Slow dynamics in glasses

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Abstract

We will review some of the theoretical progresses that have been recently done in the study of slow dynamics of glassy systems: the general techniques used for studying the dynamics in the mean field approximation and the emergence of a pure dynamical transition in some of these systems. We show how the results obtained for a random Hamiltonian may be also applied to a given Hamiltonian. These two results open the way to a better understanding of the glassy transition in real systems.

1 Introduction

Many systems (among them glasses, rubber, spin glasses...) show at low temperature a very slow approach to equilibrium. Our aim is to understand this kind of behaviour, in particular the peculiar properties of the glass transition.

At the present moment in the framework of the mean field approximation the static of spin glasses is well understood. We start to have a reasonable understanding of the dynamics. We hope that these progresses will lead to a better understanding of the behaviour of glasses. However this goal seemed to be unreachable for two reasons.

- (a) The behaviour of spin glasses and real glasses is rather different near the transition.

  In real glasses a very interesting phenomenon happens: if the temperature is decreased fast enough, the system goes into an amorphous state that has an extremely large mean life; moreover under very slow cooling some of these systems go into an ordered crystal phase. The crystal phase does not exist in general, it exists only if the parameters of the interactions among the atoms are *intentionally* chosen in such a way that this phase is energetically favoured. Independently from the possible existence of the crystal phase, the dynamics in the glassy phase becomes extremely slow at low temperature.

  Moreover the internally energy in the amorphous phase depends on the cooling speed in a strong way, also for very slow cooling. These effects have never observed in spin glasses. The spin glass transition can also be characterised by the divergence of a static quantity (the non linear susceptibility) while no anomalous behaviour has been observed in the static quantities in real glasses.

- (b) From the theoretical point of view the two systems seem to be extremely different.

  Spin glasses are systems with a random Hamiltonian. They are studied by averaging over the disorder in the Hamiltonian using *ad hoc* methods, e.g. the replica technique. Real glasses have a given Hamiltonian and the disorder is not present in the Hamiltonian, but comes out from the freezing of some of the relevant degrees of freedom.

Recently there have been some progresses which show that the previous difficulties are less serious than it was believed.

- (a) It has been found that in some disordered systems (e.g. modified spin glasses) there is a dynamical transition which is characterised by the divergence of the time needed for equilibrate the system. Near this transition temperature the static quantities do show no anomaly. The temperature at which the equilibration time diverges is higher than the temperature at which a transition is present for the static quantities. This static transition cannot be observed because the system takes to much time to equilibrate.
- (b) In some cases the replica method can be applied also to system without intrinsic disorder in the Hamiltonian. The behaviour of those system is very similar to that of really disordered systems, apart from the possible existence of a low energy ordered crystal phase

Some of these effects cannot be understood using only the tools of standard equilibrium statistical mechanics, because they are non- equilibrium phenomena. In this note I will present a coherent picture of the dynamics of these systems. The results have been obtained in these recent years mainly in the framework of spin glasses theory [1, 2] and I will show how they can be extended to other systems like glasses. Some of the statements are well proven, while other are still conjectural.

In the second section of this note I will give a general qualitative description of the dynamics based on the hypothesis that systems evolve in time jumping from one to an other quasi-equilibrium state. In the third section I will review some very interesting results obtained by a direct computation of the dynamical evolution of the system using more powerful methods; I will also compare these results with those obtained in the previous section. Finally in the fourth section I will address to the old problem of comparing the behaviour of a system with random Hamiltonian (like spin glasses), with that of system with a fixed Hamiltonian (like glasses). This comparison will be done in a model system: one finds that the properties of the system with fixed Hamiltonian are very similar to that of the systems with random Hamiltonian. The only difference is the possible existence of a crystal phase for specific choices of the parameters of the fixed Hamiltonian; the crystal phase does not exists for the random Hamiltonian. Some brief conclusions are presented at the end.

2 Local Equilibrium States

We consider Ising spin models in which there are N variables σ_i, which take the values ± 1 [1] There are many possible kinds of Hamiltonian that we can write down. In the simplest case the interaction involves only two spins,

[1] Similar consideration can also be done for interfaces or manifolds in a random medium [3].

$$H_J(\sigma) = -\sum_{i,k} J_{i,k}\sigma_i\sigma_k, \tag{1}$$

and all the pairs i,k are equivalent.

If the J are randomly distributed Gaussian variables, with variance $1/N$, we obtain the SK model, otherwise one has a different model.

At low temperature these models have a corrugated free energy landscape, with many local minima, separated by high barriers. In this situation general arguments imply a very slow dynamics because the system may be trapped in a valley and it takes quite a long time to escape from it.

The jumping from a valley to an another valley is a controlled by the height of the barriers and the time needed (neglecting prefactors) is

$$\tau = \exp(\beta\Delta F), \tag{2}$$

where ΔF is the minimum barrier in free energy that the system has to cross in going from one valley to an other valley [2].

The best characterisation of a valley [3] is a region of the phase space in which the system spends a long time. In this case it reasonable to define the local magnetizations in the valley α as

$$m_i^\alpha = \langle\sigma_i\rangle_\alpha, \tag{3}$$

where the average is taken inside the valley α.

In long range models these magnetizations satisfies the mean field equations. Neglecting the Onsager reaction field [4], they are are

$$m_i = th(\beta\sum_k J_{i,k}m_k) \tag{4}$$

Alternatively we can define a free energy as function of the m_i:

$$F[m] = -\sum_{i,k} J_{i,k}m_im_k - T\sum_i s(m_i), \tag{5}$$

where the local entropy is simply given by

$$s(m) = -\frac{1+m}{2}\ln(\frac{1+m}{2}) - \frac{1-m}{2}\ln(\frac{1-m}{2}). \tag{6}$$

The local minima of the free energy $F[m]$ are solutions of the mean field equations .

The free energy landscape can be characterised by the structure of the set of the solutions (which we will label by Greek indices). Generally speaking the most important parameters are the free energy of the solution (f^α, the local magnetizations m_i^α in a given solution, the overlap among two solutions α and γ ($q_{\alpha,\gamma} = \frac{1}{N}\sum_{i=1,N} m_i^\alpha m_i^\gamma$) and the self overlap ($q_{EA} = q_{\alpha,\alpha}$), which in most of the models is independent from the solution.

At equilibrium it is reasonable to assume that different valleys may be populated, and the probability that the system is in one of this valley is given by

$$w_\alpha \propto w(f_\alpha) \equiv \exp(-\beta f_\alpha). \tag{7}$$

[2]This is not the only method for having a slow dynamics. For alternative possibilities see [4, 5].

[3]Sometimes one uses the terminology *local equilibrium state* or *quasi-equilibrium state*.

[4]If we add the Onsager reaction field we obtain the TAP equations.

It is evident that

$$\sum_\alpha w_\alpha = 1. \tag{8}$$

In many disordered systems the number of valleys as function of the free energy ($\mathcal{N}(f)$) increases as

$$\mathcal{N}(f) \sim \exp(y(f - f_0) + O((\frac{f - f_0)^2}{V}), \tag{9}$$

in the region where

$$1 << f - f_0 << V \tag{10}$$

where V is the volume of the system.

At a given temperature there are two possibilities

- (a) If $y < \beta$ the integral
$$\int df \mathcal{N}(f) w(f) \tag{11}$$
is dominated by f near f_0. Only few valleys dominate the sum in equation(8), although an infinite number of them give a non zero contribution. In this situation we say that the replica symmetry is broken.

- (b) If $y > \beta$ the integral
$$\int df \mathcal{N}(f) w(f) \tag{12}$$
would be divergent if we neglect terms of $O((\frac{f-f_0)^2}{V})$. In reality the integral is dominated by the region where $f - f_0$ of order of the size V of the system. In this case the number of valleys which dominates the sum in equation (8) is exponentially large and each of the valley has a weight which is exponentially small. In this case the replica symmetry is not broken.

Let us consider the case where the valleys are separated by very high barriers (e.g. diverging with N) in the region where the temperature T is smaller than T_D. Depending on the nature of the problem we may enter or in the region (a) or (b) when we decrease the temperature from above to below T_D.

If we enter in the region (a), as it happens in the usual SK model for spin glasses, a phase transition is present from the equilibrium point of view at T_D.

On the contrary, as happens in other spin glass models [7]-[**?**], if we enter in the region (b), no phase transition is present from the equilibrium point of view at T_D, and a static transition is present only at smaller temperature, T_R, where y becomes smaller that β and we pass from region (a) to region (b). This transition can be easily understood. At temperatures greater that T_R the valleys populated at equilibrium have a free energy density greater than minimal possible because of entropic effects. The relevance of these entropic effects disappear by decreasing the temperature and for temperatures less than T_R the valleys have the smallest possible free energy.

In this last case we have two transition one for the statics and the other for the dynamics. If we quench the system at temperature smaller than T_D coming from an high temperature region, the internal energy (for an infinite system) does not go to the equilibrium value and the system remains trapped in a metastable state [8, 9].

In this case for the infinite system independently from the speed of cooling we always find the energy of the metastable states and therefore we do not observe any strong dependence of the energy on the cooling. This is an artefact of the mean field approximation, which is correct only for infinite range forces. We shall see later how this behaviour may be changed for more realistic model.

It is also possible that there is an other isolated solution to the mean field equation, with a free energy density F_C smaller than F_0 and there are no solutions in the region

$$F_C < F < F_0. \tag{13}$$

In many cases this isolated solution describes an highly ordered state, which we call the crystalline state. The existence of this states does not change the properties of the system in the region where $f > f_0$.

From this point of view in order to compute the approach to equilibrium one should evaluate the free energy barriers which separate one valley from an other valley. This computation is rather difficult, especially if we take care that the system is still slightly out of equilibrium. However in the next section we shall see that a direct computation of the non equilibrium properties can be done.

3 The non equilibrium equations

It was found quite recently [8, 9] that the non equilibrium behaviour of the system can be described directly for the infinite system (i.e. after having taken the limit $N \to \infty$), by introducing the average correlation function and the response function defined as

$$C(t,t') = \lim_{N\to\infty} \frac{\sum_{i=1,N} \sigma_i(t)\sigma_i(t')}{N},$$
$$G(t,t') = \lim_{N\to\infty} \frac{\sum_{i=1,N} \frac{\delta\sigma_i(t')}{\delta h_i(t)}}{N}. \tag{14}$$

In the equilibrium regime time translation invariance implies that these functions depend only on the time difference. We consider here the case where the system at time zero starts from a random configuration. Only positive times are possible and time translation is explicitely broken.

Closed equation can be written for these two functions. They are

$$\frac{\partial C(t,t')}{\partial t'} = E_C[C,G],$$
$$\frac{\partial G(t,t')}{\partial t'} = E_G[C,G], \tag{15}$$

where $E_C[C,G]$ and $E_G[C,G]$ have an explicit form (non local in time) which depend on the problem. In some case one can expand $E_C[C,G]$ and $E_G[C,G]$ in powers of C and G. The solution of these equations can be computed numerically and one can obtain a great amount of information in this way.

From the analytic point of view one can study these equation in the adiabatic approximation, where one set to zero the time derivative. This approximation is justified in the large time region. The resulting equations are non trivial; they are

$$E_C[C,G] = E_G[C,G] = 0. \tag{16}$$

The solution of these equations can be simplified [3, 8, 9] by noting that they are *reparametrization invariant*, i.e. if C and G are a solution also the functions

$$
\begin{aligned}
C_h(t,t') &= C(h(t),h(t')), \\
G_h(t,t') &= G(h(t),h(t'))\frac{dh(t')}{dt'},
\end{aligned}
\tag{17}
$$

are an other solution of the adiabatic equations, for an arbitrary choice of the function h.

Reparametrization invariance strongly simplifies the study of the adiabatic equations and many results can be obtained in this limit. In some case it can be proved that for large times the internal energy tends to the equilibrium value, while in other case finds that there is dynamical transition at a temperature T_D. At lower temperature one finds that the dynamical energy does *not* tend at large times at the equilibrium value and therefore metastable states are present.

The evaluation of the reparametrization invariant quantities morally corresponds to the evaluation of the properties of the solutions of the mean fields equations of the previous section, although it contains more information.

The more difficult part, which at the present moment we can do only numerically, consists in computing quantities that are not reparametrization invariant, as the time dependence of the energy. This computation morally corresponds to the evaluation of the barriers separating the solutions of the mean fields equations of the previous section and it is not a surprise that it turns out to be much more difficult. Technically one ends up with a well defined and difficult mathematical problem, very similar in spirit, but more complicated, of the non linear velocity selection problem, which has been widely studied in the past.

It is extremely satisfactory that the very difficult problem of computing analytically the non equilibrium dynamics in these systems is now under control and I am convinced that the mathematical difficulties may be surmounted, may be with some help from our more mathematically minded friends.

The results obtained from this dynamical approach have the advantage to be easily compared with those obtained experimentally in spin glasses, where the condition N very large with respect to t is certainly satisfied. A very interesting phenomenon which appears is aging, i.e. the dependence of the experimental results on the age of the system [10, 11, 12]. A detailed discussion of this point would make this note too long.

4 Glasses in the mean field approximation

In spin glasses the Hamiltonian is random as an effect of quenched random disorder. In real glasses the Hamiltonian is not random and the quenched disorder is dynamically generated at low temperature. We can ask how much of the qualitative and quantitative results which have obtained in spin glasses may be transferred to glasses.

In order to understand this point we have started to study models in which the Hamiltonian does not contain quenched disorder and to compare the results with those coming of random Hamiltonian [13].

Our strategy is the following. We want to study the properties of a given Hamiltonian H_G which is not random. We consider a class of Hamiltonians H_R, of which H_G is a particular case. We choose the class H_R in such a way that the statistical properties of

H_G and that of a generic Hamiltonian in H_R are as similar as possible. In the best case we can obtain that the two corresponding free energies coincide in the high temperature expansion [5].

After having constructed H_R in an appropriate way, we can suppose that the statistical properties of H_G and H_R are the same or, if they are different, we can construct a perturbative expansion which compute this difference. It is clear that this approach may be successfully in the high temperature region (more or less by construction) and it may also reproduce the behaviour in the glassy region, included the dynamic and static transitions. However it is cannot certainly reproduce the possible existence of a crystal phase.

I will present now a simple model in which this approach works very well at all the temperature and it misses only the crystal phase, which exists only for *intentionally* chosen Hamiltonians H_G [14]. The Hamiltonian is is the same as in eq. (1).

In the case of H_G we have

$$J_{i,k} = N^{-1/2} \sin(\frac{2\pi ik}{N}), \tag{18}$$

while in the case of H_R we have that J is a random orthogonal symmetric matrix, i.e. a random symmetric matrix which satisfies the constraint

$$\sum_k J_{i,k} J_{k,j} = \delta_{i,j}. \tag{19}$$

It is easy to check that the first Hamiltonian is a particular realization of the second one.

A details computation (partially analytic and partially numeric) for the Hamiltonian H_G shows that in the low temperature phase there are two different limits when N goes to infinity, one for generic N and an other for N odd, such that $p = 2N + 1$ is prime. Only in this second case there is a crystalline phase at low temperature. At all temperatures the model for generic N behaves in the same way as the model described by H_R and it undergoes a replica symmetry breaking transition. On the contrary the dynamical glassy transition is present for all N. The strategy of computing the properties of a given system by approximating it by a random system works very well in the glassy region and it misses the crystal phase, which exists only for non generic values of N.

There are many other system which can be studied using this stategy [15, 16], but I will not discuss them.

5 Conclusions

We have seen that we begin to control the off equilibrium dynamics in many model systems. There are cases in which we have a glass transition with metastability. This feature is present only in the mean approximation, which is correct in the infinite range limit.

A crucial and open problem is to understand how this feature of the infinite range approximation appears in more realistic finite range models, in which metastable states cannot exists. Let us describe a possible scenario for the (fragile) glass transition.

The correlation time τ diverges algebraically at T_D, which is not the situation for real glasses where a divergence of the form

$$\tau \propto \exp(\frac{A}{(T - T_G)}) \tag{20}$$

[5]In general the behaviour of the system can be better controlled in the high temperature phase.

is observed.

On the other hands metastability is present in the mean field approximation as soon as $T < T_D$. Generally speaking metastable states do decay in short range model by tunnelling effects. If we apply these ideas to the present case we find that

$$\tau \propto \exp(g(T)), \tag{21}$$

where $g(T)$ is a smooth function, which quite likely diverges at the temperature T_R as

$$g(T) \propto (T - T_R)^{-\gamma}. \tag{22}$$

From this point of view the glass transition temperature should be identified with the temperature at which in the mean field approach the replica symmetry is broken. The dynamical transition found in the mean field approach is no more a real transition and denotes the onset of very slow dynamics.

This line of thinking should be seriously investigated and one should develop the theoretical techniques needed to compute the function $g(T)$. The dependence of the exponent γ on the dimensions of the space is a rather interesting issue, which unfortunately it has not been studied up to now. Experiment on four dimensional glasses are notoriously rather difficult to be done, however the comparison of numerical simulations for three and four dimensional glass models should give rather interesting information and may be crucial to test further developments of the theory. For example the theory could predict that in d-dimensions $\gamma = d - 2$, i.e.

$$\tau \propto \exp(\frac{A}{(T - T_G)^{(d-2)}}). \tag{23}$$

The only possibility for a new testing this kind of predictions (apart from the known three dimensional case) would be to do accurate numerical simulations in higher dimensions.

The study of off equilibrium dynamics in glass related models has started only recently. Very interesting results have been obtained and I am confident that this approach will lead to a better understanding of real glasses.

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