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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 seem to be asymptotically compatible with the relations that were derived by Cugliandolo and Kurchan for generalized spin glasses.

1. Introduction

The behaviour of a Hamiltonian system (with dissipative dynamics) approaching equilibrium is well understood in a mean-field approach for infinite-range disordered systems [1–3]. In this case we must distinguish a high and low-temperature region. In the low-temperature phase the correlation and response functions satisfy some simple relations derived by Cugliandolo and Kurchan (CK) [1]. In this paper we present the first investigation of the relations among these quantities for binary glasses. We find indications of the existence of a phase transition. The numerical data are compared with the theory. The results of this comparison point towards 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 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 follows the laws of evolution at a given temperature T. If the initial configuration is not at equilibrium at temperature T, the system will display an off-equilibrium behaviour. In many cases the initial configuration is at equilibrium at a temperature $T' > T$; different results will be obtained as functions of T'. In this paper we will only consider the case $T' \gg T$ (in particular we will study the case $T' = \infty$).

We can define a correlation function

$$C(t, t_w) \equiv \langle A(t_w) A(t + t_w) \rangle \tag{1}$$

and the response function

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

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where we consider the evolution in the presence of a time-dependent Hamiltonian in which we have added the term

$$\int \mathrm{d}t\, \epsilon(t) A(t). \tag{3}$$

The off-equilibrium fluctuation dissipation relation of the CK theory describes some properties of the correlation functions and of the response function in the limit t_w going to infinity. The usual equilibrium fluctuation dissipation (FDT) relation tells us that

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

where

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

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

It is convenient to define the integrated response:

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

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

We can also define the quantities

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

The static FDT relation is

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

which can also be written naively as

$$R(\infty) = \beta(\langle A^2 \rangle - \langle A \rangle^2). \tag{9}$$

Here the brackets denote the usual equilibrium expectation value. If there is only one equilibrium state (or two that have opposite values $\langle A \rangle$ and are related by a symmetry operation), the previous formula (equation (9)) is correct, otherwise a more lengthy discussion is needed.

A very interesting situation occurs when the quantity $\langle A \rangle$ is identically zero because of symmetry arguments in the high-temperature phase. 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 [4–6], where the magnetic susceptibility can be written at zero magnetic field as $\chi = \beta/N \sum_{i=1,N} (\langle \sigma_i^2 \rangle - \langle \sigma_i \rangle^2) = \beta(1-q)$.

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 (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 glass systems CK proposed that the response function and the correlation function satisfy the following relation:

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

which can also be written in the 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 gives us much 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 ageing 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.

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

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

We note that we must be quite careful when exchanging limits in the low-temperature phase: the correlation function C must 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 same way, we have that in the region where t and t_w are *both* large

$$\begin{aligned} R(t, t_w) &\approx R(\infty) = \beta(C(0) - C(\infty)) \qquad \text{for } t \ll t_w \\ R(t, t_w) &\approx R_{eq} = \beta \int_0^C dC\, X(C) \qquad \text{for } t \gg t_w. \end{aligned} \tag{17}$$

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

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

Sometimes simple ageing is also assumed [7, 8], 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 ageing may be correct, but it is not a necessary consequence of the previous relations and its verification is not the primary aim of this paper (a discussion of simple ageing in the same system can be found in [9]).

The aim of this paper is to show that binary mixtures 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 and the function $X(C)$ is compatible to be given by the one-step formula (15), in agreement with the conjecture of [10].

This paper is organized as follows. In section 2, we define the model, the relevant quantities (i.e. the asymmetry or stress) and we present some general considerations. In section 3 we study the approach to equilibrium of quantities defined at given times, for example the energy and equal-time fluctuations of the stress. We show that the fluctuations of the stress are strongly indicative of a phase transition. In section 4 we make a comparison of our data with the CK theory of ageing. Finally, in section 5 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 made with the finding of this paper.

2. The model

2.1. The Hamiltonian

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

$$H = \sum_{i<k}\left(\frac{(\sigma(i)+\sigma(k))}{|\boldsymbol{x}_i - \boldsymbol{x}_k|}\right)^{12} \tag{20}$$

where the radius (σ) depends on the type of particles. This model has been carefully studied [11–14] and it is known that a choice of the radius such that $\sigma_B/\sigma_A = 1.2$ strongly inhibits crystallization and the system goes into a glassy phase when it is cooled. Using the same conventions of the previous investigators we consider particles of average radius 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, where T and ρ are respectively the temperature and density. For definiteness we have taken $\rho = 1$. The model has been widely studied especially for this choice of parameters. It is usual to introduce the quantity $\Gamma \equiv \beta^4$. The glass transition is known to occur around $\Gamma = 1.45$ [12].

Our simulations 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 0.4. 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 concentrate our attention is the asymmetry in the energy (or stress):

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

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

$$\langle A \rangle = 0. \tag{23}$$

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 also in this case the stress density a vanishes in this limit:

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

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 equation (20).

It is convenient to also consider the following Hamiltonian:

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

where

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

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 of $1+\epsilon$, in this way maintaining the volume as constant.

As long 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

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

At the order ϵ the Hamiltonian in equation (26) coincides with the previous one in equation (25).

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

- The equilibrium response function $R_{\rm eq}$ is exactly given by $\frac{36}{5}e(0)$ at all temperatures.

• If there is only one equilibrium state, and this occurs in the high-temperature phase, we have at $\epsilon = 0$

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

• If we define (at $\epsilon = 0$)

$$C(t, t_{\mathrm{w}}) = 12\beta \frac{\langle A(t + t_{\mathrm{w}}) A(t_{\mathrm{w}}) \rangle}{N} \tag{30}$$

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

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

It is convenient to define the quantity

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

and investigate its limit for large times ($W \equiv \lim_{t \to \infty} W(t)$). 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 section 3 we shall see that there is a transition from $q = 0$ in the high-temperature phase to a non-zero value of q at low temperatures.

3. The transition

3.1. General considerations

We have performed 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 points; for $N = 66$ we have used only 250 samples. The evolution was done using the Monte Carlo method, with an acceptance rate fixed around 0.4. At the end of each Monte Carlo sweep all the particles are shifted by the same vector in order to keep the centre of mass fixed [14]. This last step is introduced in order to avoid drifting of the centre of mass and it would not be 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 by equation (35), are not affected by this shift.

Four observations are in order.

• We need to 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 only be obtained by a careful finite-size analysis for large N, strong indications of the existence of a transition can also be obtained 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 degrees of freedom are more or less equivalent to our 54 continuous degrees of freedom for $N = 18$.

• The limit $t \to \infty$ may be tricky. All the previous theoretical discussions were done for an infinite system. In practice we need N to be greater than 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 a region of time whose size increases with N. Finite-size corrections sometimes become much more severe at large times [15, 9].

• In this paper we have explored a region of not very large times and we have extrapolated the data to infinity by assuming simple power corrections at large times. The real situation is probably more complicated. It is quite possible that when we fast cool the system, as we have done here, we end up in a metastable state of energy higher than the equilibrium one, and that the system is going to relax to the equilibrium values with a much slower process. This effect cannot be seen on the timescale of our simulations and it produces a drift of the energy which is only observable on much slower cooling. In this situation our results do not involve the real equilibrium value of the energy (and of the other quantities), but involves their value in a metastable state.

3.2. The energy

Let us consider the time dependence of the energy. In figure 1 we see the energy for $\Gamma = 1.4, 1.6, 1.8, 2.0$, which are near or below the value $\Gamma = 1.45$ at which the phase transition is estimated from the behaviour of the equilibrium correlation functions.

The data are plotted as functions of $y \equiv t^{(-0.7)}$. The data are quite linear as functions of y at $N = 34$. Similar data for $N = 18$ (not shown here) display some curvature at large t and small y. 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 we have reason to suppose that $N = 34$ is nearly asymptotic. This is confirmed by a run at $N = 66$ for $\Gamma = 1.8$: a comparison of the three runs ($N = 18$, $N = 34$ and $N = 66$) at $\Gamma = 1.8$ is shown in figure 2.

The results seem to be puzzling. The energy goes to its asymptotic values with a power correction, the exponent of which is independent of the temperature when the temperature

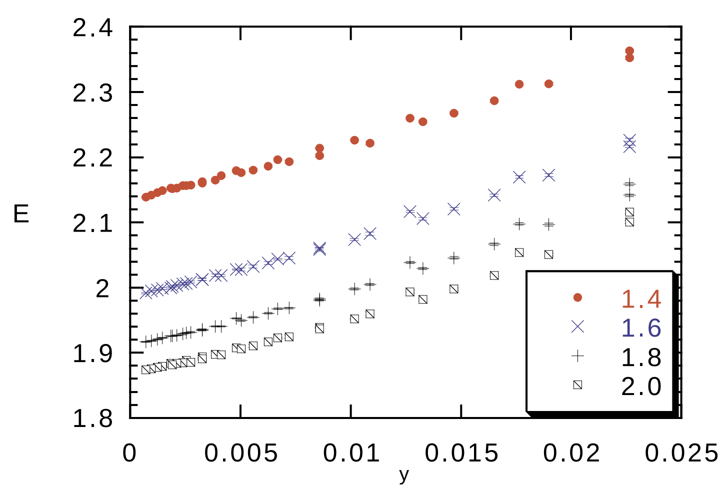

Figure 1. The value of $E(t)$ versus $y \equiv t^{(-0.7)}$ for values of $\Gamma = 1.4, 1.6, 1.8, 2.0$ at $N = 34$.

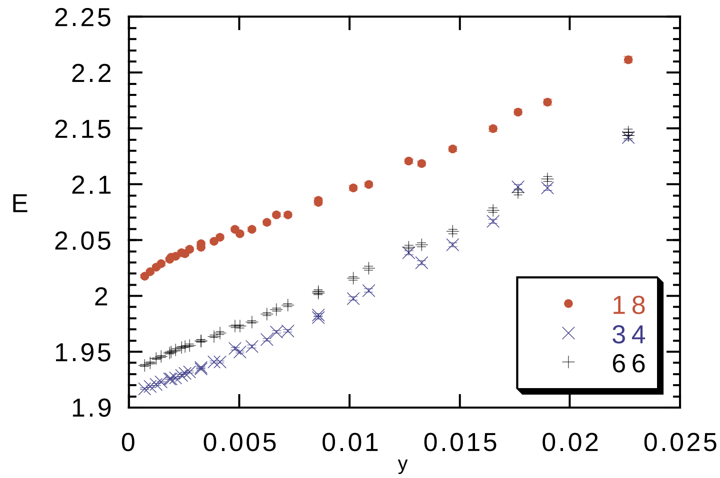

Figure 2. The value of $E(t)$ versus $y \equiv t^{(-0.7)}$ for values of $N = 18, 34, 66$ at $\Gamma = 1.8$.

changes by a factor of about 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 timescale. Moreover, the temperature independence of the exponent strongly suggests that the process is not dominated by activated processes which become dominant at much 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 [16]. We can thus suppose that here we also converge to a metastable state, whose energy may be larger than the equilibrium one. It would be interesting to verify this point by careful computation of the true equilibrium energy by more tuned simulations. We can thus tentatively conclude that our large-time extrapolations involve some kind of metastable state. If this happens, it is quite remarkable that the two timescales (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 section 3.2 for the quantity $W(t)$ defined in equation (32), but we are very interested in finding the exact value of extrapolation at infinite time. In the high-temperature region we find that W extrapolates to a value very near 1, as expected from the previous considerations.

New phenomena appear when we decrease the temperature below the one corresponding to $\Gamma = 1.4$. In figure 3 we show the data of $W(t)$ versus $y \equiv t^{(-0.7)}$ for $\Gamma = 1.8$ for $N = 18$ and 66.

Here we also have 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 (i.e. 0.7) 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 lattices show a curvature in the plot versus y, which is absent in the larger sample. This is a finite-volume effect which indicates the times range for which we

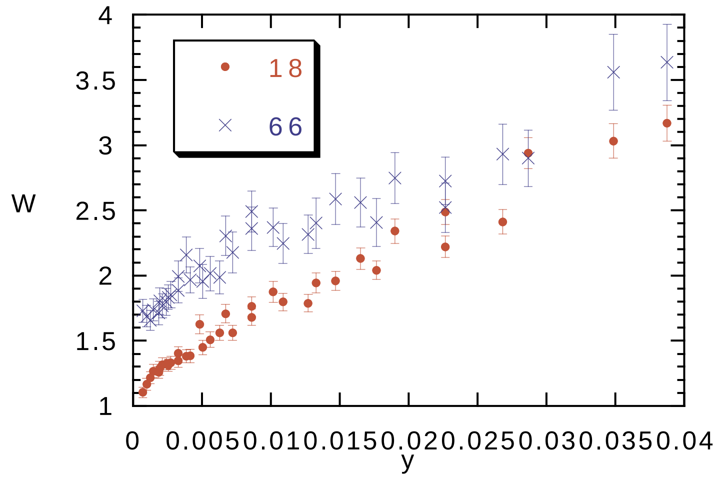

Figure 3. The value of $W(t)$ versus $y \equiv t^{(-0.7)}$ for $\Gamma = 1.8$ for $N = 18$ and 66.

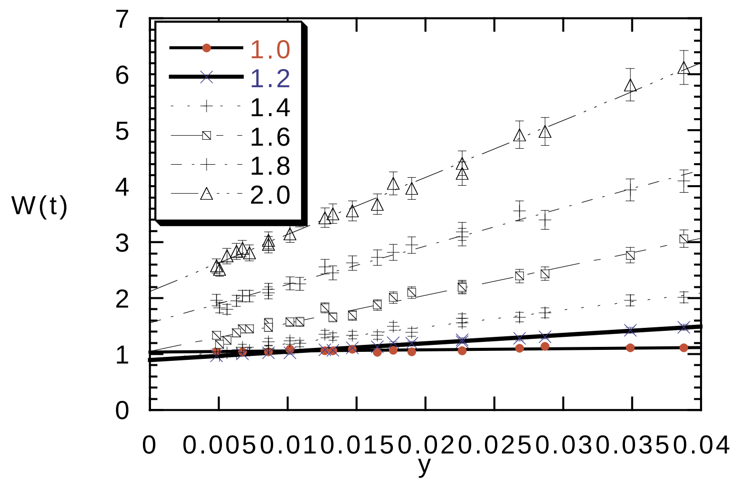

Figure 4. The value of $W(t)$ versus $y \equiv t^{(-0.7)}$ for values of $\Gamma = 1.0, 1.2, 1.4, 1.6, 1.8, 2$ at $N = 34$.

can comfortably assume that the volume is sufficiently large.

In figure 4 we show the value of $W(t)$ versus $y \equiv t^{(-0.7)}$ for different values of Γ at $N = 34$. A linear fit is rather good and the extrapolated values of $W(\infty)^{-1}$ are shown in figure 5.

It is clear from figures 4 and 5 that $W(\infty)$ becomes different from 1 in the low-temperature region. If we assume that it diverges at low temperatures, the data are compatible with the usual situation where $W(\infty)$ is roughly proportional to the temperature at small temperatures. This result should be taken as an indication that, at least in the metastable region there is a transition to a region where $W(\infty) \neq 1$.

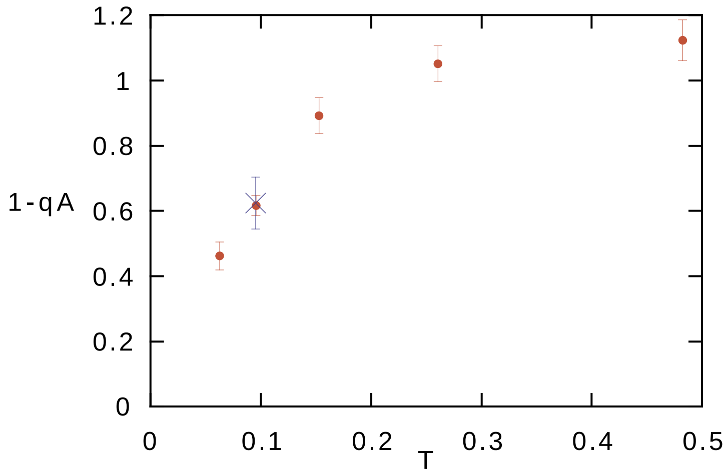

Figure 5. The value of $1 - q_A = W(\infty)^{-1}$ as a function of the temperature using the data of $N = 34$ extrapolated from the region of time 200–2000, i.e. the linear fits of the previous figures. The cross at $\Gamma = 1.8$ is the value extrapolated from the region of time 200–6400 at $N = 66$.

4. The comparison with the CK theory

4.1. The correlation functions

Up until now we have considered equal-time correlation functions. Let us see what happens 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 ageing 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 $s \to 0$ gives 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 always placed in the region where $t \gg 1$.

In figure 6 we plot the correlation function at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 512, 2048, 8912$ as a function of $s^{0.5} \equiv (t/t_w)^{0.5}$. We have plotted the data as a function of $s^{0.5}$ and not of s in order to decompress the FDT region at $s = 0$.

As we can see, the two regions (FDT and ageing) 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 the correlation function also shows a residual dependence on t_w at $s = 0$.

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

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

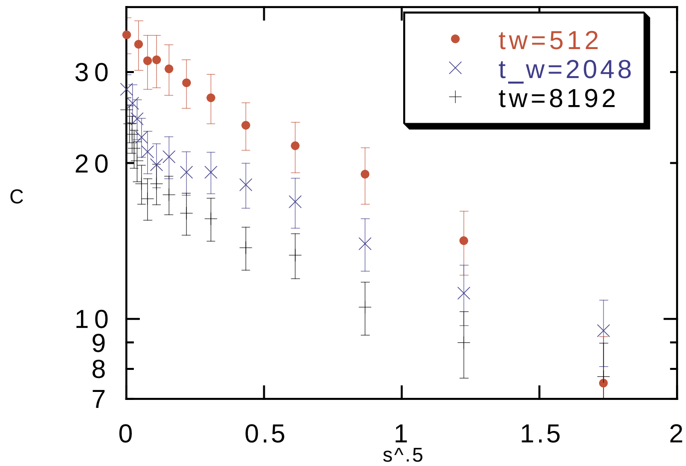

Figure 6. On a logarithmic scale we see the correlation function at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 512, 2048, 8912$ as a function of $s^{0.5} \equiv (t/t_w)^{0.5}$.

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 $d = 0.3$. The function f is very small when $x > 0.3$ and near 1 for $x < 0.3$.

The value of Q will be a number very near 1 for similar configurations (in which the particles have moved less than a) and it will be a much smaller value (less than 0.1) for unrelated configurations; using the same terminology as in spin glasses [17, 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 figure 7. We see that in this case also we have some violation of simple scaling, but the violations are definitely smaller, also, due to its definition, the quantity Q is normalized to 1 at $s = 0$.

4.2. The response function

We have followed a standard procedure [18, 19] to measure the off-equilibrium response function in simulations: we have kept the system in the presence of an external field ϵ up to time t_w and we have removed the field just at this time.

If ϵ is sufficiently small, we have that the stress as a 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 long as the limit of $R(t, t_w)$ does not depend on t_w when $t \to \infty$ the quantity defined in equation (37) goes to zero when $t \to \infty$. In this way we can obtain the value of the integrated response by measuring the stress density as a 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 than the third. At time t_w we change the form of the box to a cubic one. In this way we deform the system and induce a stress

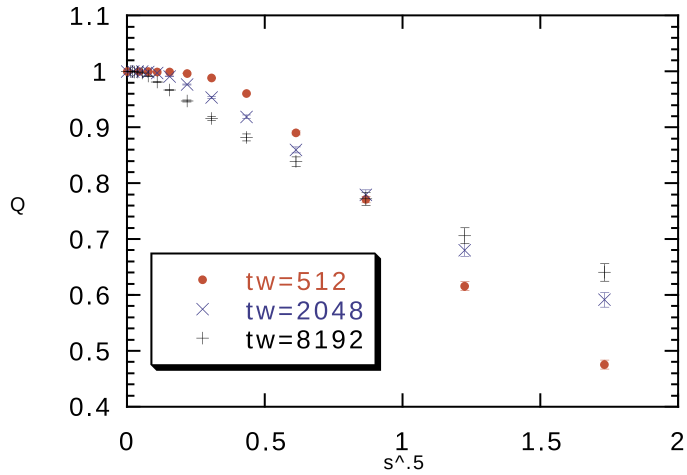

Figure 7. The overlap Q at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 512, 2048, 8912$ as a function of $s^{0.5} \equiv (t/t_w)^{0.5}$.

which will be eventually decay. In the high-temperature phase, where the system is liquid, the stress will disappear in a short time. In contrast, in the glassy phase, the stress remains for a much longer time (as expected [8]) and it shows an interesting ageing 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 value of ϵ that is too large we enter a nonlinear region. The analysis of the nonlinear dependence of the stress as a function of ϵ would be very interesting, but it goes beyond the scope of this paper. Here we restrict ourselves to the linear region. We have taken data at $\epsilon = 0.1$ and $\epsilon = 0.05$ and we have seen that there are some non-linear effects. No nonlinear effects have been detected at $\epsilon = 0.02$ and $\epsilon = 0.01$. All the data we present in this paper come from $\epsilon = 0.01$ and they are reasonably free of systematic effects. As a further check we have compared the value of Q measured at $\epsilon = 0$, as in section 4.1 with the value of Q at $\epsilon = 0.01$ and found that they differ by less than 1%.

In figure 8 we plot the response function S at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 128, 512, 2048$ as a function of $s^{0.5} \equiv (t/t_w)^{0.5}$. In this case ageing shows 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 the building of a discontinuity at $s = 0$ followed by a smooth function of s.

4.3. Fluctuations and response together

The crucial step now would be to plot the fluctuations and response together. The previous equation tells 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 $X(C)$.

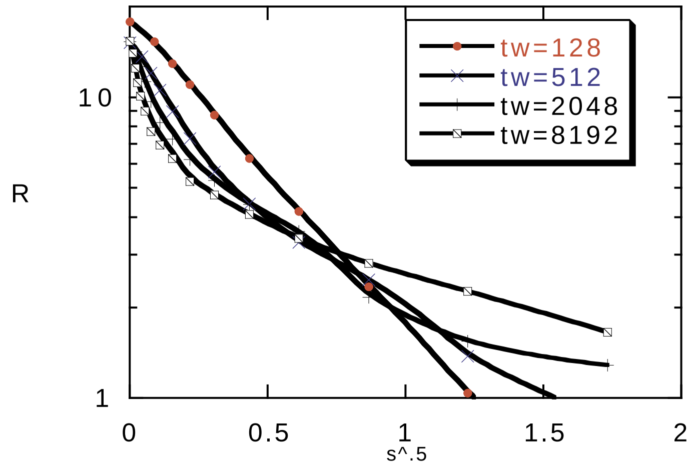

Figure 8. On a logarithmic scale we see the response function at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 128, 512, 2048, 8192$ as a function of $s^{0.5} \equiv (t/t_w)^{0.5}$.

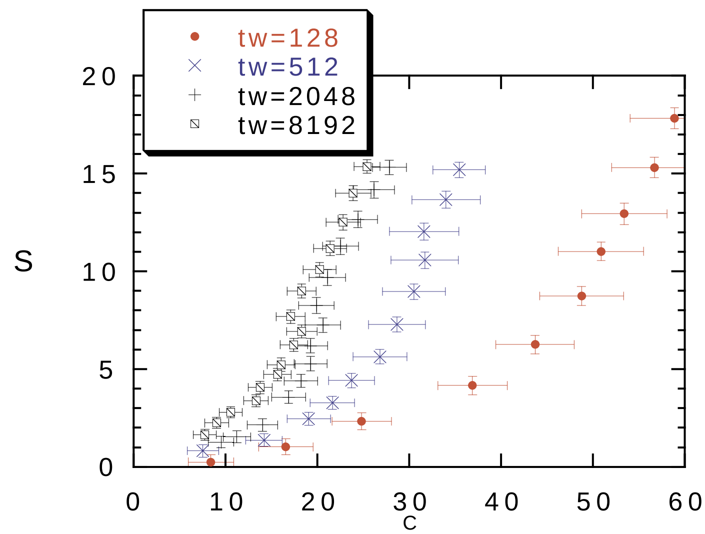

Figure 9. The response S as a function of C at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 128, 512, 2048, 8192$.

In the one-step replica symmetry-breaking scheme (conjectured in [10]) we expect that:

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

In figure 9 we find the data for the response S as a function of C at $\Gamma = 1.8$ for $N = 66$ at values of $t_w = 128, 512, 2048, 8912$. We can distinguish two regions:

- a high C region (typically $C > C(\infty)$), where the function S has a gradient of almost 1;
- a region of smaller C, where the dependence of S on C is more complex.

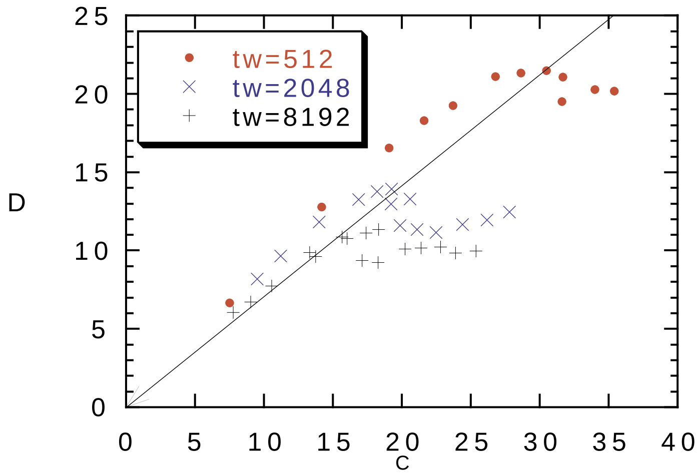

Figure 10. The difference $D \equiv C - S$ as function of C at $\Gamma = 1.8$ for $N = 34$ at values of $t_w = 512, 2048, 8912$. The straight line corresponds to one-step replica symmetry breaking with $m = 0.3$.

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

Similar data (not shown here) for the response S as a function of C at $\Gamma = 1.8$ for $N = 34$ behave in a qualitatively similar way, but have a much stronger dependence on the waiting time. In the case where $N = 66$ the data at $t_w = 2048$ and 8192 are similar, showing that the result will be near to the asymptotic limit in this case.

In order to expose the existence of a region where the FTD is valid [19], 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 verify the existence of a region where the FDT relation holds, in figure 10 we plot the the function D versus S at $\Gamma = 1.8$ for $N = 34$ at values of $t_w = 512, 2048, 8912$. A plateaux region is quite evident, the level of which is still dependent on t_w. The straight line corresponds to one-step replica symmetry breaking with $m = 0.3$.

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

- The function $S(C)$ is zero for $C < C(\infty)$. This corresponds to the simple situation where replica symmetry is not broken.
- The function $S(C)$ is linear for $C < C(\infty)$ with gradient m. This corresponds to one-step replica symmetry breaking.
- The function $S(C)$ has a power behaviour for $C < C(\infty)$ with an exponent greater than 1. In this case the replica symmetry is broken in a continuous way.

If we plot the previous data for $S(C)$, 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 be safely done. A value of m around 0.3 is compatible with the data. The study of the behaviour of the function $X(C)$ at small C is an interesting problem that must be investigated further.

5. Conclusions

In the previous section it was shown that there is a low-temperature region where the large-time extrapolation of the energy and of the stress autocorrelation function can be carried out by assuming simple power-law corrections. The extrapolated values most probably do not correspond to equilibrium values, but to metastable values and the real equilibrium values are reached only at much longer times.

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 ageing is found. The function $X(C)$ of the CK theory has been studied. This function also 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 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 needs to increase the time t_w by a factor of 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 as the time increases†. One probably needs a factor of 100 or more in computer time, which is not a very large amount (considering that this computation has taken a few weeks on a workstation), but it would certainly go outside the exploratory aim of this work and of the capabilities of the hardware we have used.

Something smarter can probably be done and two possibilities are as follows.

- We can repeat the same procedure where the temperature is slow cooled in steps of total length t_w starting from a finite temperature to the final temperature. In this way it is possible that ageing and the other phenomena survive, but the finite-time corrections could be much smaller [20].
- 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 simple ageing much better with much smaller corrections.

It would appear that there is much to investigate in the study of equilibrium of glasses. It will be interesting to see if the indications given in this paper are confirmed by more accurate and lengthy computations.

Acknowledgments

I would like to thank S Franz and D Lancaster for useful discussions and L Cugliandolo and J Kurchan for suggesting measuring the stress after changing the form of the box.

Appendix. Spin glasses

This appendix will briefly recall the situation for spin glasses. Ageing and the predictions of the CK theory were carefully analysed in [19]: a comparison of their results with ours would be instructive. Here we limit ourselves to the following general remark.

In spin glasses the relevant quantity is the total magnetization

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

† We should also increase the value of s in order to explore in more detail the region where C becomes small.

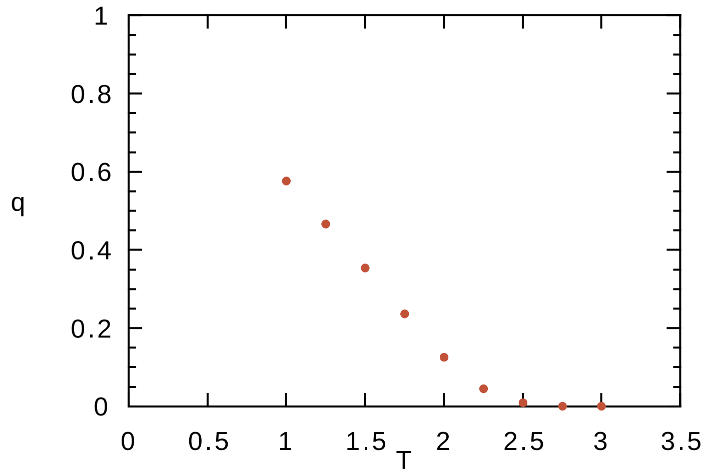

Figure A1. The value of q as function of the temperature in a four-dimensional spin glass.

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

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

We can now compute in simulations the magnetic susceptibility (χ), i.e. by inserting a small magnetic field h and measuring the ratio $\langle M\rangle/h$. 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 shown in figure A1, where the data are taken from [20].

There is a striking difference between spin glasses and the case of binary glasses presented here, which is noteworthy.

• 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 a present response (i.e. the susceptibility).

However, it seems that this difference does not have deep physical consequences and is just an effect of the different choice of observables.

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