition at a higher temperature T_D below which equilibrium is never reached [4,3,6]. In addition, the temperature T_D whose significance is a priori purely dynamical may be computed from the Gibbs partition function using the so-called "marginality condition" [6]. This is related to the intuitive feeling that the dynamical transition should arise when the free–energy landscape becomes "rough" and includes many states separated by extensive barriers while at the same time the replica symmetry remains unbroken ($T_D > T_S$). Recently, it has been shown that these results may be extended to mean–field spin models with complicated but non–random interactions [7]. A glassy system, once trapped in a metastable state, is indeed partially frozen and its slow degrees of freedom may act as self-induced "quenched" constraints with respect to the fast ones [2,4,7].

In this letter, we wish to investigate the metastable states in the equilibrium free-energy landscape in any glassy system with or without quenched disorder. More precisely, we shall define the entropy $\mathcal{S}_{hs}$ as the logarithm of the number of these "hidden" metastable states and present a general scheme to compute this quantity. It will be shown that for mean-field disordered models $\mathcal{S}_{hs}$ is extensive in the range of temperatures $T_S < T < T_D$ only, and gives also some important information about the structure of the states below T_S. We shall argue that the same holds in the absence of disorder and that these two temperatures then correspond to the ideal calorimetric and kinetic temperatures T_G and T_C respectively. The replica formalism will then be adapted to the case of systems without disorder to derive their metastable states entropy $\mathcal{S}_{hs}$ and the glassy correlation functions inside these states. An example of such a calculation will be given for a simple 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 $T = \frac{1}{\beta}$ is given by

$$F_\phi(\beta) = -\frac{1}{\beta} \log \int d\phi(x)\; e^{-\beta H[\phi]} \tag{1}$$

For a usual ferromagnet, the emergence of a spontaneous magnetization at low temperature coincides with the breaking of the symmetry $\phi(x) \to -\phi(x)$ of the Hamiltonian. 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

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

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 ($g \rightarrow 0$). 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

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

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

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

where $g^{\rho\lambda} = g(\frac{1}{m} - \delta^{\rho\lambda})$. Let us define two more quantities related to the field σ : its internal energy $W(m,\beta) = \frac{\partial(mF_\sigma)}{\partial m}$ and its entropy $S(m,\beta) = \beta m^2\frac{\partial F_\sigma}{\partial m}$. Since the case $m = 1$ will be of particular interest, we shall use hereafter $F_{hs}(\beta) \equiv W(m = 1,\beta)$ and $\mathcal{S}_{hs}(\beta) \equiv S(m = 1,\beta)$ where hs stands for "hidden states". We stress that $S(m,\beta)$ and $\beta^2\frac{\partial F_\phi}{\partial\beta}$ which are respectively the entropies of the fields σ and ϕ are two distinct quantities with different physical meanings.

When the pinning field $\sigma(x)$ is thermalized at the same temperature as $\phi(x)$, that is when $m = 1$, one sees from eqn.(4) that $F_\phi(\beta) = F_\sigma(m = 1,\beta)$. The basic idea of this letter is to decompose F_σ into its energetic and entropic contributions to obtain

$$\mathcal{S}_{hs}(\beta) = \beta\Big[F_{hs}(\beta) - F_\phi(\beta)\Big] \tag{5}$$

To get some insights on the significance of the above relation, we shall now turn to the particular case of disordered mean-field systems. We shall see how it rigorously gives back some analytical results derived within the mean-field TAP and dynamical approaches [3,6,8,9,11]. We shall then discuss 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 [5] to end up with $F_\phi(\beta) = \lim_{n\to 0} \mathop{\mathrm{Ext}}_{\{q^{ab}\}} \mathcal{F}_\phi(\{q^{ab}\})$. $q^{ab} = \frac{1}{V}\int dx \phi^a(x)\phi^b(x)$ are the overlaps between the n replicas ($V \equiv \int dx$ is the volume of the system). Above the static transition temperature T_S, the physical saddle-point of $\mathcal{F}_\phi$ is replica symmetric (RS) $q^{a\neq b} = q$ (for simplicity a spherical normalization $q^{aa} = 1$ has been assumed). 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 eqn.(4) the same free-energy functional $\mathcal{F}_\phi$ where the number of replicas $\phi^{a\rho}(x)$ now equals $n \times m$ and with the additional term $\frac{V}{2}\sum_{a=1}^{n}\sum_{\rho,\lambda=1}^{m} g^{\rho\lambda} q^{a\rho,a\lambda}$. This interaction term explicitly breaks the symmetry of permutations of the $n \times m$ replicas [15] 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

$$F_\sigma(m,\beta) = \mathop{\mathrm{Ext}}_{q_0,q_1} \; \mathcal{F}_\phi(q_0, q_1, m, \beta) \tag{6}$$

when $g \to 0^+$. 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 [12] for a related case where σ acquires a simple geometrical interpretation). Let us now send $m \to 1$ 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 $F_\sigma(m = 1, \beta) = F_\phi(\beta) = \mathrm{Extr}_q\, \mathcal{F}_\phi(q,\beta)$ as expected. Defining $\mathcal{V}(q_1) \equiv \beta \dfrac{\partial \mathcal{F}_\phi}{\partial m}(q_0 = q, q_1, m = 1, \beta)$, 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 $\mathcal{S}_{hs} = \mathcal{V}(q_1)$. It turns out that $\mathcal{V}$ defined above is equal to the potential recently introduced in mean-field glasses [9,10] to compute the marginality temperature T_D at which the relaxational dynamics exhibits a drastic slow down [3,6] as mentioned in the introduction. The typical behaviour of the entropy $\mathcal{S}_{hs}(\beta)$ is as follows. At high temperature, there is only the RS solution $q_1 = q, \mathcal{S}_{hs} = 0$. At a given T_D, there appears a non trivial saddle-point q_1 (which shifts the free–energy (6) by an extensive amount of order gV [15]) and the entropy $\mathcal{S}_{hs}$ shows a first order jump. When T

decreases, $\mathcal{S}_{hs}$ goes down and vanishes at T_S. Note that $\mathcal{S}_{hs}(T=T_S)=0$ is mathematically equivalent to the usual optimization condition of the one-step free–energy with respect to m. This is an important remark we shall comment on in the following.

The marginality condition [6,9] tells us that $T = T_D$ is the temperature of the onset of an exponential number of such metastables states. Using the TAP formalism [11], one can indeed write the set of equations that the mean-field local magnetizations $\{M(x)\}$ must satisfy. The paramagnetic solution $M(x) = 0$ (for simplicity we suppose that $q = (\frac{1}{V}\int dx M(x))^2$ vanishes in the RS phase) gives the RS free–energy density as expected. Below T_D the RS free–energy density is also achieved by the sum of an exponential number of solutions with a higher free–energy and an internal overlap $q_1 = \frac{1}{V}\int dx M(x)^2$ [3]. It has been recently verified in the particular case of the random orthogonal model [8] that the logarithm of the number of these solutions [13] - which is sometimes called complexity or configurational entropy [3,14] - coincides with the entropy $\mathcal{S}_{hs}$ defined in this letter.

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 $\mathcal{S}_{hs}(\beta) = 0$. Physically, there exists only one state. When the temperature goes down, there may appear some high barriers which 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_D, their number $e^{\mathcal{S}_{hs}}$ 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_D is not complete. The partial freezing of collective modes inside the metastable states makes the dynamics very slow but does not forbid some microscopic changes (the so-called activated processes) [3]. Thus, no discontinuties occur at T_D for the thermodynamic quantities and it is reasonable to think that T_D coincides with the ideal kinetic transition temperature T_C for glassy systems. Below T_D, $F_\phi(\beta)$ comes from the superposition of many states with high free–energies. The number $e^{\mathcal{S}_{hs}}$ 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 $\mathcal{S}_{hs}$ is not extensive anymore [14]. The true thermodynamical transition therefore takes place at T_S which corresponds to the usual calorimetric glass transition temperature T_G. 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 (non exponential) number of states will still occur and that $\mathcal{S}_{hs}(T < T_S) = 0$. As a consequence, the effective temperature of the states, that is of the field σ, becomes higher than the temperature of the field ϕ and m is determined through the condition that the hidden states' entropy vanishes. If one goes back to the case of mean-field disordered systems, one finds that m is such that the one-step free–energy derivative with respect to m equals zero. Therefore, we have obtained a simple physical interpretation of the usual optimization condition of $\mathcal{F}_\phi$ with respect to m in the RSB phase, whose meaning has always been far less clear than the optimization with respect to the overlaps q_0 and q_1 [5]. Furthermore, let us notice that if $\mathcal{S}_{hs}$ is already non extensive at T_D then T_D and T_S must coincide. This is what happens for systems with a continuous RSB transition [5] where the intermediate phase $T_S < T < T_D$ is skipped. Such systems seem therefore to exhibit a less generic behaviour [3,4].

Formula (4) is a convenient starting point to compute $\mathcal{S}_{hs}$ in systems without quenched disorder. 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 : $G^{\rho\lambda}(x-y) \equiv \langle \phi^\rho(x)\phi^\lambda(y)\rangle = \delta^{\rho\lambda} G(x-y)$. 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 metastable states in which the expectation value $\langle\phi(x)\rangle$ does not vanish anymore and therefore by the emergence of non zero off-diagonal propagators

$$G_{hs}(x-y) = \langle\phi(x)\rangle\langle\phi(y)\rangle = \langle\phi^\rho(x)\phi^\lambda(y)\rangle \quad (\rho \neq \lambda) \tag{7}$$

in the limit $m \to 1$ [16]. As discussed above, the diagonal correlation function $G(x-y)$ 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 more delicate since a perturbative expansion of the original Hamiltonian will never be able to generate an effective coupling between the replicas and to detect the first order glass transition. We shall now present a simple self-consistent calculation which permits us to obtain $\mathcal{S}_{hs}$ and $G_{hs}(x-y)$.

Let us consider a system of N particles at positions x_i ($i=1...N$) interacting through a two–body potential $\sum_{i<j} V(|x_i-x_j|)$. In the grand-canonical ensemble, this system is described by the Hamiltonian $H[\phi]=\frac{1}{2}\int dxdy\ \phi(x)V^{-1}(x-y)\phi(y)-\mu\int dx\exp i\phi(x)$ where μ is the chemical potential and $\phi(x)$ the conjugated field to the density of particles at point x. To obtain an analytically tractable problem, we shall make two simplifications. First, while the previous general expression contains interactions at all orders in ϕ, we shall keep only the quartic vertex. Secondly, we shall consider a $O(N)$ version of the above Hamiltonian and compute the free–energy $F_\sigma(m,\beta)$ using Bray's self-consistent screening approximation [17]. The expansion parameter $1/N$ plays the role of the chemical potential μ. 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 which are related to $N\to 0$ [18] are known to have a glassy behaviour at low temperatures. Bray's calculation is exact to order $1/N$ and contains a partial resummation of an infinite class of diagrams [17] and is thus well defined in the whole range $0<N<\infty$. With the Ansatz $G^{\rho\lambda}(k)=\delta^{\rho\lambda}G(k)+(1-\delta^{\rho\lambda})G_{hs}(k)$ [16], one obtains the free–energy $F_\sigma(m,N)$ as an extremum over the set of all propagators $G(k)$ and $G_{hs}(k)$ [19]. When $m\to 1$, the diagonal propagators are solutions of the implicit equations

$$\frac{1}{G(k)}=\frac{1}{V(k)}+\int dq\ G(q)+\frac{2}{N}\int dq\ \frac{G(k-q)}{1+\Pi(q)} \tag{8}$$

where $\Pi(k)\equiv\int dqG(k-q)G(q)$. Eqn.(8) is identical to Bray's result as expected [17]. The entropy of the metastable states then reads

$$\mathcal{S}_{hs}(N)=\operatorname*{Ext}_{G_{hs}(k)}\int dk\left[s\left(\frac{G_{hs}(k)}{G(k)}\right)-\frac{1}{N}s\left(\frac{\Pi_{hs}(k)}{1+\Pi(k)}\right)\right] \tag{9}$$

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 steming from eqn.(8,9) in dimension $D = 3$ shows that a non zero set of propagators G_{hs} may appear when N becomes lower than a given N_C which depends on the bare propagator $V(k)$. Despite different choices of $V(k)$, we have always found $N_C < 1$. A more careful analysis of the equations would however be useful. 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 one. If for instance we choose the bare mass $V = -0.2$, $\mathcal{S}_{hs}$ is equal to zero when $N > N_C \simeq 0.65$ and jumps discontinuously to 0.31 at the transition with $G_{hs}/G \simeq 0.91$. The entropy then decreases smoothly when N gets smaller and vanishes at $N_G \simeq 0.54$ where $G_{hs}/G \simeq 0.96$. We notice that the ratios N_C/N_G and G_{hs}/G are remarkably similar to the values of T_D/T_S and q_1 which may be found in mean-field disordered models [6–8]. 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 $(\vec{\phi}^2)^2$ model may be complicated at small N ($N < 1$), even above the ferromagnetic transition temperature. This is strongly reminiscent of the random field Ising model which is recovered here if $N = 1$ and g keeps a finite value [19].

A deeper and more rigorous understanding of the mechanism of the ergodicity breaking occurring at T_C is still to be found. In this respect, one could try to transpose the TAP approach to non disordered models. Let us call $\Gamma(M) = g \int dx \sigma(x) M(x) + F_\phi[\sigma, g, \beta]$ the Legendre transform of the "Hamiltonian" of the field σ. The free–energy $F_\phi(\beta)$ is equal to the minimum of the effective potential Γ at $M(x) = \langle \phi(x) \rangle$. It may well happen that at T_C there appear many different minima of Γ while at higher temperatures the only solution is $M(x) = 0$. If so, the presence of the source σ would lift this degeneracy by selecting the closest solution $M(x) \neq 0$ (i.e. having the largest overlap with σ). The propagator $G_{hs}(x-y)$ would then be the average of $M(x)M(y)$ over all these solutions, that is over all possible fields σ. A natural idea is thus to define a partition function $Z_{solutions}$ as the sum of the Gibbs weights $e^{-\beta\Gamma(M)}$ of all the solutions of $\frac{\partial\Gamma}{\partial M(x)} = 0$. It would be very interesting to confirm or disprove that the equality between $Z_{solutions}$ and the partition function of the field ϕ eqn.(1) also holds in the glassy phase below T_C.

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