On the mean field approach to glassy systems

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Abstract

In these lectures I will study some properties that are shared by many glassy systems. I will shown how some of these properties can be understood in the framework of the mean field approach based on the replica method and I will discuss which are the difficulties which we have to face when we apply the replica method to realistic short range models. We finally present a partially successfully application of the replica method to soft sphere glasses.

1 Introduction

In these lecture I will study some systems which present some of the relevant characteristics of glasses. The aim is to construct simple microscopic models which can be studied in details and still behave in an interesting way. I will start from the simplest models, where only some of the observed characteristics are reproduced and we will later go to more complex systems.

The basic idea is to learn as much it is possible from mean field theory results and to try to understand the extent of the overlap among the rather complex phenomenology displayed by glasses and the exact results which are obtained for model with infinite range interaction. It is remarkable that the two cases have many points in common (with a few very interesting differences!) so that it seems to be a quite natural and reachable goal to construct a theory of glasses based on mean field tools. This construction is in progress and here I will review our present understanding.

This note is organized as follows: after this introduction we recall some of the main results which have been obtained in the framework of the mean field theory, both for systems with and *without* quenched disorder. In section III I will show which are the difficulties to extend these results to short range models, which properties are maintained and which are modified. Finally in the last section I will stress some of the properties of real glasses and I will describe a first tentative of doing esplicite computations for a soft sphere glass.

2 Mean field results

In these recent years there have been many progresses on the understanding of the behaviour of glassy systems in the mean field approximation. The mean field approximation is correct when the range of the interaction is infinite and this property allows us to write self consistent equations whose solution gives the solution of the model. The techniques that can be used are of various types, the replica method, a direct probabilistic method based of the cavity (Bethe) equations [2, 3] and the direct study of the dynamical equations [4, 5].

The main results have been the following:

- Model with random quenched disorder have been well understood both from the equilibrium and from the dynamical point of view.
- Some of the results obtained for systems with random quenched disorder have been extended to non disordered system. This step is crucial in order to have the possibility of extending these models to real glasses.

Let us see in details the results that have been obtained.

2.1 Disordered systems

In this case the thermodynamical properties at equilibrium can be computed using the replica method [2, 3]. A typical example of a model which can be solved with the replica method is a spin model with p spin interaction. The Hamiltonian we consider depends on some control variables J, which have a Gaussian distribution and play the same role of the random energies of the REM (i.e. the random energy model [6, 7]) and by the spin variable σ. For $p = 1, 2, 3$ the Hamiltonian is respectively

$$H_J^1(\sigma) = \sum_{i=1,N} J_i \sigma_i \tag{1}$$

$$H_J^2(\sigma) = \sum_{i,k=1,N}{}' J_{i,k} \sigma_i \sigma_k \tag{2}$$

$$H_J^3(\sigma) = \sum_{i,k,l=1,N}{}' J_{i,k,l} \sigma_i \sigma_k \sigma_l$$

where the primed sum indicates that all the indices are different. The N variables J must have a variance of $O(N^{(1-p)/2})$ if we want to have a non trivial thermodynamical limit. The variables σ are usual Ising spins, which take the values ± 1. From now on we will consider only the case $p > 2$.

In the replica approaches one assumes that at low temperatures the phase space breaks into many valleys, (i.e. regions separated by high barriers in free energy). One also introduces the overlap among valley as

$$q(\alpha, \gamma) \equiv \frac{\sum_{i=1,N} \sigma_i^\alpha \sigma_i^\gamma}{N}, \tag{3}$$

where σ^α and σ^γ are two generic configurations in the valley α and γ respectively.

In the simplest version of this method [8, 9] one introduces the typical overlap of two configurations inside the same valley (sometimes denoted by q_{EA}. Something must be said about the distribution of the valleys. Only those which have minimum free energy are relevant for the thermodynamics. One finds that these valleys have zero overlap and have the following probability distribution of *total* free energy of each valley:

$$P(F) \propto \exp(\beta m(F - F_0)), \tag{4}$$

where F_0 is the total free energy of the valley having lower free energy.

Indeed the average value of the free energy can be written in a self consistent way as function of m and q ($f(q,m)$) and the value of these two parameters can be found as the solution of the stationarity equations:

$$\frac{\partial f}{\partial m} = \frac{\partial f}{\partial q} = 0. \tag{5}$$

The quantity q is of order $1 - \exp(-A\beta p)$ for large p, while the parameter m is 1 at the critical temperature, and has a nearly linear behaviour al low temperature. The only difference is that m is no more strictly linear as function of the temperature.

The thermodynamical properties of the model are the same as is the Random Energy Model (indeed we recover the REM when $p \to \infty$): there is a transition at T_c with a discontinuity in the specific heat, with no divergent susceptibilities.

A very interesting finding is that if we consider the infinite model and we cool it starting at high temperature, there is a transition at a temperature $T_D > T_c$ [4, 5]. At temperatures less than T_D the system is trapped in a metastable state. The correlation time (not the equilibrium susceptibilities) diverges at T_D and the mode-mode coupling become exact in this region [10] .

It was suggested some time ago [11, 12, 13] that these properties of the p-spin model strongly hint that this model may be considered a mean field realization of a glassy system and it should share with real glasses the physical origine of this behaviour.

It is interesting to note that although in the original approach the dynamical transition was found by using explicitly the equation of motions now we have techniques which allow the determination of the dynamical transition and of some of the properties of the exponentially large times needed to escape from a metastable state using only equilibrium computations [14, 15, 16, 17]. The main technical tool consists in computing the properties of a system with coupled replicas [18].

2.2 Model without quenched disorder

We could ask how much of the previous results can be carried to models without quenched results. It has been found in the framework of the mean field theory (i.e. when the range of the interaction is infinite), that there a the partial equivalence of Hamiltonians with quenched and random disorder. More precisely it often possible to find Hamiltonians which have the same properties (at least in a region of the phase space) of the Hamiltonian without disorder [19] - [26] . An example of this intriguing phenomenon is the following.

The configuration space of our model is given by N Ising spin variables [19]. We consider the following Hamiltonian

$$H = \sum_{i=1,N} |B_i|^2 - 1|^2, \tag{6}$$

$$\text{where} \quad B_i = \sum_{k=1,N} R_{i,k}\sigma_k. \tag{7}$$

Here R is an unitary matrix, i.e.

$$\sum_{k=1,N} R_{i,k}\overline{R_{k,m}} = \delta_{i,m}. \tag{8}$$

We could consider two different cases [19] :

- The matrix R is a random orthogonal matrix.
- The matrix R is given by
$$R(k,m) = \frac{\exp(2\pi i\ km)}{N^{1/2}} \tag{9}$$
  In other words B is the Fourier transform of σ.

The second case is a particular instance of the first one, exactly in the same way that a sequence of all zeros is a particular instance of a random sequence.

The first model can be studied using the replica method and one finds results very similar to those of the p-spin model we have already studied.

Now it can be proven that the statistical properties of the second model are identical to those of the first model, with however an extra phase. In the second model (at least for some peculiar value of N, e.g. N prime [20, 19, 21]) there are configurations which have exactly zero energy. These configuration form isolated valleys which are separated from the others, but have much smaller energy and they have a very regular structure (like a crystal). An example of these configurations is

$$\sigma_k \equiv_{\mathrm{mod} N} k^{(N-1)/2} \tag{10}$$

(The property $k^{(N-1)} \equiv 1$ for prime N , implies that in the previous equations $\sigma_k = \pm 1$). Although the sequence σ_k given by the previous equation is apparently random, it satisfies so many identities that it must be considered as an extremely ordered sequence (like a crystal). One finds out that from the thermodynamical point of view it is convenient to the system to jump to one of these ordered configurations at low temperature. More precisely there is a first order transition (like a real crystalization transition) at a temperature, which is higher that the dynamical one.

If the crystallisation transition is avoided by one of the usual methods, (i.e. explicit interdiction of this region of phase space or sufficient slow cooling), the properties of the second model are exactly the same of those of the first model. Similar considerations are also valid for other spin models [23, 24, 25] or for models of interacting particles in very large dimensions, where the effective range of the force goes to infinity [26, 27, 28, 29] .

We have seen that when we remove the quenched disorder in the Hamiltonian we find a quite positive effect: a crystallisation transition appears like in some real systems. If we neglect crystalization, which is absent for some values of N, no new feature is present in system without quenched disorder.

These results are obtained for long range systems. As we shall see later the equivalence of short range systems with and without quenched disorder is an interesting and quite open problem.

3 Short range models

The interest of the previous argument would be to much higher if we could apply them to short range models. In order to discuss this point it is convenient to consider two classes of models:

$$H = \sum_{x,y,z} J(x,y,z)\sigma(x)\sigma(y)\sigma(z)$$
$$H = \sum_{x,y,z} J(x-y,x-z)\sigma(x)\sigma(y)\sigma(z). \tag{11}$$

In both cases the sum is restricted to triplets spins which are at distance less than R (i.e. $|x-y|<R$, $|x-z|<R$, $|z-y|<R$). In the first case the model is not translational invariant while in the second case the Hamiltonian is translational invariant. Moreover in the second case the Hamiltonian depends only on a *finite* number of J also when the volume goes to infinity, so that the free energy density will fluctuates with J. The second model looks much more similar to real glasses than the first one. A careful study of the difference among these two models has not yet been done. In any case it is clear that the phenomenon of metastability which we have seen in the previous section for the infinite range models is definitely not present in these short range models. No metastable states with infinite mean life do exist in nature.

Let us consider a quite simple argument. Let us suppose that the system may stay in phase (or valleys) which we denote as A and B. If the free energy density of B is higher than that of A, the system can go from B to A in a progressive way, by forming a bubble of radius R of phase A inside phase B. If the surface tension among phase A and B is finite, has happens in any short range model, for large R the volume term will dominate the free energy difference among the pure phase B and phase B with a bubble of A of radius R. This difference is thus negative at large R, it maximum will thus be finite.

In the nutshell a finite amount of free energy in needed in order to form a seed of phase A starting from which the spontaneous formation of phase A will start. For example, if we take a mixture of H_2 and O_2 at room temperature, the probability of a spontaneous temperature fluctuation in a small region of the sample, which lead to later ignition and eventually to the explosion of the whole sample, is greater than zero (albeit quite a small number), and obviously it does not go to zero when the volume goes to infinity.

We have two possibilities open in positioning the mean field theory predictions of existence of real metastable states:

- We consider the presence of these metastable state with *infinite* mean life an artefact of the mean field approximation and we do not pay attention to them.

- We notice that in the real systems there are metastable states with very large (e.g. much greater than one year) mean life. We consider the *infinite* time metastable states of the mean field approximation as precursors of these *finite* time metastable states. We hope (with reasons) that the corrections to the mean field approximation will give a finite (but large) mean life to these states (how this can happen will be discussed later on).

Here we suppose that the second possibility is the most interesting and we proceed with the study of the system in the mean field approximation. We have already seen that in a short range model we cannot have real metastable states. Let us see in more details what happens.

Let us assume that $\Delta f < 0$ is the difference in free energy among the metastable state and the stable state. Now let us consider a bubble of radius R of stable state inside the metastable one. The free energy difference of such a bubble will be

$$F(R) = -\Delta f \; V(R) - I(R) \tag{12}$$

where the interfacial free energy $I(R)$ can increase at worse as $\Sigma(R)$. The quantities $V(R) \propto R^D$ and $\Sigma(R) \propto R^{D-1}$ are respectively the volume and the surface of the bubble; σ is the surface tension, which can also be zero (when the surface tension is zero, we have $I(R) \propto R^\omega$, with $\omega < D-1$).

The value of $F(R)$ increases at small R, reaches a maximum a R_c, which in the case $\sigma \neq 0$ is of order $(\Delta f)^{-1}$ and it becomes eventually negative at large R. According to enucleation theory, the system goes from the metastable to the stable phase under the formation and the growth of such bubbles, and the time to form one of them is of order (neglecting prefactors)

$$\ln(\tau) \propto \Delta f \; R^D \propto (\Delta f)^{(D-1)} \tag{13}$$

$$\tau \propto \exp\left(\frac{A}{(\Delta f)^{(D-1)}}\right) \tag{14}$$

where A is constant dependent on the surface tension. In the case of asymptotically zero surface tension we have

$$\tau \propto \exp\left(\frac{A}{\Delta f^\lambda}\right) \tag{15}$$

$$\lambda = \frac{D}{\omega} - 1 \tag{16}$$

This argument for the non existence of metastable states can be naively applied here. The metastable states of the the mean field approximation now do decay. The dynamical transition becomes a smooth region which separates different regimes; an higher temperature regime where mode mean field predictions are approximately correct and a low temperature region where the dynamics is dominated by barriers crossing. There is no region where the predictions of mean field theory are exact but mean field theory is only an approximated theory which describe the behaviour in a limited region of relaxation times (large, but not too large).

The only place where the correlation time may diverge is at that the thermodynamical transition T_c, whose existence seems to be a robust prediction of the mean field theory. It follows that the only transition, both from the static and the dynamical point of view, is present at T_c.

In order to understand better what happens near T_c we must proceed in a careful matter. The nucleation phenomenon which is responsible of the decay of metastable states is of the same order of other non-perturbative corrections to the mean field behaviour, which cannot be seen in perturbation theory. We must therefore compute in a systematic way all possible sources of non perturbative corrections. This has not yet been done, but it should not be out of reach.

One of the first problem to investigate is the equivalence of systems with and without random disorder. In systems with quenched disorder there are local inhomogeneities which correspond to local fluctuations of the critical temperature and may dominate the thermodynamics when we approach the critical temperature.

It is quite possible, that systems with and without quenched disorder, although they coincide in the mean field approximation, they will be quite different in finite dimension (e.g. 3) and have different critical exponents. The scope of the universality classes would be one of the first property to assess.

It is not clear at the present moment if the strange one order and half transition is still present in short range model or if it is promoted to a bona fide second order transition. If the transition remains of the order one and half (for example is conceivable that this happens only for systems without quenched disorder). It could also possible that there is appropriate version of the enucleation theory which is valid near T_c and predicts:

$$\tau \propto \exp(\frac{A}{(T-T_C)^{\alpha}}). \tag{17}$$

A first guess for α is $D-2$ [13, 14] , although other values, e.g. 2/3, are possible. A more detailed understanding of the static properties near T_c is needed before we can do any reliable prediction.

4 Toward realistic models

4.1 General considerations on glasses

I would like now to shortly review the properties of real glasses, which, as we shall see, have many points in common with the systems that we have considered up to now. As usual we must select which of the many characteristics of glasses we think are important and should be understood. This is a matter of taste. I believe that the the following facts are the main experimental findings about glasses that a successfully theory of glasses should explain:

1. If we cool the system below some temperature (T_G), its energy depends on the cooling rate in a significant way. We can visualize T_G as the temperature at which the relaxation times become of the order of a hour.

2. No thermodynamic anomalies (i.e. divergent specific heat or susceptibilities) are observed: the entropy (extrapolated at ultraslow cooling) is a linear function of the temperature in the region where such an extrapolation is possible. For finite value of the cooling rate the specific heat is nearly discontinuous. Data are consistent with the possibility that the true equilibrium value of the specific heat is also discontinuous at a temperature T_c lower than T_G. This results comes mainly from systems which have also a crystal phase (which is reached by a different cooling schedule) under the very reasonable hypothesis that the entropy of the glass phase cannot be smaller than that of the crystal phase.

3. The relaxation time (and quantities related to it, e.g. the viscosity, which by the Kubo formula is proportional to the integral of the correlation function of the stress energy tensor) diverges at low temperature. In many glasses (the fragile ones) the experimental data can be fitted as

$$\tau = \tau_0 \exp(\beta B(T)), \tag{18}$$

$$B(T) \propto (T - T_c)^{-\lambda}, \tag{19}$$

where $\tau_0 \approx 10^{-13}s$ is a typical microscopic time, T_c is near to the value at which we could guess the presence of a discontinuity in the specific heat and the exponent λ is of order 1. The so called Vogel-Fulcher law [1] states that $\lambda = 1$. The precise value of λ is not too well determine. The value 1 is well consistent with the experimental data, but different values are not excluded.

Points 1 and 2 can be easily explained in the framework of the mean field approximation. Point 3 is a new feature of short range models which is not present in the mean field approximation. It is clearly connected to the non-existence of infinite mean life metastable states in a finite dimensional world. One needs a more careful analysis in order to find out the origine of this peculiar behavior and obtain quantitative predictions.

It is interesting to find out if one can construct approximation directly for the glass transitions in liquids. Some progresses have been done in the framework of mean field theory in the infinite dimensional cases. Indeed the model for hard spheres moving on a sphere can be solved exactly in the high temperature phase when the dimension of the space goes to infinity in a suitable way [26, 27, 29].

4.2 A first attempt to use the replica method for glasses

One of the most interesting results is the suggestion that the replica method can be directly applied to real glasses. The idea is quite simple [30]. We assume that in the glassy phase a finite large system may state in different valleys (or states), labeled by α. The probability distribution of the free energy of the valley is given by eq. (4). We can speak of a probability distribution because the shape of the valleys and their free energies depends on the total number of particles. Each valley may be characterized by the density

$$\rho(x)_\alpha \equiv < \rho(x) >_\alpha . \tag{20}$$

In this case we can define two correlation functions.

$$\begin{aligned} g(x) &= \frac{\int dy < \rho(y)\rho(y+x >>_\alpha}{V} \\ f(x) &= \frac{\int dy < \rho(y) >_\alpha < \rho(y+x >>_\alpha}{V}. \end{aligned} \tag{21}$$

A correct description of the low temperature phase must take into account both correlation functions. The replica method does it quite nicely: g is the correlation function inside one replica and f is the correlation function among two different replicas.

$$\begin{aligned} g(x) &= \frac{\int dy < \rho_a(y)\rho_a(y+x >>}{V} \\ f(x) &= \frac{\int dy < \rho_a(x)\rho_b(y+x >>}{V}, \end{aligned} \tag{22}$$

with $a \neq b$.

The problem is now to write closed equation for the two correlation functions f and g. Obviously in the high temperature phase we must have that $f = 0$ and the non-vanishing of f is a signal of entering in the glassy phase.

The first attempt in this direction was only a partial success [30]. A generalized hypernetted chain approximation was developed for the two functions f and g. A non trivial solution was found at sufficient low temperature both for soft and hard spheres and the transition temperature to a glassy state was not very far from the numerically observed one. Unfortunately the value of the specific heat at low temperature is not the correct one (it strongly increases by decreasing the temperature). Therefore the low temperature behaviour is not the correct one; this should be not a surprise because an esplicite computation show that the corrections to this hypernetted chain approximation diverge at low temperature.

These results show the feasibility of a replica computation for real glasses, however they point in the direction that one must use something different from a replicated version of the hypernetted chain approximation. At the present moment it is not clear which approximation is the correct one, but I feel confident that a more reasonable one will be found in the near future.

References

[1] H. Vogel, Phys. Z, **22**, 645 (1921); G.S. Fulcher, J. Am. Ceram. Soc., **6**, 339 (1925).

[2] M.Mézard, G.Parisi and M.A.Virasoro, *Spin glass theory and beyond*, World Scientific (Singapore 1987).

[3] G.Parisi, *Field Theory, Disorder and Simulations*, World Scientific, (Singapore 1992).

[4] L.Cugliandolo, J.Kurchan, Phys. Rev. Lett.**71** (1993) 173.

[5] A. Crisanti, H. Horner and H.-J. Sommers, *The Spherical p-Spin Interaction Spin-Glass Model: the Dynamics*, Z. Phys. **B92** (1993) 257.

[6] B.Derrida, Phys. Rev. **B24** (1981) 2613.

[7] L. R. G. Fontes, Y. Kohayakawa, M. Isopi, P. Picco *The Spectral Gap of the REM under Metropolis Dynamics* Rome preprint (1996).

[8] D. J. Gross and M. Mézard, *The Simplest Spin Glass*, Nucl. Phys. **B240** (1984) 431.

[9] E. Gardner, *Spin Glasses with p-Spin Interactions*, Nucl. Phys. **B257** (1985) 747.

[10] J.-P. Bouchaud, L. Cugliandolo, J. Kurchan, Marc Mézard, cond-mat 9511042.

[11] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. Lett. **58**, 2091 (1987).

[12] T. R. Kirkpatrick and D. Thirumalai, Phys. Rev. **B36**, 5388 (1987).

[13] T. R. Kirkpatrick, D. Thirumalai and P.G. Wolynes, Phys. Rev. **A40**, 1045 (1989).

[14] G. Parisi, *Gauge Theories, Spin Glasses and Real Glasses*, Talk presented at the Oskar Klein Centennial Symposium, cond-mat 9411115.

[15] S.Franz and G.Parisi, J. Phys. **I** (France) **5**(1995) 1401.

[16] E. Monasson Phys. Rev. Lett. **75** (1995) 2847.

[17] A. Cavagna, I. Giardina and G. Parisi, cond-mat 9611068.

[18] J. Kurchan, G. Parisi and M.A. Virasoro, J. Physique **3**, 18 (1993).

[19] E.Marinari, G.Parisi and F.Ritort, J.Phys.A (Math.Gen.) **27** (1994), 7615; J.Phys.A (Math.Gen.) **27** (1994), 7647.

[20] G. Migliorini, *Sequenze Binarie in Debole Autocorrelazione*, Tesi di Laurea, Università di Roma *Tor Vergata* (Roma, March 1994).

[21] I.Borsari, S.Graffi and F.Unguendoli, J.Phys.A (Math.Gen.), to appear and *Deterministic spin models with a glassy phase transition*, cond-mat 9605133.

[22] G. Parisi and M. Potters, J. Phys. A: Math. Gen. **28** (1995) 5267, Europhys. Lett. **32** (1995) 13.

[23] S. Franz and J. Hertz; Nordita Preprint, cond-mat 9408079.

[24] E. Marinari, G. Parisi and F. Ritort, J. Phys. **A**: Math. Gen. **28** 1234 (1995).

[25] E. Marinari, G. Parisi and F. Ritort J. Phys. **A**: Math. Gen. **28** 327 (1995).

[26] L.Cugliandolo, J.Kurchan, G.Parisi and F.Ritort, Phys. Rev. Lett. **74** (1995) 1012.

[27] L.Cugliandolo, J.Kurchan, E.Monasson and G.Parisi, Math. Gen. **29** (1996) 1347.

[28] G. Parisi, cond-mat 9701032.

[29] G.Parisi and F.Russo, work in progress.

[30] M. Mézard and G. Parisi cond-mat 9602002.