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# Inherent structures, configurational entropy and slow glassy dynamics

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Received 18 December 2001

Published 7 February 2002

Online at [stacks.iop.org/JPhysCM/14/1381](http://stacks.iop.org/JPhysCM/14/1381)

## Abstract

We give a short introduction to the inherent structure approach to glassy systems, with particular emphasis on the Stillinger and Weber (SW) decomposition. We present some of the results obtained in the framework of spin-glass models and Lennard-Jones glasses. We discuss how to generalize the standard SW approach by including the entropy of inherent structures. Finally we discuss why this approach is probably insufficient to describe the behaviour of some kinetically constrained models.

## 1. Introduction

If we are asked what is a glass we will most probably think of window glass. The glassy state is, however, rather common in nature and many apparently unrelated systems such as structural glasses, spin glasses, disordered and granular materials or proteins—among others—present what is called *glassy behaviour*. All these systems have as a common feature a dramatic slowing down of the equilibration processes when some control parameter, e.g., the temperature or density, is varied. The equilibration process is frequently non-exponential, and correlation functions show power-law and stretched-exponential behaviour as opposed to a simple exponential decay. As the characteristic relaxation time may change by several orders of magnitude, it easily exceeds the observation time. The residual very slow motion leads to a non-equilibrium phenomenon which changes the properties of the systems, a process commonly called aging. The greatest difficulty in understanding the slow glassy relaxation dynamics is that a general non-equilibrium theory to deal with this class of systems is still lacking, and approximations to the problem remain partial. They usually work either in a limited range of timescales or in a limited range of temperatures (for instance, mode-coupling theory (MCT) [1]).

Following the ideas formulated more than 30 years ago by Goldstein [2], a convenient framework for understanding the complex phenomenology of glassy systems is provided by

energy landscape analysis. The trajectory of the representative point in the configuration space can be viewed as a path in a multidimensional potential energy surface. The dynamics is therefore strongly influenced by the topography of the potential energy landscape: local minima, barriers, basins of attraction and other topological properties all influence the dynamics.

The idea of Goldstein, formulated at a qualitative level, was formalized years later by Stillinger and Weber (SW) [3, 4], who proposed a procedure for identifying basins of the potential energy surface of supercooled liquids. The recipe is rather simple: the set of all configurations connected to the same local energy minimum by a steepest-descent path uniquely defines the basin associated with this minimum, which SW named *inherent structure* (IS) to stress its intrinsic nature.

The physical motivation behind their proposal follows from the observation that the potential energy surface of a supercooled liquid contains a large number of local minima. Therefore the time evolution of the system can be seen as the result of two different processes: thermal relaxation into basins (*intra-basin* motion) and thermally activated potential energy barrier crossing between different basins (*inter-basin* motion). When the temperature is lowered down to the order of the critical MCT temperature  $T_{\text{MCT}}$  the typical barrier height is of the order of the thermal energy  $k_B T_{\text{MCT}}$  and the inter-basin motion slows, dominating the relaxation dynamics. If the temperature is further reduced, the relaxation time eventually becomes of the same order as the physical observation time and the system falls out of equilibrium since there is not enough time to cross barriers and equilibrate. This defines the *experimental glass transition* temperature  $T_g$ .

With this picture in mind, it is natural to view the IS as the natural elements for describing the slow glassy dynamics. If we think of the glassy system as a dynamical system, then the SW decomposition is a mapping of the true dynamics at a given temperature onto the IS dynamics. This approach is rather appealing since it naturally leads to universality: all glassy systems with similar IS dynamics must have similar glassy behaviour.

The recent increase in computational power has significantly improved the analysis of the energy surface, and IS analysis of the energy surface has been performed for several systems. The results are both positive and negative; indeed, while the IS formalism has been successful for the description of the off-equilibrium dynamics and the FDT violations in structural glass models [5–9], it fails for some kinetically constrained glassy systems [10].

To understand this success/failure we have to analyse the idea behind the SW approach. The main question that we would like to answer is: *what is a good description for the long-time slow glassy dynamics?* The natural approach is to look for some ‘reduced dynamics’ which includes only those details of the full dynamics relevant on the long timescales. This obviously implies a coarse graining of the phase space. For example within Mori’s projection method used to derive the MCT, the phase space is coarse grained by projecting it onto the subspace spanned by the ‘slow variables’. It is clear that even though the phase space can be always coarse grained, not all possible coarse grainings will lead to a relevant reduced dynamics. This is a well known problem in the theory of dynamical systems, where the associated reduced dynamics is called *symbolic dynamics*. Indeed from the theory of dynamical systems we know that a symbolic dynamics gives a good description of the full dynamics only if the mapping between the full phase space and the coarse-grained one defines what is called a *generating partition*; see e.g. [11]. In general for a generic system not only is it not trivial to demonstrate that a generating partition exists but, even when it does exist, its practical identification remains a highly non-trivial task with the result that we can answer this question only *a posteriori*: we first define a partition and then check whether it reproduces the desired features of the dynamics.

The SW mapping identifies configurations in an IS basin with the IS itself. Therefore to be a plausible mapping the systems must spend a lot of time inside the basin. Under this assumption the dynamics on timescales larger than the typical residence time inside a IS basin could be quite well described by the IS dynamics. This scenario is typical, e.g., of a many-valley energy landscape with activated dynamics. This, however, is only one of the plausibility conditions since other requirements on the dynamics must be satisfied, as discussed later in this work.

To illustrate our discussion we shall report results from numerical simulations of the *finite-size* fully connected Ising spin random orthogonal model (ROM) [12] and binary mixtures of Lennard-Jones (BMLJ) particles [13]. The former, belonging to the  $p$ -spin class [14], is a fully connected Ising spin-glass model with a random orthogonal interaction matrix, whose high-temperature dynamics is described in the thermodynamic limit by the MCT [15]. The latter, a typical system used for studying the structural glass transition, is a system composed by a mixture of type A and type B particles interacting via a Lennard-Jones potential. One of the main advantages is that with a suitable choice of the Lennard-Jones potential parameters for AA, AB and BB interactions, the system does not crystallize simplifying the analysis of the glass transition.

## 2. The Stillinger and Weber decomposition

### 2.1. The SW configurational entropy

The recipe for the SW decomposition is rather simple [3]: the set of all configurations connected to the same local energy minimum (IS) by a steepest-descent path uniquely defines the basin associated with the minimum. The phase space is then partitioned into a disjoint set of basins, usually labelled by  $e_{IS}$ , the energy of the IS. Under broad assumptions, e.g., that boundaries between basins are sub-extensive, this decomposition covers almost all the energy surface and, collecting all IS with the same energy, the partition sum is written as a sum of basin partition functions:

$$Z_N(T) \simeq \int de \exp N[s_c(e) - \beta f_b(T, e)] \quad (1)$$

where  $Ns_c(e)$  accounts for the entropic contribution arising from the number of basins with energy  $e_{IS} = e$ . We shall call  $s_c(e)$  the *SW configurational entropy or complexity* to distinguish it from other possible definitions taken from mean-field concepts [16, 17]. The term  $f_b(T, e)$  is the typical free energy of the basins with energy  $e_{IS} = e$ . If all such basins have similar statistical properties, then  $f_b(T, e)$  is the free energy of the system when constrained to any one characteristic basin with  $e_{IS} = e$ .

In equilibrium at each temperature  $T = 1/\beta$  the system will visit an  $e_{IS}$ -basin with probability (see equation (1))

$$P_N(e_{IS}, T) = \exp N[s_c(e_{IS}) - \beta f_b(T, e_{IS})]/Z_N(T). \quad (2)$$

Therefore, in the thermodynamic limit, it will populate mainly IS with energy  $e(T)$  fixed by the condition

$$s_c(e) - \beta f_b(T, e) = \text{maximum} \quad (3)$$

and the free energy (density) of the system becomes

$$f(T) = f_b(T, e(T)) - Ts_c(e(T)). \quad (4)$$

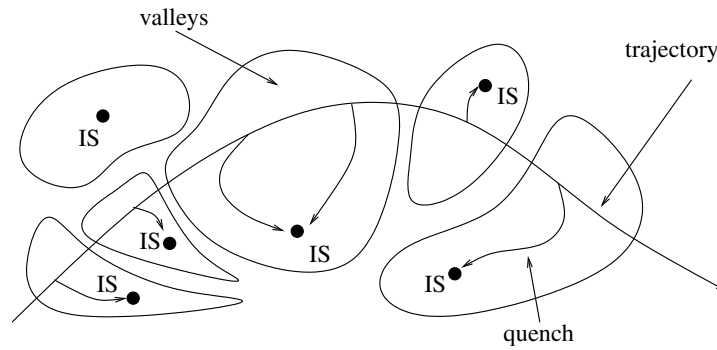


Figure 1. SW decomposition.

The separation of the free energy into two contributions reflects the timescale separation between inter-basin and intra-basin motions. Condition (3) is equivalent to that of  $f(T)$  being minimal, i.e.,

$$\frac{\partial f}{\partial e} = \frac{\partial f_b(T, e)}{\partial e} - T \frac{\partial s_c(e)}{\partial e} = 0. \quad (5)$$

Note that the minimum condition follows from the balance between the change with energy of the shape of the basins ( $\partial f_b(T, e)/\partial e$ ) and of their number ( $\partial s_c(e)/\partial e$ ).

Often it is useful to write the basin free energy as  $f_b(T, e_{\text{IS}}) = e_{\text{IS}} + f_v(T, e_{\text{IS}})$  to emphasize the contribution from the motion inside the basins. Indeed, from (4) the average internal energy density reads  $u(T) = \partial(\beta f_b)/\partial\beta = e(T) + \partial(\beta f_v)/\partial\beta$ , where the first term is the (average) energy of the IS relevant at temperature  $T$  while the second term is the contribution from fluctuations inside the IS basins. The contribution  $f_v$  is called ‘vibrational’.

The main advantage of the SW decomposition is that it can be easily transformed into a numerical algorithm, and the recent increase in computational power has greatly helped to advance the IS analysis of the energy surface. The scheme, summarized in figure 1, follows directly from the definition.

First we equilibrate the system at a given temperature  $T$ ; then, starting from an equilibrium configuration, the system is instantaneously quenched down to  $T = 0$  by decreasing the energy along the steepest-descent path. The procedure is repeated several times starting from uncorrelated equilibrium configurations. In this way, the IS are identified and quantities such as the  $e_{\text{IS}}$ -probability distribution or  $e(T)$  computed.

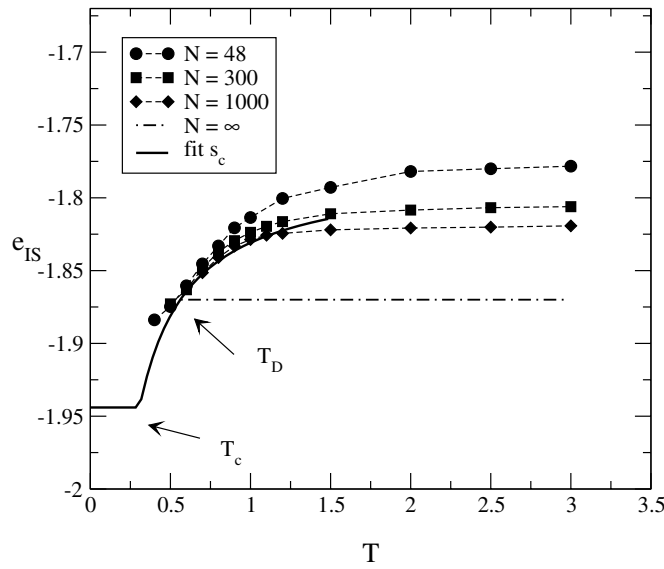
In figure 2 we report  $e(T)$  as a function of temperature  $T$  for the ROM of different sizes, while in figure 3 the same quantity is shown for a BMLJ particles.

From the figures we see a sharp drop in the IS energy as temperature is lowered. For all systems studied so far—both with discrete and continuous variables—that display a fragile glass transition, the drop turns out to be strongly correlated with the onset of slow dynamics [18]. Indeed the decrease of  $e_{\text{IS}}$  is a clear indication that the system explores deeper and deeper basins.

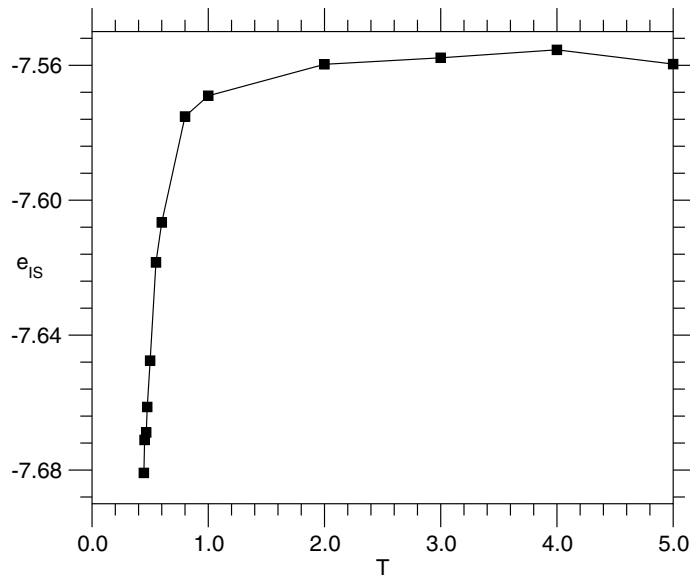
From the knowledge of the  $e_{\text{IS}}$ -distribution we can reconstruct the SW complexity  $s_c(e)$  simply by inverting equation (2):

$$s_c(e) = \ln P_N(e, T) + \beta e + \beta f_v(T, e) + \ln Z_N(T). \quad (6)$$

If the energy dependence of  $f_v(T, e)$  can be neglected, then it is possible to superimpose the curves for different temperatures. The resulting curve is, except for an unknown constant, the SW complexity  $s_c(e)$ . This is shown for the ROM in figure 4(a). The data collapse is

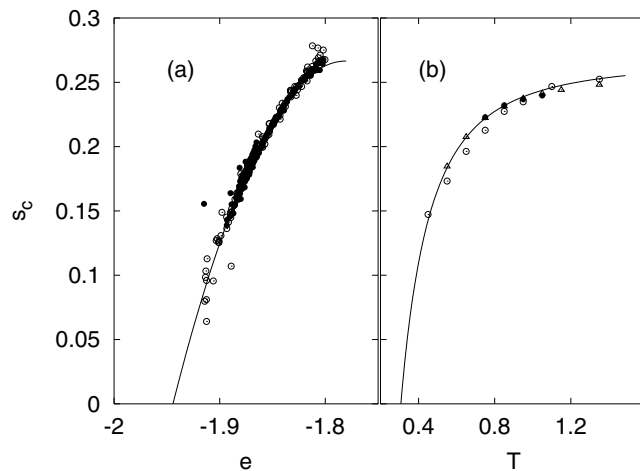


**Figure 2.** Temperature dependences of  $e(T)$  for the ROM with  $N = 48$  (circles),  $N = 300$  (squares) and  $N = 1000$  (diamonds). The horizontal line is the  $N \rightarrow \infty$  limit. The arrows indicate the critical temperatures  $T_D$  (dynamic or mode coupling) and  $T_c$  (static or Kauzmann). The full line is the curve obtained from the configurational entropy for large  $N$  (see also [6]).



**Figure 3.** Temperature dependences of  $e(T)$  for a binary (80:20) mixture of Lennard-Jones particles. Simulations were done for 1000 particles at a fixed density of 1.2 (data courtesy of Kob *et al*; see also [19]).

rather good for  $e < -1.8$ , while above this value the energy dependence of  $f_v(T, e)$  cannot be neglected. The line is the quadratic best fit which gives the value  $e_c \simeq -1.944$  for the critical energy where  $s_c(e)$  vanishes, in good agreement with the theoretical result  $e_{lrsb} = -1.936$  [12].



**Figure 4.** (a) Configurational entropy as a function of energy for the ROM. The data are for system sizes  $N = 48$  (empty circles) and  $N = 300$  (filled circles), and temperatures  $T = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$  and  $1.0$ . For each curve the unknown constant has been fixed to maximize the overlap between the data and the theoretical result [12]. The curve is the quadratic best fit. (b) Configurational entropy density as a function of temperature. The curve is the result from the best fit of  $s_c(e)$  while the symbols show the results from the temperature integration of equation (7) for  $N = 48$  (empty circles),  $N = 300$  (empty triangles) and  $N = 1000$  (filled circles) (see also [6]).

A direct consequence of the relation  $f_v(T, e) \simeq f_v(T)$  for  $e < -1.8$  is that it drops out from equation (5), so the minimum condition simply reads

$$\frac{ds_c(e)}{de} = \frac{1}{T}. \quad (7)$$

From this relation, by integrating the  $T$ -dependence of  $de/T$ , we can compute  $s_c$  as a function of  $T$ . The result obtained using the data of figure 2 is shown in figure 4, panel (b). The line is the result valid for large  $N$  obtained using the quadratic best fit of panel (a).

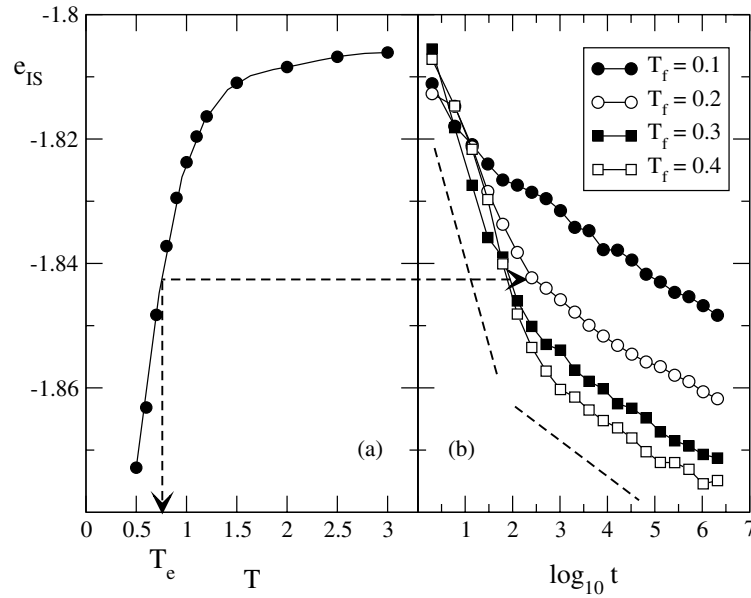
As discussed above, the vibrational contribution  $f_v$  follows from the motion inside the IS basins. Its independence of  $e_{IS}$  means that all basins are equivalent, i.e., have the same shape. In general, this is not the case and the contribution of  $f_v$  must be included. For systems with continuous variables, for example BMLJ particles,  $f_v$  can be calculated at low  $T$  in the harmonic approximation by expanding the energy about the IS configuration:

$$f_v(T, e_{IS}) = k_B T \sum_{i=1}^{3N-3} \ln[\hbar\omega_i(e_{IS})/k_B T] \quad (8)$$

where  $\omega_i(e_{IS})$  is the frequency of the  $i$ th normal mode in the  $e_{IS}$ -basin, which in general depends on the specific IS configuration, i.e., different IS with the same  $e_{IS}$  may have different normal modes. If all basins had the same curvature, then  $f_v$  would only be a function of  $T$  and we would be back to the previous case. In the BMLJ system, basins with different  $e_{IS}$  have different curvatures [9] and hence, in contrast with the ROM case,  $f_v$  is a function of both  $T$  and  $e_{IS}$ .

## 2.2. Violation of FDT and effective temperature

More information on the structure of the energy surface can be obtained from non-equilibrium relaxation processes. We shall consider here the non-equilibrium behaviour of the system



**Figure 5.** (a) Equilibrium average  $e_{IS}$  as a function of temperature. The arrows indicate the construction of the effective temperature  $T_e(e_{IS})$ . (b) Average IS energy for the ROM as a function of time for initial equilibrium temperature  $T_i = 3.0$  and final temperature  $T_f = 0.1, 0.2, 0.3$  and  $0.4$ . The average is over 300 initial configurations. The system size is  $N = 300$ . The dashed lines indicate the two regimes, see also [7].

following an instantaneous quench from an equilibrium state at a temperature  $T_i$  above the glass transition  $T_g$  to a temperature  $T_f$  below it.

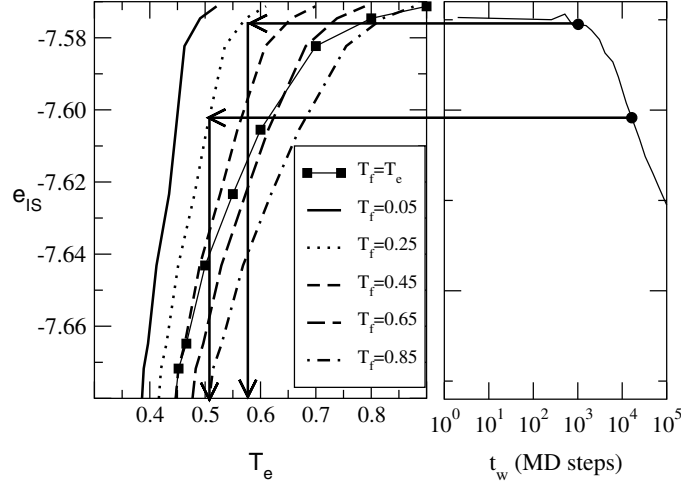
For temperatures close to the mode-coupling critical temperature, where the intra-basin and inter-basin timescales become well separated, the vibrational intra-basin dynamics quickly equilibrates at the thermal bath temperature  $T_f$ . The equilibration of the entire system on the other hand is rather slow, being dominated by the inter-valley processes. Therefore the fast equilibration of the intra-basin degrees of freedom is followed by a much slower process during which the system populates deeper and deeper  $e_{IS}$ -levels.

In the right-hand panel of figure 5 we show the average  $e_{IS}$ -energy as a function of time after the quench for the ROM. The figure reveals that the relaxation process can be divided into two different regimes: a first regime with a power law independent of  $T_f$ ; and a second regime with a power law independent of both  $T_i$  and  $T_f$ . The final temperature  $T_f$  controls the crossover between the two regimes. A similar behaviour has been observed in molecular dynamics simulations of supercooled liquids [19].

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  $k_B T_f$ . This part depends only on the initial equilibrium temperature  $T_i$  and should slow down as  $T_i$  decreases since, as is reasonable, lower states are surrounded by higher barriers. This process stops when all barrier heights become  $O(k_B T_f)$ ; the relaxation then slows down since it can proceed only via activated inter-valley processes.

Under the assumption of a fast equilibration of the intra-basin motion, we can define an *effective temperature*  $T_e$  as the temperature that the system would have when populating the basins of depth  $e_{IS}$ . The temperature  $T_e$  can be obtained from (5) with the vibrational





**Figure 6.** Left: solutions of equation (9) for several values of  $T_f$  for the BMLJ system. Right:  $e_{IS}$  as a function of time, following the temperature quench. The arrows show graphically the procedure which connects the value of  $e_{IS}(t)$  to the  $T_e$ -value, once  $T_f$  is known (data courtesy of Sciortino and Tartaglia; see also [9]).

contribution evaluated at the bath temperature  $T_f$ , since we assume local equilibrium of the intra-basin motion, and solving for  $T$  [9]:

$$T_e(e_{IS}, T_f) = \frac{1 + (\partial/\partial e_{IS})f_v(T_f, e_{IS})}{(\partial/\partial e_{IS})s_c(e_{IS})}. \quad (9)$$

The effective temperature  $T_e$  for the BMLJ particles is shown in figure 6. If  $f_v$  is not a function of  $e_{IS}$ , as in the case of the ROM, the above equation reduces to [6–8]

$$T_e(e_{IS})^{-1} = \frac{\partial s_c(e_{IS})}{\partial e_{IS}} \quad (10)$$

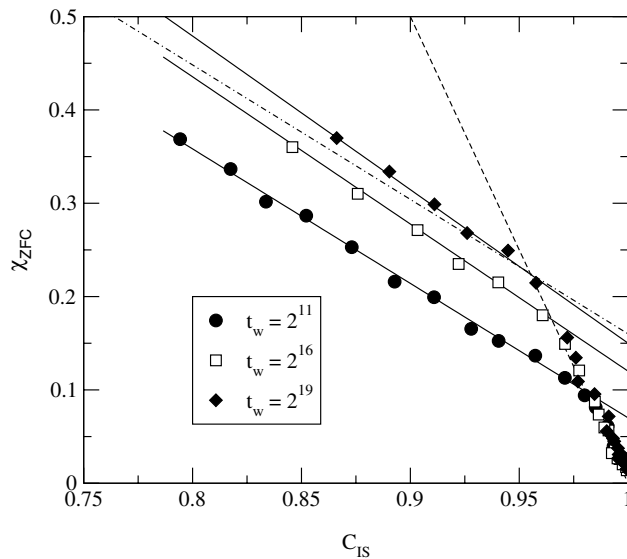
and curves with different  $T_f$  coincide; see figure 5. In the non-equilibrium relaxation process the value of  $e_{IS}$  will vary with time, making  $T_e$  a function of time, since the rhs of equations (9) and (10) must be evaluated at  $e_{IS}(t)$ . For each time  $t$  the value of  $T_e(t)$  can then be obtained graphically as shown in figures 5 and 6.

The predictions of the quasi-equilibrium assumption can be tested by studying the response of a system that is quenched to  $T_f$  at time  $t = 0$  to a perturbation switched on at some later time  $t_w$ . In the linear response regime the average value of any observable  $A$  at time  $t$  to a perturbation field  $h_A$  conjugate to  $A$  switched on at  $t_w < t$  is  $\langle A(t) \rangle = \chi_{ZFC}(t, t_w)h_A$ , where the zero-field-cooled susceptibility  $\chi_{ZFC}(t, t_w)$  is related to the  $AA$  correlation function through the famous fluctuation-dissipation formula [20]<sup>4</sup>

$$\chi_{ZFC}(t, t_w) = \frac{1}{T} [\langle A(t)A(t) \rangle - \langle A(t)A(t_w) \rangle] \Big|_{h_A=0} \quad (11)$$

which predicts that the response is proportional to  $T^{-1}$ . Under the assumption that the intra-valley motion quickly equilibrates to the thermal bath temperature  $T_f$ , while the equilibration of the entire system is dominated by the slow inter-valley processes, it follows that for short

<sup>4</sup> This expression and its differential counterpart are valid in the equilibrium regime. In the non-equilibrium regime the validity is based on the existence of an equiprobability principle which asserts that all basins with the same free energy are equiprobable [28].



**Figure 7.** Integrated response function as a function of IS correlation function, i.e., the correlation between different IS configurations, for the ROM. The dashed line has slope  $T_f^{-1} = 5.0$ , while the full lines are the predictions from (10):  $T_e(2^{11}) \simeq 0.694$ ,  $T_e(2^{16}) \simeq 0.634$  and  $T_e(2^{19}) \simeq 0.608$ . The dot-dashed line is  $T_e$  for  $t_w = 2^{11}$  drawn for comparison, see also [7].

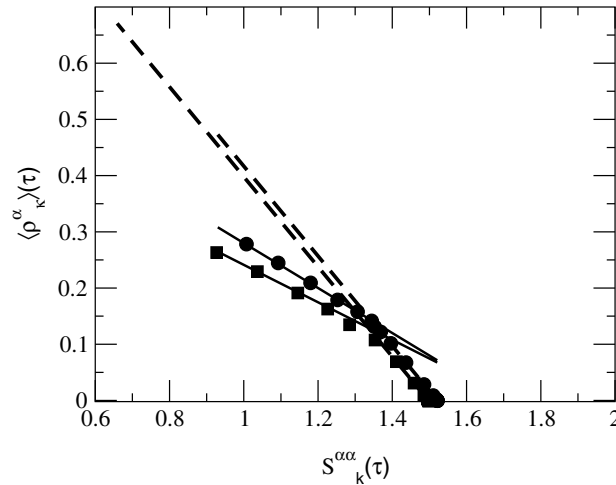
times,  $T = T_f$ , since the intra-basin motion is being probed, while for long times,  $T = T_e$ , since now it is the inter-basin motion that is to be probed. The first regime corresponds to the region where the correlation function assumes values between the equal time and plateau values, while in the second regime it assumes values below the plateau value.

In figure 7 we show the response versus correlation plot for the ROM. The analogous plot for the BMLJ particles is in figure 8. As follows from both figures, for short times the plot is linear with the expected  $T_f^{-1}$ -slope, properly describing the equilibrium condition of the intra-basin dynamics with the external bath. At larger times, the inter-basin motion sets in and the slope becomes  $T_e^{-1}$ , in very good agreement with the value predicted by equation (9).

### 3. Beyond the Stillinger and Weber projection: the free-energy landscape

In the previous sections the main effort has been to characterize glassy dynamics by studying the structure of minima of the potential energy landscape. Nevertheless, as has been said already, valleys are not only characterized by their energy at the bottom but also by the size of the basins of attraction. The decomposition proposed by SW is meaningful if the typical time required to explore a given IS or valley depends only on the energy of that valley (defined, for instance, by the energy  $e_{IS}$  of its associated minimum). But one can imagine a situation where IS with the same energy have completely different basins of attraction. In that case the probability of exploring a given IS depends not only on its energy but also on the size of the basin of attraction or its associated entropy. The most natural approach in which these considerations are properly taken into account is to assume that every IS is characterized by its free energy  $F_{IS}(T)$  defined as

$$\exp(-\beta F_{IS}(T)) = \sum_{C \in IS} \exp(-\beta E(C)) \quad (12)$$



**Figure 8.** Response  $\langle \rho_k^\alpha \rangle(\tau)$  versus the dynamical structure factor  $S_k^{\alpha\alpha}(\tau) \equiv \langle \rho_k^\alpha(t) \rho_k^{\alpha*}(0) \rangle$ , where  $\rho_k^\alpha$  is the Fourier transform component of the density of  $\alpha = A, B$  particles at wave-vector  $\mathbf{k}$ , for the binary mixture Lennard-Jones particles system for  $T_i = 0.8$ ,  $T_f = 0.25$  and two waiting times  $t_w = 1024$  (squares) and  $t_w = 16384$  (circles). Dashed lines have slope  $T_i^{-1}$  while full lines have slope  $T_e^{-1}$ . Data courtesy of Sciortino and Tartaglia; see also [9].

which corresponds to the free energy of the portion of the whole phase space containing all configurations belonging to the specific IS. We can now extend [21] the ideas of SW to include the free energy in the formulation by using the following equiprobability assumption: when the system is in equilibrium at a given temperature, valleys with the same free energy have the same probability of being explored. Both the number of configurations contained in each valley and the number  $g(F, T)$  of valleys with a given free energy grow exponentially with the size of the system, leading to a proper thermodynamic formulation in the large-volume limit. The equilibrium partition function can be written in terms of the IS free energies (12) as

$$\mathcal{Z} = \sum_C \exp(-\beta E(C)) = \sum_{\text{IS}} \sum_{C \in \text{IS}} \exp(-\beta E(C)) = \sum_{\text{IS}} \exp(-\beta F_{\text{IS}}(T)). \quad (13)$$

At a given temperature, the average free energy among all valleys is determined by a balance between the probability of exploring valleys with free  $F$  (proportional to the Boltzmann factor  $\exp(-\beta F)$ ) and the number  $g(F, T)$  of valleys with that free energy. Hence, the equilibrium free energy is given by

$$\begin{aligned} \exp(-\beta F_{\text{eq}}) &= \sum_{\text{IS}} \exp(-\beta F_{\text{IS}}(T)) = \sum_F g(F, T) \exp(-\beta F) \\ &= \sum_F \exp(S_c(F, T) - \beta F) = \sum_F \exp(-\beta \Phi(F, T)) \end{aligned} \quad (14)$$

where  $S_c(F, T) = \log(g(F, T))$  defines the configurational entropy while the function  $\Phi(F, T) = F - T S_c(F, T)$  is the thermodynamic potential associated with it. Because  $\Phi$  is an extensive quantity, the leading contribution to (14) is in the large-volume limit determined by the minimum of  $\Phi(F, T)$  as a function of  $F$ :

$$F_{\text{eq}}(T) = \Phi(F^*, T) = F^* - T S_c(F^*, T) \quad (15)$$

$$\frac{1}{T} = \left. \frac{\partial S_c(F, T)}{\partial F} \right|_{F=F^*}. \quad (16)$$

Note that the average free energy  $F^*$  does not coincide with the equilibrium free energy  $F_{\text{eq}}(T)$ : it is always higher,  $F^* = F_{\text{eq}}(T) + T S_c(F^*, T)$ , the difference being the configurational entropy evaluated at  $F^*$ .

It is interesting to note the parallelism of this coarse-grained description and the standard equilibrium theory. In that case, the relevant entities are the configurations and the equilibrium energy is given by a balance between the Boltzmann factor  $\exp(-\beta E)$  and the degeneracy  $g(E) = \exp(S(E))$  where  $S(E)$  is the entropy. The relation  $1/T = \partial S(E)/\partial E$  yields the thermodynamics. Nevertheless, an important difference between the standard equilibrium theory and the present free-energy valley decomposition must be stressed. Both the equilibrium entropy  $S(E)$  and the SW configurational entropy  $S_c(E)$  are only functions of the energy while the configurational entropy  $S_c(F, T)$  in this new formalism depends on both the free energy and the temperature. Therefore the configurational entropy turns out to be a more complicated object when expressed in terms of the free energy than in terms of the energy of the valleys.

A natural question arises now: what are the assumptions behind the validity of this free-energy decomposition? The main assumption in Boltzmann theory is the equiprobability assumption, i.e., all configurations with identical energy have the same probability in equilibrium. This introduces the equilibrium measure used in ensemble theory which is at the root of statistical mechanics. For glassy systems a similar idea lies behind the physical meaning of the present free-energy decomposition. One assumes [21] the validity of an equiprobability hypothesis stating that valleys with identical free energy have the same probability of being explored. This gives a flat measure in equilibrium which, if extended to the non-equilibrium case, is analogous to the Edwards measure proposed in the context of granular media [22–24]. The main difference between the Edwards measure and this new free-energy measure is that the former occurs in a non-stationary sheared situation [25] or even in a stationary one (for instance, under tapping [26]) at zero temperature, while the latter occurs in a non-stationary relaxational regime at finite temperature.

In recent work [21] the validity of this free-energy measure has been explicitly tested by studying the configurational entropy of simple models. This has been done by introducing a probabilistic argument to compute the free energy of the IS. In equilibrium, the probability of exploring a given IS is given by  $p_{\text{IS}}(T) = \exp(-\beta(F_{\text{IS}}(T) - F_{\text{eq}}(T)))$ . Then one can run a simulation and, after equilibrating, collect the number of times  $N_{\text{IS}}$  that a particular IS is found among a total number of quenches  $N_{\text{run}}$ . This yields  $p_{\text{IS}}(T) = N_{\text{IS}}/N_{\text{run}}$  from which we have an estimate of the IS free energy:  $F_{\text{IS}}(T) = -T \log(p_{\text{IS}}(T)) + F_{\text{eq}}(T)$ . By using this method, the configurational entropy  $S_c(F, T)$  has been computed in [21] for the ROM and the Sherrington–Kirkpatrick model, a model with a completely different energy surface topology [27]. The average free energy of the IS,  $F^*$ , can be obtained from the minimum of the potential  $\Phi(F, T)$ . The difference between the minimum  $F^*(T)$  and the equilibrium free energy  $F_{\text{eq}}(T)$  yields the configurational entropy at the given temperature  $S_c(F^*, T)$ . Moreover, from the shape of  $\Phi(F, T)$  it is possible to infer both the type of transition of the model (one step or infinite replica symmetry breaking) and the critical or Kauzmann temperature. We note that, as in the case of the SW results discussed in the previous section, the method works only for finite-sized systems where the number of different IS is not too large.

As a generalization of this free-energy scenario to the dynamics, it has been proposed that the effective temperature in structural glasses is related to their fragility [28]. Moreover, the effective temperature is also given by the slope of the configurational entropy evaluated at the threshold free energy. This off-equilibrium scenario complements the new measure discussed above and offers a scenario for the glass transition driven by entropic barriers.

#### 4. Models with kinetic constraints

Another class of interesting models are the kinetically constrained models. These models are characterized by extremely simple thermodynamic behaviour without any type of phase transition, but with complicated slow dynamics due to the existence of kinetic constraints. The constraints are such that detailed balance and ergodicity are preserved despite the infinite energy barriers that they introduce. In some senses they are similar to hard-sphere models where some configurations are excluded from the configurational space, although with much simpler static properties. The simplest example of this family of models is the kinetically constrained Ising paramagnet where there is no interaction between the spins (and hence there is no critical point even at  $T = 0$ ) but some transitions are excluded in the dynamics. The description of these models within an IS formalism has been studied in detail in [10]. Here we only want to make some general comments on the validity of the IS description of the dynamics; for a more detailed discussion we refer the reader to [10].

In general, in most of the dynamically constrained models the energy function can take only a discrete set of values; therefore there is accidental degeneracy in the density of states. One of the main problems related to this and discussed in [10] is that it is difficult to properly define the IS decomposition itself. The steepest-descent procedure for mapping a configuration onto a valley is not well defined because it is not unique. From a physical point of view this does not seem to be a serious problem. Suppose we add to the original Hamiltonian a random perturbation term  $P$  which lifts the degeneracy. If the system is stochastically stable (the dynamical behaviour in the limit  $P \rightarrow 0$  coincides with the dynamical behaviour of the unperturbed system), then one can work with the perturbed system and make the perturbation vanish at a later stage. Because the dynamics of the vast majority of glassy systems is probably stochastically stable, we believe that this is not a serious problem of the approach.

But there is another problem which seriously compromises the validity of the IS approach. One can show that the IS decomposition is completely identical for some models with completely different dynamical constraints, with the result that the SW configurational entropies are exactly the same. Because the dynamics of these models are known to be extremely different, it is then clear that the configurational entropy cannot describe their relaxational dynamics. Obviously, to cope with this problem one can go further and describe the dynamical behaviour in terms of the configurational entropy, but now defined in terms of the free energy. This route could eventually solve the problem because now, although the energies of the different IS are identical for all models, the entropic contributions (as explained in the preceding section) can be completely different. Nevertheless, we believe that going beyond the standard SW description will not really solve another more essential problem present in systems of this kind. One of the main features of these models is that relaxation occurs by the coarsening of a typical length scale. This length scale reflects the typical size of spatial regions which are ordered into the ground-state structure. As relaxation proceeds, the configuration of the system approaches that of the ground state. Now the ground state in this class of systems corresponds to the crystal structure in structural glasses. So the relevant question is: how important is the existence of a crystalline configuration in structural glasses as far as the glass transition phenomenology is concerned? Light scattering measurements suggest that relaxation in the supercooled region does not proceed by crystallization of larger and larger regions and that the structure of the glass is always that of a liquid. This result is in agreement with the very well known fact that some spin glasses with disorder (which do not have a crystalline structure) display a behaviour similar to that of structural glasses. Hence we must conclude that the slow dynamics in glasses is not necessarily related to a coarsening

process towards a single and unique structure. The physical mechanism behind relaxation must then be some kind of thermally activated entropic search, but without any kind of growing order in the system. On the other hand, the existence of a some kind of coarsening process in the relaxation will preclude the validity of the equiprobability hypothesis, and hence the existence of a flat measure for the free energy. Therefore kinetically constrained models, while displaying non-equilibrium behaviour strikingly similar to that of glasses, cannot be described in a framework such as that proposed in the previous section. Nevertheless, a careful study of the constrained Ising chain in terms of the free energy could certainly be interesting to clarify this issue.

## 5. Conclusions

There is still more work to be done. Most of the lines of research presented here will clearly see a fast development in the near future when our understanding of the validity of general scenarios for the description of glassy systems improves. The most important results that we have tried to propose in this paper can be summarized in the form of answers to the following set of selected questions:

- *When can the SW decomposition be expected to work fairly well?* A statistical description of valleys in terms of IS seems to be useful for systems where valleys are very narrow (which means that they contain an exponentially large number of configurations scaling like  $\exp(\alpha N)$ , but with  $\alpha \ll 1$  to ensure that the entropic contribution to the valley free energy is small) or valleys are very large but with very similar shape. The latter assumption corresponds to the claim that the distribution of instantaneous frequency modes computed in the harmonic approximation for those valleys is not too broad. This is indeed the case for, e.g., BMLJ [29] systems. Obviously, glassy systems where there is a highly heterogeneous distribution of basins of attraction for the IS cannot be described within the usual SW approach.
- *How can one improve the standard SW approach?* Basins of attraction can be included in the dynamical formulation by supposing that basins are visited according to their free energy. Therefore, in equilibrium at temperature  $T$ , the probability of visiting a valley with free energy  $F$  is proportional to the Boltzmann factor  $\exp(-\beta F)$  and to the number  $g(F, T) = \exp(S_c(F, T))$  of such valleys, where  $S_c(F, T)$  defines the configurational entropy. This free-energy measure can be further extended to deal with non-equilibrium processes where the probability of jumping among valleys is simply given by the entropic term  $g(F^*, T)$  evaluated at the time-dependent threshold free energy  $F^* = F(t)$ . This description offers an interpretation of the violation of FDT in terms of a single timescale, given by the effective temperature evaluated at the threshold  $1/T_e(t) = (\partial S_c(F, T)/\partial F)_{F=F^*}$ . The validity of this flat measure in terms of the free energy in the off-equilibrium regime remains one of the most fascinating problems when trying to construct a general theory for slowly relaxing non-equilibrium processes in complex free-energy landscapes.
- *What is the utility of investigating relatively small systems?* As we have stressed in the previous point, a description of basins in glassy systems must be constructed in terms of the free-energy landscape. The appropriate configurational entropy is then a function of both the free energy and temperature. Within the IS formalism an estimate of the free energy of each IS can be obtained by sampling the IS space. A good sampling requires that each IS is visited with a finite frequency. If the number of IS is too large, this is not possible. Remembering that the total number of IS becomes exponentially large with

increasing volume of the system, we conclude that sizes must be modest for the procedure to be implemented. Moreover, in the case of mean-field models, one can do careful checks of the main theoretical assumptions by comparing numerical results with analytical ones. Furthermore, a theoretical analysis of finite- $N$  corrections in mean-field systems could give a theoretical framework for activated processes in glassy systems.

- *Is the IS formalism relevant for coarsening models?* In principle, for systems where a given pattern grows with time the dynamics cannot be expressed in terms of jumps among uncorrelated structures. Therefore, the entropic assumption is not justified and a dynamical measure in terms of the free-energy landscape does not hold any longer. In this respect it would be extremely interesting to find a coarsening model where the IS formalism in terms of the free energy works. To our knowledge, such an example has not yet been provided.

In summary, the IS description of dynamics in terms of the energy and, more generally, in terms of the free energy of basins provides the first approximate scheme to deal with the dynamics of complex systems. There are still points which are obscure and not well understood, but these will we hope be progressively clarified in the near future. This will then provide a more complete understanding of the main physical mechanisms behind the elusive glass transition problem.

### Acknowledgments

We thank for useful discussions B Coluzzi, C Donati, U Marini Bettolo, E Marinari, A Rocco, F Sciortino, M Sellitto and P Tartaglia. Special thanks go to F Sciortino for having given us the data for BMLJ systems. FR acknowledges funding from project PB97-0971 and Acciones Integradas collaboration HI2000-0087.

### References

- [1] Götze W 1989 *Liquid, Freezing and the Glass Transition (Les Houches Lectures)* ed J-P Hansen, D Levesque and J Zinn-Justin (Amsterdam: North-Holland)
- [2] Goldstein M 1969 *Phys. Rev.* **51** 3728
- [3] Stillinger F H and Weber T A 1982 *Phys. Rev. A* **25** 978
- [4] Stillinger F H 1995 *Science* **267** 1935
- [5] Wales D J, Miller M A and Walsh T R 1998 *Nature* **394** 758
- [6] Crisanti A and Ritort F 2000 *Europhys. Lett.* **51** 147
- [7] Crisanti A and Ritort F 2000 *Europhys. Lett.* **52** 640
- [8] Crisanti A and Ritort F 2000 *J. Phys.: Condens. Matter* **12** 6413  
Crisanti A and Ritort F 2000 *Physica A* **280** 155
- [9] Sciortino F and Tartaglia P 2001 *Phys. Rev. Lett.* **86** 107
- [10] Crisanti A, Ritort F, Rocco A and Sellitto M 2000 *J. Chem. Phys.* **113** 10615
- [11] Beck C and Schlögl F 1993 *Thermodynamics of Chaotic Systems: an Introduction (Cambridge Nonlinear Science Series)* (Cambridge: Cambridge University Press) p 4
- [12] Marinari E, Parisi G and Ritort F 1994 *J. Phys. A: Math. Gen.* **27** 7847  
Parisi G and Potters M 1995 *J. Phys. A: Math. Gen.* **28** 5267
- [13] Kob W and Andersen H C 1994 *Phys. Rev. Lett.* **73** 1376  
Kob W and Andersen H C 1995 *Phys. Rev. E* **51** 4626  
Kob W and Andersen H C 1995 *Phys. Rev. E* **52** 4134  
Nauroth M and Kob W 1997 *Phys. Rev.* **55** 675  
Gleim T, Kob W and Binder K 1998 *Phys. Rev. Lett.* **81** 4404
- [14] Kirkpatrick T R and Thirumalai D 1987 *Phys. Rev. Lett.* **58** 2091  
Kirkpatrick T R and Wolynes P G 1987 *Phys. Rev. B* **36** 8552  
Crisanti A, Horner H and Sommers H J 1993 *Z. Phys. B* **92** 257

- [15] Bouchaud J P, Cugliandolo L F, Kurchan J and Mezard M 1998 *Spin Glasses and Random Fields* ed A P Young (Singapore: World Scientific)
- [16] Mezard M and Parisi G 1998 *Phys. Rev. Lett.* **82** 747  
Mezard M and Parisi G 1999 *J. Chem. Phys.* **111** 1076
- [17] Mezard M 1999 *Physica A* **265** 352  
Coluzzi B, Mezard M, Parisi G and Verrochio P 1999 *J. Chem. Phys.* **111** 9039
- [18] Sastry S, Debenedetti P G and Stillinger F H 1998 *Nature* **393** 554
- [19] Kob W, Sciortino F and Tartaglia P 2000 *Europhys. Lett.* **49** 590
- [20] See also Franz S and Virasoro M 2000 *J. Phys. A: Math. Gen.* **33** 891
- [21] Crisanti A, Marinari E, Ritort F and Rocco A 2001 *Preprint* cond-mat/0105391
- [22] Edwards S F and Mehta A 1989 *J. Physique* **50** 2489
- [23] Monasson R and Pouliquen O 1997 *Physica A* **236** 395
- [24] Sellitto M 2002 *J. Phys.: Condens. Matter* **14**
- [25] Barrat A, Kurchan J, Loreto V and Sellitto M 2000 *Phys. Rev. Lett.* **85** 5034  
Barrat A, Kurchan J, Loreto V and Sellitto M 2001 *Phys. Rev. E* **63** 051301
- [26] Dean D S and Lefevre A 2001 *Phys. Rev. Lett.* **86** 8639  
Lefevre A and Dean D S 2001 *Eur. Phys. J. B* **21** 121
- [27] See for example Mézard M, Parisi G and Virasoro M (ed) 1987 *Spin Glass Theory and Beyond* (Singapore: World Scientific)  
Fischer K H and Hertz J A 1991 *Spin Glasses* (Cambridge: Cambridge University Press)
- [28] Crisanti A and Ritort F 2001 *Preprint* cond-mat/0102104
- [29] Sciortino F 2001 private communication