Numerical indications for the existence of a thermodynamic transition in binary glasses

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Abstract

In this note we present numerical simulations of binary mixtures and we find indications for a thermodynamic transition to a glassy phase. We find that below the transition point the off equilibrium correlation functions and response functions seems to be asymptotically compatible with the relations that were originally derived Cugliandolo Kurchan for generalized spin glasses.

1 Introduction

The behaviour of an Hamiltonian system (with dissipative dynamics) approaching equilibrium is well understood in a mean field approach for infinite range disordered systems [1, 2, 3]. In this case we must distinguish an high and low temperature region. In the low temperature phase the correlation and response functions satisfy some simple relations derived by Cugliandolo e Kurchan [1]. We present in this note the first investigation of the relations among these quantities for binary glasses. We find indications for the existence of a phase transition. The numerical data are compared to the theory. The results of this comparison point toward the applicability of the results of the CK dynamical theory to binary glasses.

Generally speaking in a non equilibrium system it is natural to investigate the properties of the correlation functions and of the response function. Let us concentrate our attention on a quantity $A(t)$, which depends on the dynamical variables $x(t)$. Later on we will make a precise choice of the function A.

Let us suppose that the system starts at time $t = 0$ from a given initial condition and subsequently it follow the laws of the evolution at a given temperature T. If the initial configuration is not at equilibrium at the temperature T, the system will display an off-equilibrium behaviour. In many case the initial configuration is at equilibrium at a temperature $T' > T$; different results will be obtained as function of T'. In this note we will consider only the case $T' >> T$ (in particular we will study the case $T' = \infty$).

We can define a correlation function

$$C(t, t_w) \equiv < A(t_w)A(t + t_w) > \tag{1}$$

and the response function

$$G(t,t_w) \equiv \left.\frac{\delta A(t+t_w)}{\delta\epsilon(t_w)}\right|_{\epsilon=0}, \tag{2}$$

where we are considering the evolution in presence of a time dependent Hamiltonian in which we have added the term

$$\int dt\epsilon(t)A(t). \tag{3}$$

The off-equilibrium fluctuation dissipation theorem of the CK theory states some properties of the correlation functions in the limit t_w going to infinity. The usual equilibrium fluctuation dissipation (FDT) relation tell us that

$$G(t) = -\beta\frac{\partial C(t)}{\partial dt}, \tag{4}$$

where

$$G(t) = \lim_{t_w\to\infty} G(t,t_w), \quad C(t) = \lim_{t_w\to\infty} C(t,t_w). \tag{5}$$

In our notation the correlation and response functions which depend on two times are the off-equilibrium ones; those which depend on only one time are the equilibrium ones, i.e.they are the limit of the off-equilibrium correlations when both times goes to at infinity at fixed distance.

It is convenient to define the integrated response:

$$\begin{aligned} R(t,t_w) &= \int_0^t d\tau G(\tau,t_w), \\ R(t) &= \lim_{t_w\to\infty} R(t,t_w), \end{aligned} \tag{6}$$

which is the response of the system to a field acting for a time t.

We can also define the quantities

$$C(\infty) = \lim_{t\to\infty} C(t), \quad R(\infty) = \lim_{t\to\infty} R(t). \tag{7}$$

The static FDT relation is

$$R(\infty) = \beta\left(C(0) - C(\infty)\right). \tag{8}$$

The last equation can be naively written also as

$$R(\infty) = \beta\left(< A^2 > - < A >^2\right), \tag{9}$$

Here the brakets denote the usual equilibrium expectation value. If there is only one equilibrium state (or two that have opposite values $< A >$ and differ by a symmetry), the previous formula, eq. (9) , is correct, otherwise a more lengthy discussione is need.

A very interesting situation happens when the quantity $< A >$ is identically zero because of symmetry arguments in the high temperature. It is quite possible that there is a spontaneous symmetry breaking: two or more states of the systems may be present and the expectation of A in the appropriate state becomes different from zero. A typical example of this situation (see the appendix for more details) is given by spin glasses [4, 5, 6], where the magnetic susceptibility can be written at zero magnetic field as $\chi = \beta/N\sum_{i=1,N}(< \sigma_i^2 > - < \sigma_i >^2) = \beta(1-q)$.

In this case the following relation is valid in the high temperature phase

$$R(\infty) = \beta C(0), \tag{10}$$

where we recall that in our notations $C(0) = \lim_{t\to\infty} C(t,t)$.

The breaking at low temperature of the relation eq. (10) is a signal of a phase transition. We will denote by T_c the temperature at which the previous relation breaks. We can also introduce an order parameter defined by

$$q_A \equiv 1 - \frac{\beta C_D}{R(\infty)}, \tag{11}$$

where

$$C_D = \lim_{t\to\infty} C(t,t). \tag{12}$$

We can get further information on the nature of the transition if we stay in the framework of the CK theory for the approach to equilibrium [1]. In the study of off-equilibrium spin glasses systems Cugliandolo and Kurchan proposed that the response function and the correlation function satisfy the following relations:

$$G(t,t_w) \approx -\beta X\left(C(t,t_w)\right) \frac{\partial C(t,t_w)}{\partial t}. \tag{13}$$

The previous relation can be also written in the following form

$$R(t,t_w) \approx \beta \int_{C(t,t_w)}^{C(0,t_w)} X(C) dC. \tag{14}$$

The function $X(C)$ is system dependent and its form tell us many interesting information.

If $C(\infty) \neq 0$, we must distinguish two regions:

- A short time region where $X = 1$ (the so called FDT region) and $C > C(\infty)$.
- A large time region (usually $t = O(t_w)$ where $C < C(\infty)$ and $X < 1$ (the aging region) [7, 8].

In the simplest non trivial case, i.e. one step replica symmetry breaking, the function $X(C)$ is piecewise constant, i.e.

$$\begin{aligned} X(C) &= m \quad \text{for} \quad C < C(\infty), \\ X(C) &= 1 \quad \text{for} \quad C > C(\infty). \end{aligned} \tag{15}$$

In all known cases in which one step replica symmetry holds, the quantity m vanishes linear with the temperature at small temperature. It often happens (but it is not compulsory) that $m = 1$ at $T = T_c$.

We notice that we must be quite careful in exchange limits in the low temperature phase: the correlation function C satisfy the relation

$$\lim_{t\to\infty} C(t,t_w) = 0 \neq \lim_{t\to\infty}\left(\lim_{t_w\to\infty} C(t,t_w)\right) = C(\infty). \tag{16}$$

In the sane way we have that in the region where t and t_w are *both* large

$$R(t,t_w) \approx R(\infty) = \beta(C(0) - C(\infty)) \quad \text{for} \quad t << t_w,$$
$$R(t,t_w) \approx R_{eq} = \beta \int_0^C dC X(C) \quad \text{for} \quad t >> t_w. \tag{17}$$

Therefore it is quite possible that

$$\lim_{t\to\infty} R(t,t_w) \equiv R_{eq} \neq R(\infty). \tag{18}$$

This phenomenon is present as soon the function $X(C)$, is non zero outside the FDT region and it is the typical situation that happens when replica symmetry is broken [4, 5] .

The previous considerations are quite general. However the function $X(C)$ is system dependent and its form tell us many interesting information. Systems in which the replica symmetry is not broken are characterized by having $m = 0$ in the formula eq. (15) .

Sometime simple aging is also assumed [7], i.e. the following the scaling relation holds outside the FDT region:

$$C(t,t_w) = C_s\left(\frac{t}{t_w}\right). \tag{19}$$

Simple aging may be correct, but it is not a necessary consequence of the previous relations and its verification is not the primary aim of this note (a discussion of simple aging in the same system can be found in [9]).

The aim of this note is to show that binary mixture of spheres do have a transition in the thermodynamics sense at a temperature near the glassy transition, which can be characterized by a non zero value of the appropriate order parameter q_A. More precisely we will show that there are equilibrium quantities which have an irregular (i.e. non-analytic behaviour) at the transition point T_c. Moreover the correlation and response functions seem to satisfy the relations of the CK theory, with the function $X(C)$ is compatible to be given by the one step formula (15).

The paper is organized as follows. In section II, we define the model, the relevant quantities (i.e. the asymmetry or stress) and we present some general considerations. In section III we study the approach to equilibrium of quantities defined at given time, e.g the energy and the equal time fluctuations of the stress. We show that the fluctuations of the stress are strongly indicative of a phase transition. In section IV we make a comparison of our data with the CK theory of aging. Finally in the last section we present our conclusion. At the end of the paper there is a short appendix where some results on spin glasses are recalled and a comparison is done with the finding of this paper.

2 The model

2.1 The Hamiltonian

The model we consider is the following. We have taken a mixture of soft particles of different sizes. Half of the particles are of type A, half of type B and the interaction among the particle is given by the Hamiltonian:

$$H = \sum_{i<k} \left(\frac{(\sigma(i) + \sigma(k))}{|x_i - x_k|}\right)^{12}, \tag{20}$$

where the radius (σ) depends on the type of particles. This model has been carefully studied in the past [10, 11, 12, 13]. It is known that a choice of the radius such that $\sigma_B/\sigma_A = 1.2$ strongly inhibits crystallisation and the systems goes into a glassy phase when it is cooled. Using the same conventions of the previous investigators we consider particles of average diameter 1, more precisely we set

$$\frac{\sigma_A^3 + 2(\sigma_A+\sigma_B)^3 + \sigma_B^3}{4} = 1. \tag{21}$$

Due to the simple scaling behaviour of the potential, the thermodynamic quantities depend only on the quantity T^4/ρ, T and ρ being respectively the temperature and the density. For definiteness we have taken $\rho = 1$. The model as been widely studied especially for this choice of the parameters. It is usual to introduce the quantity $\Gamma \equiv \beta^4$. The glass transition is known to happen around $\Gamma = 1.45$ [11].

Our simulation are done using a Monte Carlo algorithm, which is more easy to deal with than molecular dynamics, if we change the temperature in an abrupt way. Each particle is shifted by a random amount at each step, and the size of the shift is fixed by the condition that the average acceptance rate of the proposal change is about .4. Particles are placed in a cubic box with periodic boundary conditions. In our simulations we have considered a relatively small number of particles $N = 18$, $N = 34$ and $N = 66$. We start by placing the particles at random and we quench the system by putting it at final temperature (i.e. infinite cooling rate).

2.2 The stress

The main quantity on which we will concentrate our attention is the asymmetry in the energy (or stress):

$$A = \sum_{i<k} \frac{(\sigma(i)+\sigma(k))^{12}}{|x_i - x_k|^{14}} \left(2(x_i-x_k)^2 - (y_i-y_k)^2 - (z_i-z_k)^2\right) = 2T_{1,1} - T_{2,2} - T_{3,3}. \tag{22}$$

In other words A is a combination of the diagonal components of the stress energy tensor. If the particles are in a cubic symmetric box, we have that

$$< A >= 0. \tag{23}$$

If the box does not have a cubic symmetry the effect of the boundary disappears in the infinite volume limit (at fixed shape of the boundary) and we have that the stress density a vanishes in this limit:

$$\lim_{N\to\infty} \frac{< A >}{N} \equiv a = 0. \tag{24}$$

What happens when we add a term ϵA to the Hamiltonian is remarkable. Let us consider the new Hamiltonian

$$H + 12\epsilon A, \tag{25}$$

where H was the old Hamiltonian eq. (20) .

It is convenient to consider the following Hamiltonian:

$$H_\epsilon = \sum_{i<k} \left(\frac{(\sigma(i)+\sigma(k))}{r_{i,k}(\epsilon)}\right)^{12}, \tag{26}$$

where

$$r_{i,k}(\epsilon)^2 = (x_i - x_k)^2(1+\epsilon)^{-4} + \left((y_i - y_k)^2 + (z_i - z_k)^2\right)(1+\epsilon)^2. \tag{27}$$

It is evident that we can recover the original Hamiltonian by contracting (for positive ϵ) the x direction by a factor $(1+\epsilon)^{-2}$ and expanding the y and z directions by a factor $1+\epsilon$, keeping in this way the volume constant.

As far as the expectation values of intensive quantities do not depend on the shape of the box, we can compute the properties of the theory with $\epsilon \neq 0$ in terms of those at $\epsilon = 0$. For example one finds that the energy and stress density are given by

$$e(\epsilon) = e(0) \qquad a(\epsilon) = \frac{36e(0)}{5}\epsilon + O(\epsilon^2). \tag{28}$$

At the order ϵ the Hamiltonian in eq. (26) coincide with the previous one eq. (25) .

We thus arrive to the following conclusion, if we consider the response of the system to adding an asymmetric term in the Hamiltonian.

- The equilibrium response function R_{eq} is exactly given by $\frac{36}{5}e(0)$ at all temperatures.
- If there is only one equilibrium state, and this happens in the high temperature phase we must have at $\epsilon = 0$

$$\frac{< A^2 >}{N} = \frac{3}{5\beta}e. \tag{29}$$

- If we define (at $\epsilon = 0$)

$$C(t, t_w) = 12\beta \frac{< A(t+t_w)A(t_w) >}{N}. \tag{30}$$

  (where the factor 12β has been added to simplify the FDT relation), we obtain that in the high temperature phase

$$\lim_{t\to\infty} C(t,t) \equiv C_D = \frac{36}{5}e. \tag{31}$$

It is convenient to define the quantity

$$W(t) = \frac{5C(t,t)}{36e(t)} \tag{32}$$

and investigate its limit for large time ($W \equiv \lim_{t\to\infty} W(t)$). In the same way as in spin glasses we can define a quantity q_A by

$$q_A = 1 - \frac{36e}{5C_D} = 1 - W^{-1} \tag{33}$$

In the next section we shall see that there is transition from $q = 0$ in the high temperature phase to a non zero value of q at low temperatures.

3 On the transition

3.1 General considerations

We have done simulations for various values of N ranging from $N = 18$ to $N = 66$. For $N = 18$ and $N = 34$ we have measured the correlations by using 1000 runs with different starting point; for $N = 66$ we have only 250 samples. The evolution was done using the Monte Carlo method, with an acceptance rate fixed around .4. At the end of each Monte Carlo sweep all the particles are shifted of the same vector in order to keep the center of mass fixed [13]. This last step in introduced in order to avoid drifting of the center of mass and it would be not necessary in molecular dynamics if we start from a configuration at zero total momentum. Most of the quantities that we measure (with only one exception, i.e. the quantity Q) to be defined later eq. (35) are not affected by this shift.

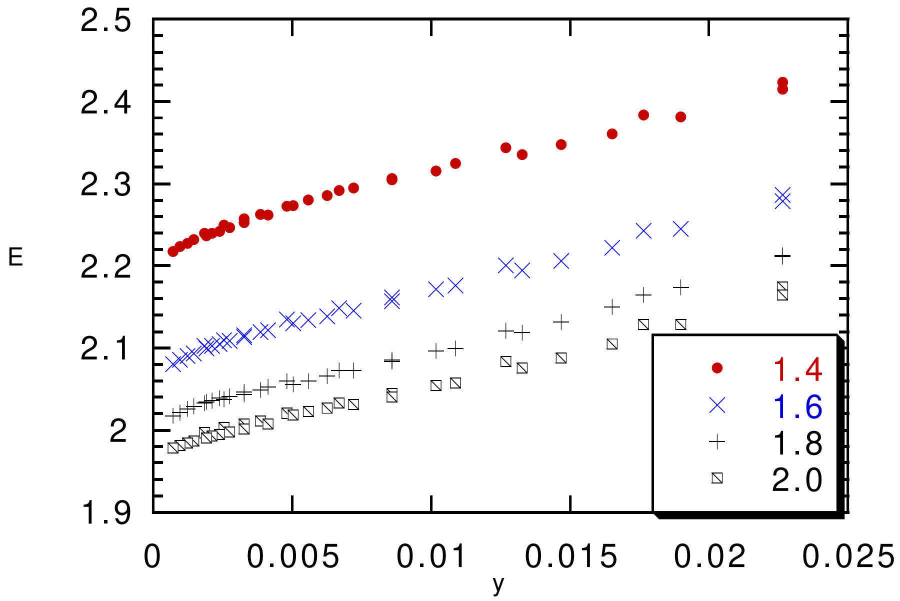

Figure 1: The value of $E(t)$ versus $y \equiv t^{(-.7)}$ for different values of Γ (1.4, 1.6, 1.8 2.0) at $N = 18$.

Four observations are in order:

- We need to do the average over many samples in order to decrease the error on the correlation $C(t,t)$. Only one run would practically give no information because for this quantity the errors do not go to zero when N goes to infinity.
- The values of N may look rather small. On the other hand our task is to show the existence of a thermodynamic phase transition. Although definite conclusions can be only obtained by a careful finite size analysis for large N, strong indications of the existence of a transition can be obtained also for small samples. For example in the Ising case the study of the susceptibility on a 4^3 lattice is enough to draw strong indications for the existence of a transition and the 64 binary degree of freedom are more or less the equivalent of our 54 continuous degrees of freedom for $N = 18$.

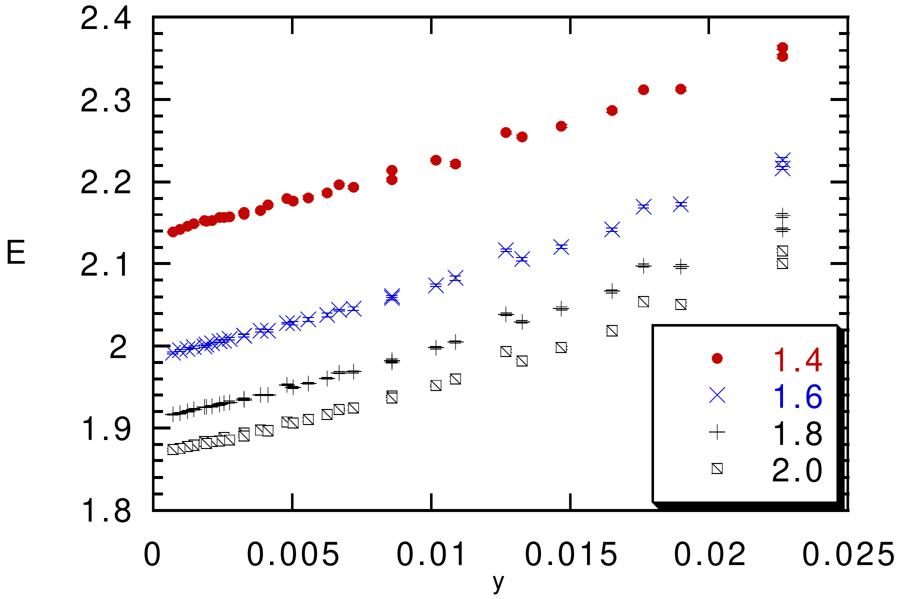

Figure 2: The value of $E(t)$ versus $y \equiv t^{(-.7)}$ for different values of Γ (1.4, 1.6, 1.8 2.0) at $N = 34$.

- The limit $t \to \infty$ may be tricky. All the previous theoretical discussion were done for an infinite system. In practice we need that that N is greater that the time to a given power, the exponent of the power being system dependent. Therefore we cannot strictly take the limit $t \to \infty$ for finite N. We have to study the behaviour of the system in region of time whose size increase with N. Finite size corrections sometimes become much more severe at large times [14, 9].

- In this note we have explored a region of not very large times and we have extrapolated the data to infinity by assuming simple powers corrections at large times. The real situation is likely more complicated. It is quite possible that when we fast cool the system we end up in a metastable state of energy higher the equilibrium one and that the system is going to relax to the equilibrium values with a much slow process, which cannot be seen on this time scale and produces a drift on a much slower scale. In this situation our results concern not the real equilibrium value of the energy (and of the other quantities), but their value in a metastable state.

3.2 The energy

Let us consider the time dependence of the energy. In fig. (1) and (2) we see the energy for $\Gamma = 1.4, 1.6, 1.8, 2.0$, which are near or below the value $\Gamma = 1.44$ at which the phase transition is estimated from the behaviour of the equilibrium correlation functions.

The data are plotted as function of $y \equiv t^{(-.7)}$. The data are quite linear as function of y at $N = 34$, while they show some curvature at large t, small y for $N = 18$. This seems to be a small finite volume effect. Apart from this effect and an overall shift, the two sets of data are quite similar so that we have reasons to suppose that the $N = 34$ are nearly asymptotic.

This is confirmed by a run at $N = 66$ for $\Gamma = 1.8$: a comparison of the three runs at $\Gamma = 1.8$ is showed in fig. (3).

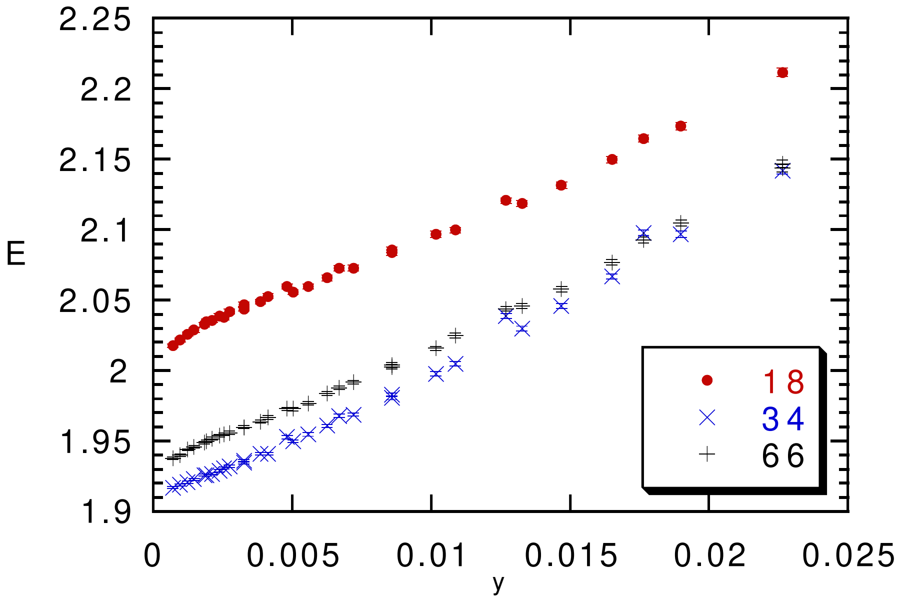

Figure 3: The value of $E(t)$ versus $y \equiv t^{(-.7)}$ for different values of N (18, 34 and 66) at $\Gamma = 1.8$.

The results seem to be puzzling. The energy goes to its asymptotic values with a power correction and the exponent of power correction is independent from the temperature when the temperature changes of about a factor 4 (and also it is not a small exponent!). On the other hand we know that in real systems the convergence of the energy to the asymptotic value is extremely slow below the glass transition. It is quite likely that we are blind to this slower process that happens on a much slower time scale. Moreover the temperature independence of the exponent strongly suggests that the process is not dominated by activated processes which become dominant at very larger times.

The situation is quite reminiscent of the mean field theory case, where the power to approach to a metastable state depends weakly on the temperature [15]. We can thus suppose that here also we converge to a metastable state, whose energy may be larger that the equilibrium one. It would be interesting to verify this point by carefully computation of the true equilibrium energy by more tuned simulations. We can thus tentatively conclude that our large time extrapolation do concern some kind of metastable state. If this happens, it is quite remarkable that the two time scales (controlling respectively the the approach to the metastable state and the slow decay of the metastable state) are so separated that the first can be studied independently from the second.

3.3 The fluctuation of the stress

Here we perform the same analysis as in the previous subsection for the quantity $W(t)$ defined in eq. (32), but we are very interested in finding the exact value of extrapolated at infinite time. In the high temperature region we find that W extrapolates to a value very near to 1, as expected from the previous considerations.

New phenomena appear when we decrease the temperature below the one corresponding to $\Gamma = 1.4$. In fig. (4) we show the data of $W(t)$ versus $y \equiv t^{(-.7)}$ for $\Gamma = 1.8$ for $N = 18$ and $N = 66$.

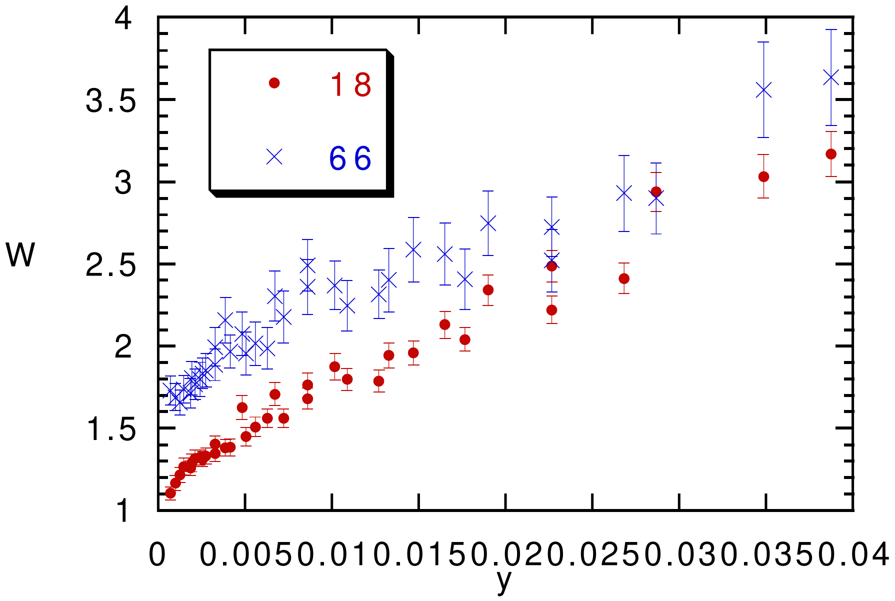

Figure 4: The value of $W(t)$ versus $y \equiv t^{(-.7)}$ for $\Gamma = 1.8$ for $N = 18$ and $N = 66$.

Here also we the same phenomena as for the energy. On the large sample the data are quite linear when plotted versus y. It is remarkable that the same choice of power which (i.e. .7) which works for the energy, is also good for W. It seems that we have the same power corrections for both quantities.

The data at small lattice show a curvature in the plot versus y, which is absent in larger sample. This is finite volume effect which indicates which is the range of time for which we can comfortable assume that the volume is sufficiently large.

We show in fig. (5) the value of $W(t)$ versus $y \equiv t^{(-.7)}$ for different values of Γ at $N = 34$. A liner fit is rather good and the extrapolated value of $W(\infty)^{-1}$ are shown in fig. (6).

It is clear from both fig. (5) and (6) that $W(\infty)$ becomes different from 1 in the low temperature region. If we assume that it diverges at low temperature, the data are compatible with the usual situation where $W(\infty)$ is roughly proportional to the temperature at small temperature. This results should be taken as an indication that, at least in the metastable region there is a transition to a region where $W(\infty) \neq 1$.

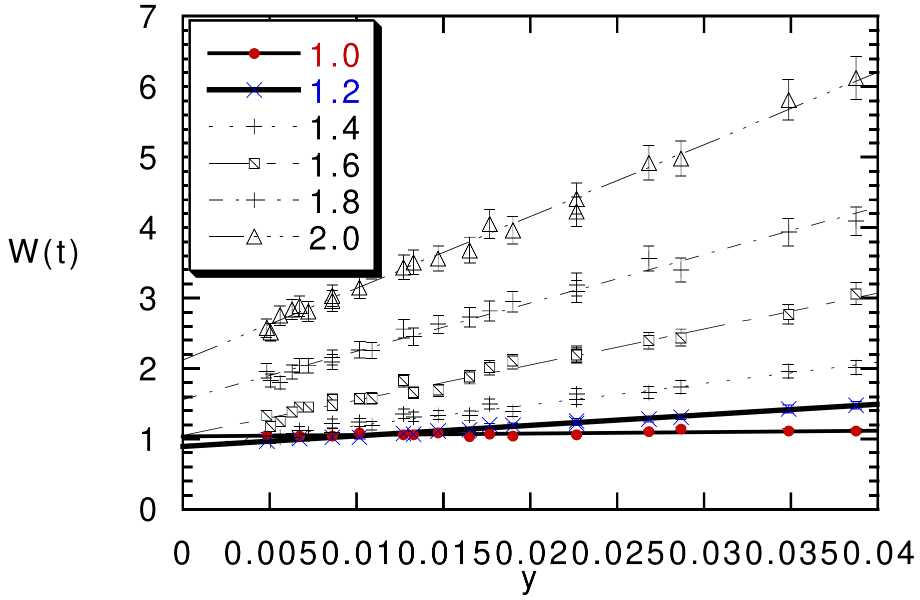

Figure 5: The value of $W(t)$ versus $y \equiv t^{(-.7)}$ for different values of Γ (1.0, 1.2, 1.4, 1.6, 1.6 and 2) at $N = 34$.

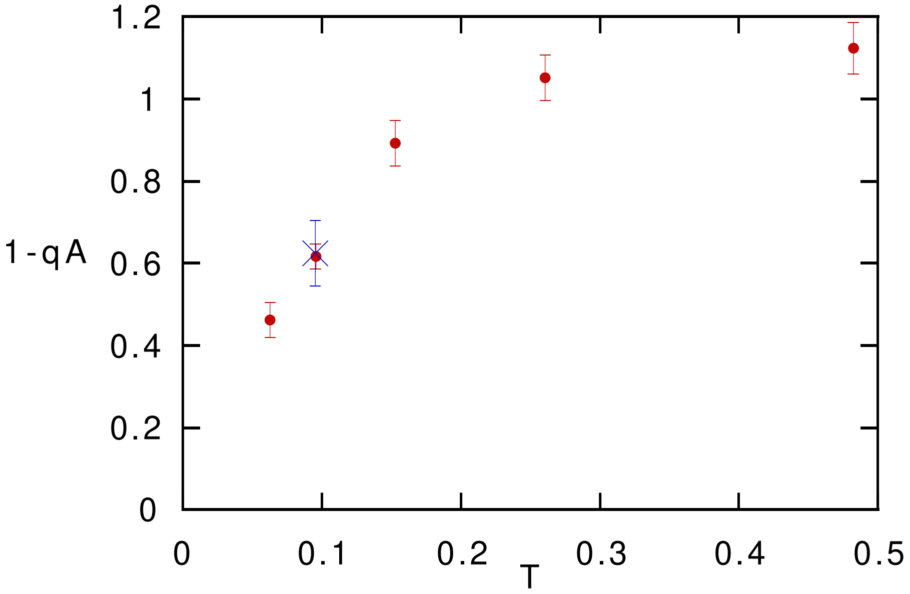

Figure 6: The value of $1 - q_A = W(\infty)^{-1}$ as function of the temperature using the data of $N = 34$ extrapolated from the region of time $200 - 2000$, i.e. the linear fits of the previous figures. The cross at $\Gamma = 1.8$ is the value extrapolated from the region of time $200 - 6400$ at $N = 66$.

4 The comparison with the CK Theory

4.1 The correlation functions

Up to now we have considered equal time correlation functions. Let us see what happen to the correlation functions at different times. We will study the correlation $C(t, t_w)$.

We introduce the variable $s = t/t_w$. According to simple aging the correlation functions should become a function of only s in the limit of large times. Of course the FDT region, which is located at finite t also when t_w goes to infinity, is squeezed at $s = 0$, so that we expect that the function C becomes discontinuous at $s = 0$. Moreover the limit $s \to 0$ give us information on the value of $C(\infty)$

$$\lim_{s \to 0} C(t, t_w) = C(\infty), \tag{34}$$

where it is understood that the limit is done always remaining in the region where $t >> 1$.

In fig (7) we plot the correlation function at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (512, 2048, 8912) as function of $s^{.5} \equiv (t/t_w)^{.5}$.

We have plotted the data as function of $s^{.5}$ and not of s for two reason:

- To decompress FDT region at s=0 in order to see better the building of the discontinuity at $s = 0$
- To expose the apparent stretched exponential decay of the correlation function for large values of s.

As we can see the two regions FDT and aging are quite clear. It is also evident that $C(\infty)$ is different from zero at this temperature (it is obviously zero in the high temperature phase; we have checked this result, but for reasons of space we do not show the corresponding data). There is an overall drift of the correlation as function t_w which seems to disappear at large times. This is not a surprise because we have seen that also the correlation function at $s = 0$ show a residual dependence on t_w.

In order to see how simple aging is satisfied for other quantities we introduce the quantity $Q(t, t_w)$ (introduced in [9]), defined as:

$$Q(t, t_w) \equiv \sum_{i,k=1,N} \frac{f(x_i(t + t_w) - x_k(t_w))}{N^2} \tag{35}$$

where we have chosen the function f in an appropriate way, i.e.

$$f(x) = \frac{d^{12}}{x^{12} + d^{12}}, \tag{36}$$

with $d = .3$. The function f is very small when $x >> .3$ and near to 1 for $x < .3$.

The value of Q will be a number very near to 1 for similar configurations (in which the particles have moved of less than a) and it will be much smaller value (less than .1) for unrelated configurations; using the same terminology as in spin glasses [16, 4, 5] Q can be called the overlap of the two configurations: with good approximation Q counts the fraction of particles which have moved less that d.

The data for Q are shown in fig. (8). We see that also in this case we have some violation of simple scaling, but the violations are definitely smaller, also because, due the its definition the quantity Q is normalized to 1 at $s = 0$.

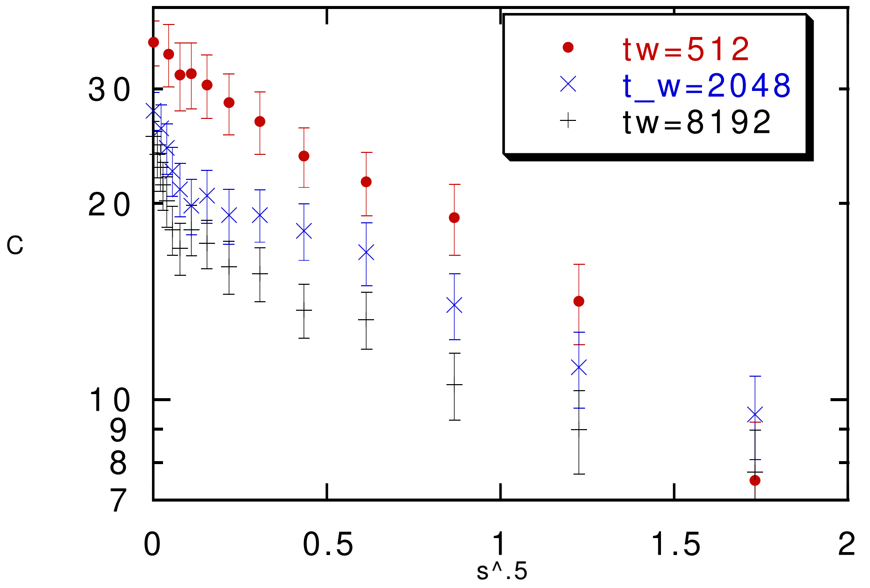

Figure 7: On a logarithmic scale we see the correlation function at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (512, 2048, 8912) as function of $s^{.5} \equiv (t/t_w)^{.5}$.

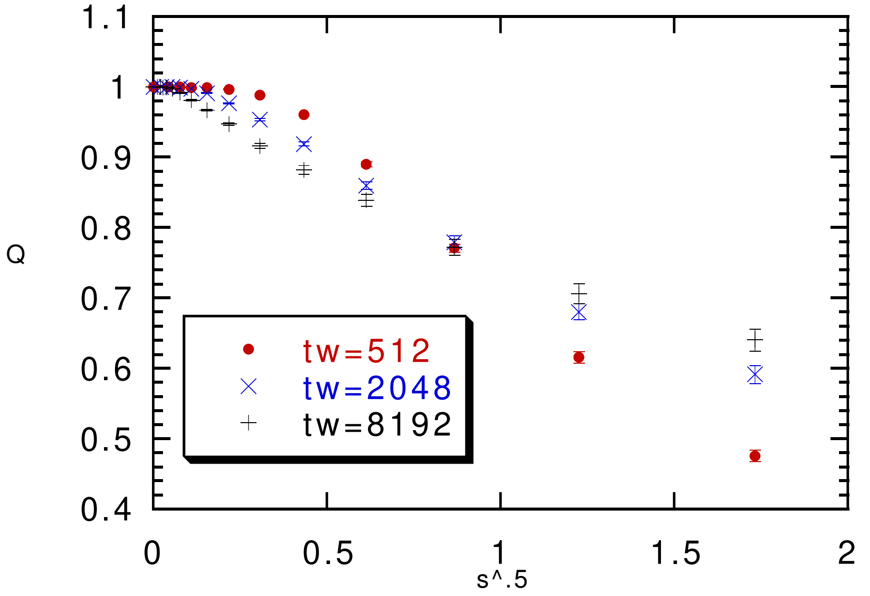

Figure 8: The overlap Q at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (512, 2048, 8912) as function of $s^{.5} \equiv (t/t_w)^{.5}$.

4.2 The response function

We have followed a standard procedure [17, 18] to measure the off-equilibrium response function in simulations: we have kept the system in presence of an external field ϵ up to time t_w and we have removed the field just at this time.

If ϵ is sufficient small, we have that the stress as function of time, is related to the integrated response R by the relation

$$\frac{a(t+t_w)}{\epsilon} \equiv S(t+t_w) = R(t+t_w,0) - R(t,t_w) \tag{37}$$

As far as the limit of $R(t,t_w)$ when $t \to \infty$ does not depend on t_w the quantity defined in eq. (37) goes to zero when $t \to \infty$. In this way we can get the value of the integrated response by measuring the stress density as function of time

In our case (where we use the stress as a perturbation) the physical interpretation of the procedure is quite clear. We start by putting the systems in a box which is not cubic (because $\epsilon \neq 0$), but two sides are slightly longer of the third. At time t_w we change the form of the box to a cubic one. In this way we deform the the system and we induce a stress which will be eventually decay. In the high temperature phase, where the system is liquid, the stress will disappear in a short time. On the contrary, in the glassy phase, we shall see that the stress remains for a much longer time (as expected [8]) and it shows an interesting aging behaviour.

The choice of ϵ is crucial. In principle its value should be infinitesimal. However the signal is proportional to ϵ while the errors are ϵ independent. The errors on the response function grow as ϵ^{-1}. On the other hand if we take a too large value of ϵ we enter in a non linear region. The analysis of the non linear dependence of the stress as function of ϵ would be very interesting, but it goes beyond the scope of this paper. Here we restrict to the linear region. We have taken data at $\epsilon = .1$ and $\epsilon = .05$ and we have seen that there are some non-linear effects. No non-linear effects have been detected at $\epsilon = .02$ and $\epsilon = .01$. All the data we present in this paper come from $\epsilon = .01$ and they are reasonable free of systematic effects. As a further check we have compared the value of Q measured at $\epsilon = 0$, as in the previous subsection, and the value of Q at $\epsilon = .01$ and they differs by less than 1%.

In fig. (9) we plot the response function S at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (128, 512, 2048) as function of $s^{.5} \equiv (t/t_w)^{.5}$. In this case aging show much smaller violations than in the case of the correlations (due the fact that the value at $s = 0$ is much less dependent on time). Also in this case we see that the building of a discontinuity at $s = 0$ followed by a smooth function of s.

4.3 Fluctuations and response together

The crucial step would be now to plot the fluctuations and the response together. The previous equation tell us that

$$\frac{\partial S}{\partial C} = X(C) \tag{38}$$

so that it is convenient to plot S versus C. The slope of the function $S(C)$ is thus $X(C)$.

In the one step replica symmetry breaking scheme we expect that:

$$\begin{aligned} S &= mC \quad \text{for} \quad C < C(\infty), \\ S &= C + (1-m)C(\infty) \quad \text{for} \quad C < C(\infty). \end{aligned} \tag{39}$$

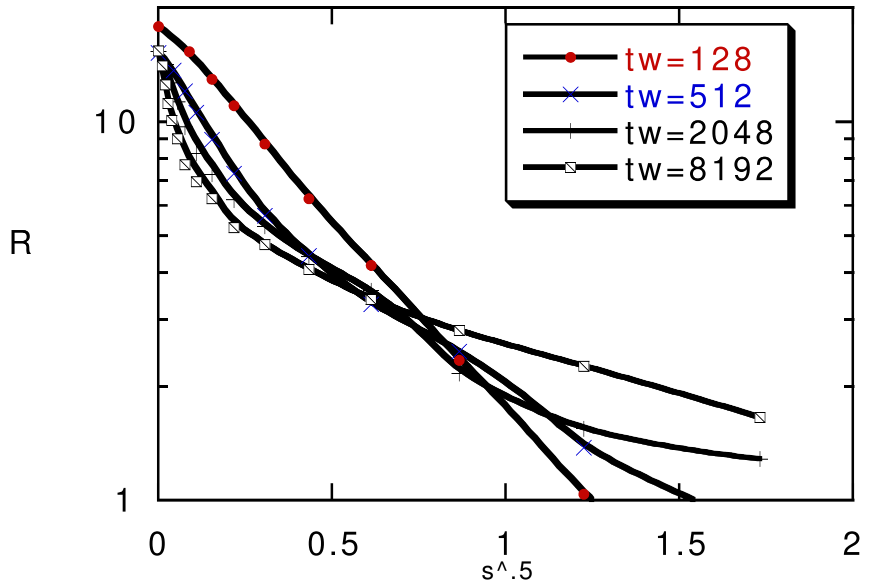

Figure 9: On a logarithmic scale we see the response function at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (128,512, 2048, 8192) as function of $s^{.5} \equiv (t/t_w)^{.5}$.

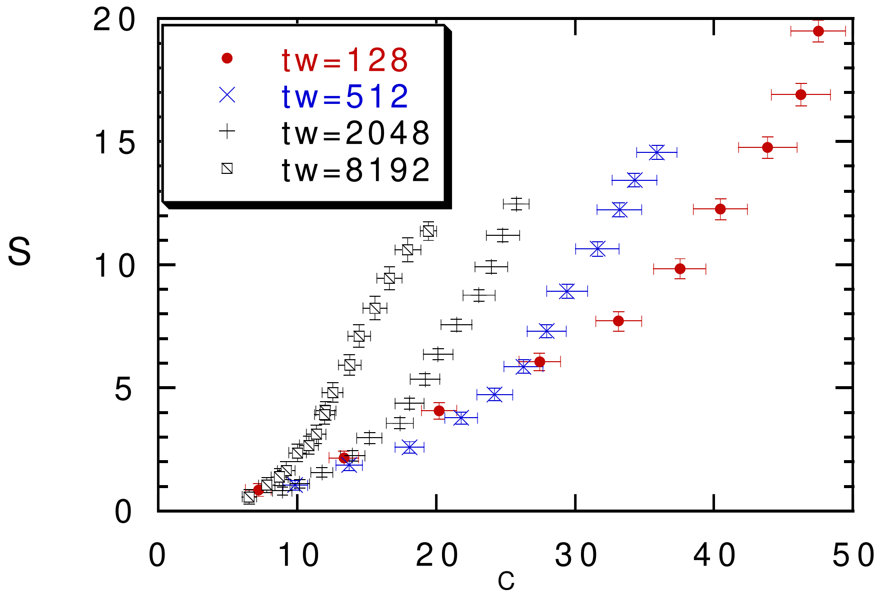

Figure 10: The response S as function of C at $\Gamma = 1.8$ for $N = 34$ at different values of t_w (128, 512, 2048, 8912).

In fig. (10) we find the data for the response S as function of C at $\Gamma = 1.8$ for $N = 34$ at different values of t_w (128, 512, 2048, 8912). We can see that also here there is strong dependance on t_w. We can distinguish two regions:

- A high C region (typically $C > C(\infty)$), where the function S has nearly slope one.
- A region of smaller C, where the dependence of S on C is more complex.

We remark that the data for smaller value of the waiting time seems to be very similar to the predictions of the one step replica theory but this conclusion is not so clear for larger values of the waiting time.

In fig. (11) we find the data for the response S as function of C at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (128, 512, 2048, 8192). We find a behaviour qualitatively similar to the one with a smaller number of particles at small waiting time; however here the data at $t_w = 2048$ and $t_w = 8192$ are much more similar, giving us the hope to be near to the asymptotic limit in the case of this larger system.

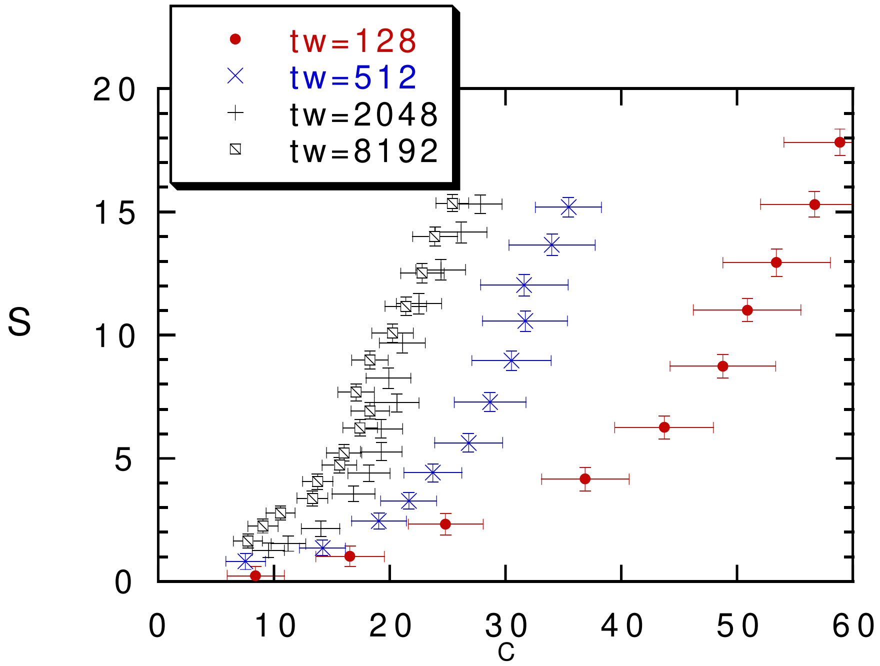

Figure 11: The response S as function of C at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (128 512, 2048, 8192).

In order to expose the existence of a region where the FTD is valid [18], it is convenient to define the function $D \equiv C - S$. It is evident that in the FDT region the function $D(C)$ must be equal to a constant. In order to test this prediction and to verify the existence of a region where the FDT relation holds, in fig. (12) we plot the the function D versus S at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (512, 2048, 8912). A plateaux region is quite evident. The level of the plateaux is still dependent on t_w. The straight line correspond to one step replica symmetry breaking with $m = .3$.

The behaviour of the function $S(C)$ at small C would be quite interesting to assess. We have three possibilities of increasing complexity

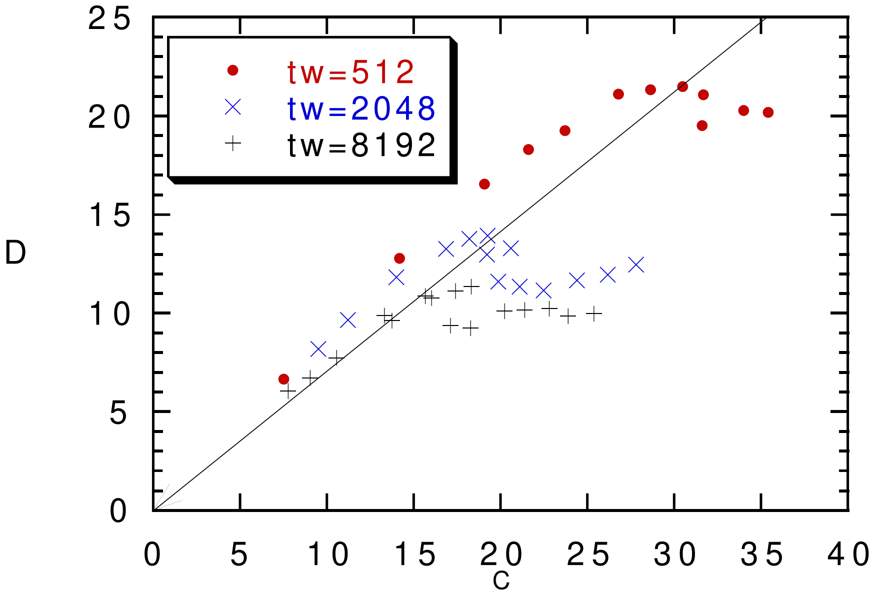

Figure 12: The difference $D \equiv C - S$ as function of C at $\Gamma = 1.8$ for $N = 34$ at different values of t_w (512, 2048, 8912). The straight line correspond to one step replica symmetry breaking with $m = .3$.

- The function $S(C)$ is zero for $C < C(\infty)$. This correspond to the simple situation where replica symmetry is not broken.
- The function $S(C)$ is linear for $C < C(\infty)$ with slope m. This correspond to one step replica symmetry breaking.
- The function $S(C)$ has a power behaviour for $C < C(\infty)$ with exponent greater than one. In this case the replica symmetry is broken in a continuous way.

The previous data for $S(C)$ plotted in double logarithmic scale may be useful to clarify this point, see fig. (13). We find that the data for small t_w seem to be linear in agreement with one step replica symmetry breaking predictions. There is a rather strong dependence on t_w in this region and the extrapolation to $t_w = \infty$ cannot safely done. A value of m around .3 (or more) is compatible with the data. This is an interesting problem that must be investigated further.

5 Conclusions

It has been shown in the previous section that there is a low temperature region where the large time extrapolation of the energy and of the stress autocorrelation function can be done by assuming simple power low corrections. The extrapolated value quite likely do not correspond to equilibrium values, but to metastable values and the real equilibrium values are reached only at much bigger time.

The behaviour in this region is quite different from the high temperature region. The autocorrelation function of the stress is bigger than the analytic continuation of its value from the high temperature region. Approximate simple aging is found. The function $X(C)$ of the CK theory has been computed. Also this function shows a dependence on the value of t_w which seems to decrease by increasing t_w. The extrapolation of the function $X(C)$ at infinite (or very large) t_w it is a delicate problem, that should be treated in a careful way. At first sight is seems likely that in order to get a reliable extrapolation one need to increase the time t_w by a factor 10, increase somewhat the statistics in order to decrease the errors and simultaneously go to larger samples in order to avoid finite volume effects, which become stronger and stronger when the time increase [1]. One probably needs a factor 100 more in computer time, which is not a very large amount (considered that this computation has taken a few weeks of a workstation), but it would certain go outside the exploratory aim of this work and of the capabilities of the hardware we have used.

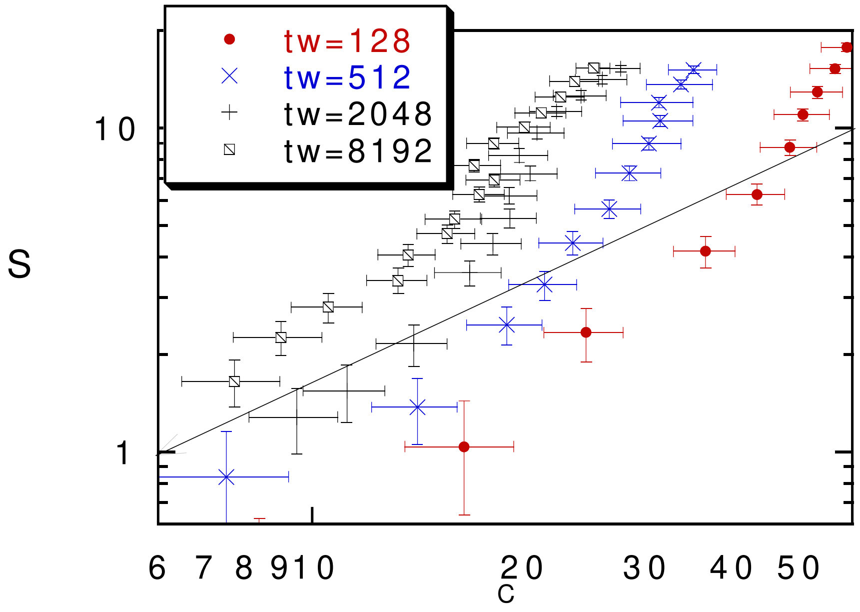

Figure 13: The response S as function of C at $\Gamma = 1.8$ for $N = 66$ at different values of t_w (128 512, 2048, 8192) on a double logarithmic scale. The straight line correspond to a linear behaviour.

It is likely that something smarter can be done. Two possibilities are immediate:

- We can repeat the same procedure where the temperature is slowed cooled in steps of total length t_w starting from a finite temperature to the final temperature. In this way is possible that aging and the other phenomena survive, but the finite time corrections could be much smaller [19].
- We could change the quantity we study. It may be possible that the stress is not the best suited quantity to investigate; indeed the quantity Q seems to satisfy much better simple aging with much smaller corrections.

[1] We should also increase the value of s in order to explore better the region where C becomes small.

It seems to me that there is a quite large amount of phenomena to investigate in the approach to equilibrium of glasses. It would be interesting to see if the indications given in this paper will be confirmed by more accurate and lengthy computations.

Acknowledgments

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Appendix: spin glasses

In this appendix I will briefly recall the situation for spin glasses. Aging and the predictions

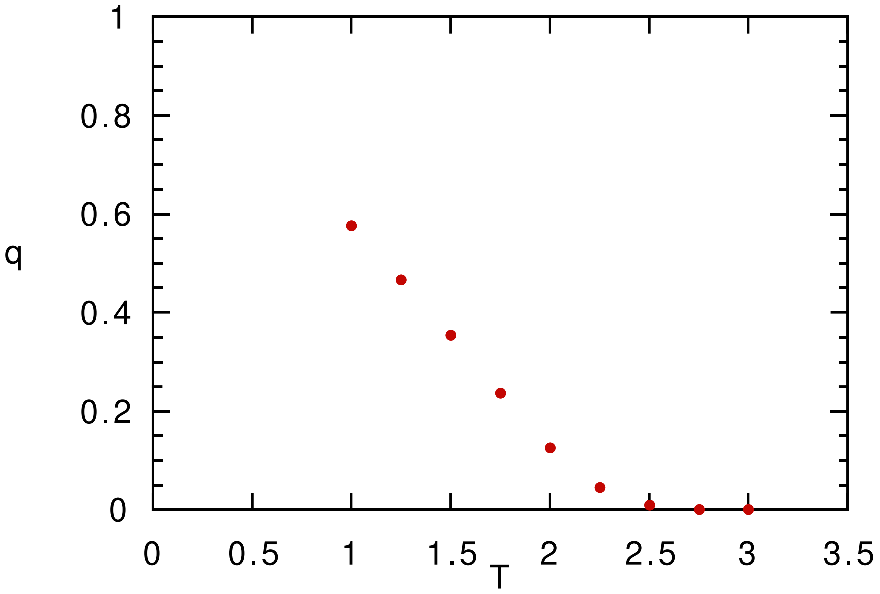

Figure 14: The value of q as function of the temperature in a 4-dimensional spin glass.

of the CK theory have been carefully analyzed in [18]: a comparison of their results with our would be instructive. Here we limit ourself to the following general remark.

In spin glasses the relevant quantity is the total magnetization

$$M = \sum_i \sigma_i. \tag{40}$$

It is easy to see that at zero magnetic field in the random bond model (due to gauge invariance) the following relation holds at all temperatures.

$$\frac{< M(t) >^2}{N} = 1. \tag{41}$$

We can now compute in simulations the magnetic susceptibility (χ), i.e. by inserting a small magnetic field h and my measuring the ratio $< M > /h$. Following the previous discussion (33) we have that

$$\chi = \beta(1-q). \tag{42}$$

An example of the function q computed in simulations for spin glasses (a four dimensional model) is showed in fig. (14), where the data are taken from [19].

There is a striking difference from spin glasses and the case of binary glasses presented here, which it is worthwhile to note:

- In glasses the response to the stress tensor is computed from symmetry arguments and the transition is present in the fluctuations.
- In glasses the fluctuations of the magnetization are computed from symmetry arguments and the transition is present response, (i.e. the susceptibility).

However it seems to me that this difference does not seem to have deep physical consequence and it is just an effect of the different choice of observables.

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