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Activated processes and Inherent Structure dynamics of finite-size mean-field models for glasses

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Abstract. – We investigate the Inherent Structure (IS) dynamics of mean-field *finite-size* spin-glass models whose high-temperature dynamics is described in the thermodynamic limit by the schematic Mode Coupling Theory for supercooled liquids. Near the threshold energy the dynamics is ruled by activated processes which induce a logarithmic slow relaxation. We show the presence of aging in both the IS correlation and integrated response functions and check the validity of the one-step replica symmetry breaking scenario in the presence of activated processes. Our work shows: 1) the violation of the fluctuation-dissipation theorem can be computed from the configurational entropy obtained in the Stillinger and Weber approach, 2) the intermediate time regime ($\log(t) \sim N$) in mean-field theory automatically includes activated processes opening the way to analytically investigate activated processes by computing corrections beyond mean field.

After many years of research on the structural glass problem a lot of experimental data has been collected but a convincing theory is still needed [1, 2]. The two most successful theories for the glass transition are the Adam-Gibbs-DiMarzio and the ideal Mode Coupling Theory (MCT) [3]. Despite their different character both are mean-field theories. In the former case the mean-field aspect lies in the notion of configurational entropy which assumes a breaking of the phase space in disconnected ergodic components. In the latter the presence of the MCT transition marks the onset of ergodicity breaking where the diverging of a characteristic time occurs. Both approaches have been successfully unified in the context of spin-glass theories [4].

To go beyond mean field, it is necessary to include activated processes, a very difficult task since it implies the knowledge of the excitations involved in the dynamics. Recent theoretical and numerical results clearly show that the slowing-down of the dynamics near the structural glass transition is strongly connected to the complex topology of the potential energy landscape [5]. In a glass-forming systems this is made by many deep valleys connected by saddles.

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The time evolution can then be divided into an *intra-valley* and an *inter-valley* motion. When the temperature is lowered down to the order of the critical MCT temperature T_{MCT} the two motions become well separated in time and relaxation dynamics, dominated by inter-valley processes, slows down displaying non-exponential behavior [6].

To deal with this picture Stillinger and Weber (SW) [7] introduced the concept of *inherent structure* (IS) defined as the local stable minima of the potential energy reached through a steepest descent energy minimization process. All configurations which under this mapping flow to the same IS define the basin (of attraction) of the IS. It is now a simple matter to define an IS-based thermodynamics by replacing the partition sum with a sum over IS [7, 8]. Direct consequence of this is the introduction of a *configurational entropy* $s_{\mathrm{c}}(e)$ which counts the number of different IS with the same energy e: $\Omega(e) = \exp(N s_{\mathrm{c}}(e))$. Note that despite the fact that the $s_{\mathrm{c}}(e)$ so defined is a *dynamical quantity*, it is far from obvious that it describes the long-time non-equilibrium behavior [9]. The reduction from the real dynamics to an IS dynamics is what, in the theory of dynamical systems, is called a *symbolic dynamics*. This describes correctly the dynamics only if it is associated to a *generating partition* [10]. In general for a generic dynamics it is not at all trivial to demonstrate that such a partition exists, and even if it does exist, how to find it. Nevertheless, we can argue that if the sampling of the inherent structures perfomed by the dynamics is unbiased then the SW mapping should be a "good" mapping. For example, coarsening systems do not meet these requirements and the SW mapping is not meaningful [11]. Under this assumption the dynamics on time scales larger than the typical residence time inside a IS-basin should be quite well described by the IS dynamics. Recent numerical results on Lennard-Jones mixture [12] supports this scenario for supercooled liquids.

In this letter we extend the analysis to *finite-size* mean-field glass models and propose that activated processes seen in supercooled liquids can be treated at a mean-field level by including *finite-size effects* in the dynamics of an infinite mean-field system going beyond the saddle-point approximation, *i.e.*, beyond the ideal MCT. This observation is quite reminiscent of the dynamical approach of Sompolinsky [13] and opens the way to address activated processes in structural glasses from mean-field theories. After the work by Sompolinsky the inclusion of activated processes from this point of view has not attracted much attention [14] and mean-field dynamical studies have mainly considered the $N \to \infty$ limit before the large-time limit [3]. Other possible approaches analyze activated process by considering instanton solutions of the mean-field equations [15].

This work is the natural continuation of a previous one [16] where we introduced finite-size mean-field glasses for the analysis of the SW configurational entropy. Here we extend our study to the long-time non-equilibrium dynamics finding that, once finite-size effects are included and activated processes appear in a natural way, relaxational dynamics is driven by the configurational entropy giving support to the one-step replica-symmetry breaking (RSB) scenario beyond mean field. The present results are in agreement with recent simulations on Lennard-Jones systems [17] although here we go further and verify the explicit connection between the violation of the fluctuation-dissipation theorem and the configurational entropy. Moreover, our results give further support to the relevance of p-spin–like models for the description of the glass transition in structural glasses.

Following ref. [16] we consider the dynamics of the Ising-spin Random Orthogonal Model (ROM) [18, 19] defined by the Hamiltonian

$$H = -2 \sum_{ij} J_{ij}\, \sigma_i\, \sigma_j\,, \tag{1}$$

where $\sigma_i = \pm 1$ are N Ising spin variables, and J_{ij} is an $N \times N$ symmetric random orthogonal

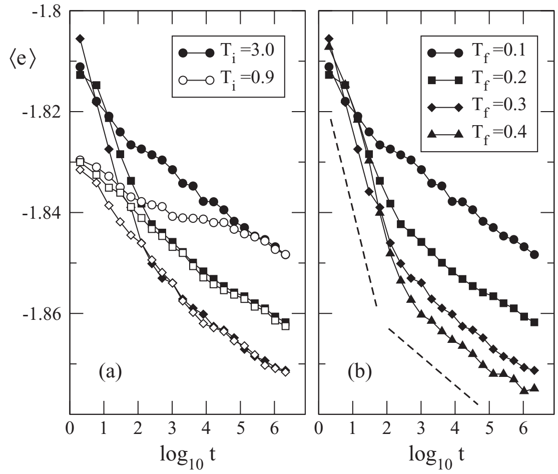

Fig. 1 – Average IS as a function of time. (a) Filled symbols: $T_{\rm i} = 3.0$, empty symbols: $T_{\rm i} = 0.9$. Final temperatures are as in panel (b). (b) $T_{\rm i} = 3.0$. The average is over different equilibrium initial configurations.

matrix with $J_{ii} = 0$. We use the heat-bath Monte Carlo scheme with random sequential spin updating. This model presents a thermodynamic glass transition typical of mean-field p-spin glasses with $p > 2$ [20] at $T_{\rm MCT} = 0.536$ with threshold energy per spin $e_{\rm th} = -1.87$. Below this temperature the system is dynamically confined into a metastable state (basin or valley) and cannot reach true equilibrium. An equilibrium transition with collapse of the configurational entropy takes place below $T_{\rm MCT}$ at the Kauzmann temperature $T_{\rm c} = 0.25$, with critical energy per spin $e_{\rm c} = -1.936$ [18, 19]. The analysis of the free-energy landscape of this model [19] reveals that the phase space is composed by an exponentially large (in N) number of different basins, separated by infinitely large (for $N \to \infty$) barriers. Above $T_{\rm MCT}$ and in the large N limit the IS with $e = e_{\rm th}$ attract most (exponentially in N) of the states and dominate the behavior of the system. For finite N basins of IS with $e \neq e_{\rm th}$ have statistical weight and may influence the dynamics [16].

To study the non-equilibrium relaxational dynamics we quench the system at time $t = 0$ from an equilibrium state at temperature $T_{\rm i} > T_{\rm g}$ to a final temperature $T_{\rm f} < T_{\rm g}$. The glass transition temperature $T_{\rm g}$ is defined, in accordance with the "experimental" definition, as the temperature below which we cannot equilibrate the system on the longest Monte Carlo run. The associated IS dynamics is obtained by regularly quenching the system down to $T = 0$ from the relaxing configuration and recording the IS associated with the instantaneous basin. We shall consider both one-time quantities, as the average IS energy, and two-time quantities, as correlation and response functions.

Relaxation of one-time quantities. – In fig. 1 the average IS energy is shown per spin $\langle e\rangle(t)$ as a function of time for a system with $N = 300$ spins. The analysis of the figure reveals that the relaxation process can be divided into two different regimes where $\langle e\rangle(t)$ decreases with different power laws. The slope of the decay in the first regime is independent of $T_{\rm f}$ while the slope in the second regime is independent of both $T_{\rm i}$ and $T_{\rm f}$ (cf. panel (a)). For a given $T_{\rm i}$ the final temperature $T_{\rm f}$ only controls the cross-over between the two regimes. A similar behavior has been observed in molecular dynamics simulations of supercooled liquids [12]. We note that since we use discrete variables, and hence a faster dynamics, the very-early regime

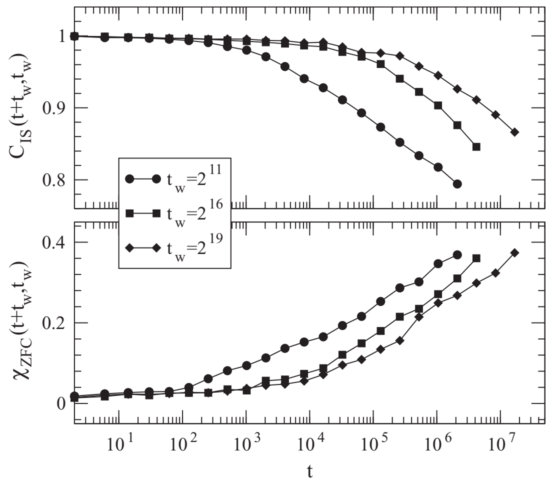

Fig. 2 – IS correlation (above) and integrated response (below) functions as a function of time for different waiting times. The system size is $N = 300$, $T_{\rm i} = 3$, $T_{\rm f} = 0.2$ and $T_{\rm g} \simeq 0.5$. Data have been averaged over about 400 dynamical histories.

observed in [12] where $\langle e \rangle(t)$ is almost independent of t is absent. Moreover since we use fully connected systems the power law exponents change with N, even if the qualitative scenario is unchanged. The two regimes are associated with different relaxation processes. In the first part the system has enough energy and relaxation is mainly due to *path search* out of basins through saddles of energy lower than $k_{\rm B}T_{\rm f}$. During this process the system explores deeper and deeper valleys while decreasing its energy. The process stops when all barrier heights become of $\mathrm{O}(k_{\rm B}T_{\rm f})$. From now on the relaxation can only proceed via activated processes and the dynamics slows down becoming logarithmic in time. Note that, for finite N, the activated regime starts already above the threshold indicating that not only stable states exist above $e_{\rm th}$ but these also influence the hopping dynamics.

Aging in correlation and response functions. – More information on the non-equilibrium activated regime can be obtained from the analysis of correlation and response functions. In order to study the relevance of the SW mapping we consider the IS-based correlation and response functions defined as

$$C_{\rm IS}(t,s) = \frac{1}{N}\sum_{i=1}^{N} \sigma_i^0(t)\,\sigma_i^0(s)\,, \tag{2}$$

$$R_{\rm IS}(t,s) = \frac{1}{N}\sum_{i=1}^{N} \frac{\delta\sigma_i^0(t)}{\delta h_i(s)}\,, \qquad t > s\,, \tag{3}$$

where $\sigma^0(t)$ is the IS at time t and h_i an external field. It can be shown that in equilibrium the fluctuation-dissipation theorem $TR_{\rm IS}(t-s) = -\partial_t C_{\rm IS}(t-s)$ holds [21]. To study the non-equilibrium response function we quench the system at time $t = 0$ from an equilibrium state at $T_{\rm i} > T_{\rm g}$ to $T_{\rm f} < T_{\rm g}$ and, after a given waiting time $t_{\rm w}$, we make a *clone* of it to which a (small) constant uniform magnetic field is applied. To reduce fluctuations the same stochastic noise is used for both replicas. The experiment is repeated for different (small) fields to control the linear response regime. Results for the correlation function and the integrated response,

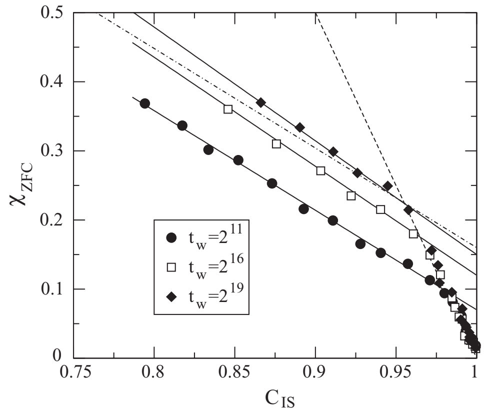

Fig. 3 – Integrated response function as a function of the IS correlation function. The data are from fig. 2. The dashed line has slope $\beta_f = 5.0$, while the full lines is the prediction (5) with $\delta(e, T) = 0$ and $s_c(e)$ from ref. [16]: $T_{\rm eff}(2^{11}) \simeq 0.694$, $T_{\rm eff}(2^{16}) \simeq 0.634$ and $T_{\rm eff}(2^{19}) \simeq 0.608$. The dot-dashed line is $\beta_{\rm eff}$ for $t_w = 2^{11}$ drawn for comparison.

or zero-field–cooled susceptibility, $\chi_{ZFC}(t, t_w) = \int_{t_w}^{t} dt' R_{IS}(t, t')$ are reported in fig. 2. The presence of aging is rather clear.

The one-step RSB scenario and the SW configurational entropy. – A way to see how equipartition is broken in the non-equilibrium regime is through the fluctuation-dissipation ratio, initially introduced in the context of spherical models for spin glasses [3, 20, 22, 23]. Usually the breaking of equipartition is expressed through an effective temperature defined as $T_{\rm eff}(t, t_w) = \partial_{t_w} C_{IS}(t, t_w)/R_{IS}(t, t_w)$, or, alternatively, as

$$T_{\rm eff}^{-1}(C_{IS}) = -\frac{\partial \chi_{ZFC}(t, t_w)}{\partial C_{IS}(t, t_w)}\,, \tag{4}$$

which is the slope of the curves χ_{ZFC} *vs.* C_{IS}. This temperature reduces to T in equilibrium and is larger when equipartition is broken.

In the context of mean-field theories for the glass transition $T_{\rm eff}$ is given by the constant temperature derivative of the free-energy with respect to the configurational entropy: $T_{\rm eff}^{-1} = [\partial s_c(f)/\partial f]_T$ [24, 25], which in the present IS analysis means

$$T_{\rm eff}^{-1} = \left[\frac{\partial s_c(f_{IS})}{\partial f_{IS}}\right]_T = \left[\frac{\partial s_c(e)}{\partial e}\right]_T \Big/ \left[\frac{\partial f_{IS}(e)}{\partial e}\right]_T\,, \tag{5}$$

where f_{IS} is the free energy of the IS with energy e, *i.e.*, obtained from the partition sum *restricted* to the configurations in the IS-basins of IS with energy e. Writing $f_{IS} = e + \Delta e(T, e) - T\, s_{IS}(T, e)$, we see that $[\partial f_{IS}(e)/\partial e]_T = 1 + \delta(e, T)$, where the last term measures how IS with different e differ from one another.

Results from our numerical simulations are shown in fig. 3. For each t_w two distinct behaviors are clearly seen. For large values of C_{IS} the slope of all the curves is $\beta_f = 1/T_f$. Below a t_w-dependent value of C_{IS} the curve changes slope and the effective temperature increases. In order to compare our results with prediction (5), we have to compute f_{IS}. This can be done from the knowledge of the probability that an equilibrium configuration at temperature $T = 1/\beta$ lies in a basin associated with IS of energy between e and $e + de$:

$P_N(e,T) = \exp N\,[-\beta f_{\rm IS} + s_{\rm c}(e) + \beta f(T)]$, where $f(T)$ is the full free energy. Using the results from refs. [16, 19] both $f_{\rm IS}$ and its derivative can be estimated. In all cases we found $\delta(e,T) \simeq 0$, within numerical errors, a result in agreement with the fact that the ROM is rather similar to the Random Energy Model [3] for which $\delta(e,T) = 0$. Using for $s_{\rm c}(e)$ the expression obtained in ref. [16] we obtain from (5) the slopes $\beta_{\rm eff} = 1/T_{\rm eff}$ shown in fig. 3. The agreement is rather good. Data for $T_{\rm f} = 0.1$ and 0.3 are more noisy, but consistent with this identification.

We therefore conclude that in the activated regime the effective temperature $T_{\rm eff}$ derived from the SW configurational entropy agree extremely well with the numerical data confirming the one-step scenario. This is a highly non-trivial result. First of all, as discussed above, it is not obvious that the SW mapping correctly describes the long-time non-equilibrium dynamics. It is plausible that it works for an activated dynamics, but plausibility is not a proof. Second, eq. (5) is derived within mean field, *i.e.*, for $N \to \infty$. Here we apply it for states which exist only for *finite* N being, as discussed above, those which govern the relaxational dynamics in this regime but disappear in the thermodynamic limit. Thus our finding gives to (5) a broader validity. We note that quite new results from numerical simulations of Lennard-Jones mixtures are in agreement with (5), but with $\delta(e,T) \neq 0$ [26].

From the discussion on the SW approach it follows that if the SW mapping defines a good mapping then it should equally well describe the long-time relaxational dynamics regardless which configuration we use to identify the IS-basin. To check this point we have repeated the simulations using slightly different definitions of IS, *i.e.*, changing the minimization rule. In all cases we have found the same results, so that in this case the SW mapping provides a good "symbolic" dynamics for the long-time non-equilibrium behavior.

We now summarize our findings. The Stillinger-Weber decomposition of phase space in terms of IS is a natural and simple statistical description of a dynamical system with activated dynamics among different basins when the time scales for motions inside a basin and between basins are well separated. Moreover, we have shown that finite-size mean-field glasses are valuable models to describe activated processes in structural glasses. In the activated regime these models display slow logarithmic relaxation with two classes of motions which confirm the one-step replica symmetry breaking scenario: a fast intra-basin motion where fluctuation-dissipation holds and a slow inter-basin motion corresponding to activated processes. The fluctuation-dissipation ratio in the activated regime can be fully described in terms of the Stillinger and Weber configurational entropy generalizing the mean-field scenario with the inclusion of activated processes. Our results suggest the possibility of investigating the glass transition in structural glasses from finite-size correction to mean-field theory justifying efforts in this direction.

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