Off-Equilibrium Fluctuation-Dissipation Relation in Fragile Glasses

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In this Letter we investigate the approach to equilibrium in fragile glasses by doing numerical simulations of binary mixtures. We study the diffusion of particles and the response to an external driving force. We find evidence for the validity of the Cugliandolo-Kurchan off-equilibrium fluctuation-dissipation relation. The results agree with the predictions of one step replica symmetry breaking and the dependence of the breakpoint parameter on temperature coincides with that found in simple generalized spin glass models. [S0031-9007(97)04473-6]

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When we suddenly decrease the temperature in a Hamiltonian system (with dissipative dynamics), many interesting phenomena happen if the initial and the final temperatures correspond to different phases. When the low temperature phase can be characterized by a simple order parameter (e.g., the magnetization for ferromagnets) we find the familiar phenomenon of spinodal decomposition characterized by growing clusters of different phases. There is a dynamical correlation length (i.e., the size of the clusters) which increases as a power of the time t after the quench and the energy approaches equilibrium with powerlike corrections [e.g., $E(t) \approx E_\infty + At^{-1/2}$]. In this region aging phenomena are also present [1,2].

The situation is more intriguing in the case of glasses and spin glasses where the low temperature phase cannot be characterized in terms of a simple order parameter and clusters cannot easily be defined. Remarkable progress in understanding the off-equilibrium dynamics and its relations to the equilibrium properties has been done by noticing that a crucial off-equilibrium feature is the presence of deviations from the well known *equilibrium* fluctuation-dissipation relations. On the basis of some analytic results for soluble models it has been conjectured that in the general case one can define a function $X(C)$, C being an autocorrelation function at different times [3–5]. This function characterizes the violations of the fluctuation-dissipation theorem (which is correct only at equilibrium). In the case of the spinodal decomposition the function $X(C)$ takes only the values 0 or 1, but different results are expected for other systems. It is remarkable that (at least in the case of spin glasses) the function $X(C)$ is equal to the function $x(q)$ (q being the overlap of two spin configurations) which plays a central role in the equilibrium computation of the free energy [6,7].

This equality is very interesting because it is rather difficult to measure the function $x(q)$ at thermal equilibrium while the function $X(C)$ can be measured relatively easily in off-equilibrium simulations [8]. The temperature dependence of the function $X(C)$ is interesting also because rather different systems can be classified in the same universality class according to the behavior of this function. It was conjectured a long time ago that the equilibrium properties of glasses are in the same universality class of some simple generalized spin glass models [9]. Here we study the dynamic function $X(C)$ in glass forming materials (in the case of a fragile glass) and we show that its properties are in agreement with the conjecture of Ref. [9] and the dynamic theory of Ref. [3]. The approach to equilibrium of the fragile glass we study (a binary mixture) conforms well to the theoretical predictions, at least in the region of time explored by these simulations. It would be very interesting to check if the same properties are present also for strong glasses.

Let us define our notations. We concentrate our attention on a quantity $A(t)$; later on we will make a precise choice of this function. We suppose that the system starts at time $t = 0$ from an initial condition and subsequently is at a fixed temperature T. If the initial configuration is at equilibrium at a temperature $T' > T$, we observe an off-equilibrium behavior. Here we will consider only 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

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

where we are considering the evolution in presence of a time dependent Hamiltonian in which we have added the term $\int dt\, \epsilon(t) A(t)$.

The usual equilibrium fluctuation-dissipation theorem (FDT) tells us that

$$G^{\mathrm{eq}}(t) = -\beta \frac{dC^{\mathrm{eq}}(t)}{dt}, \tag{3}$$

where

$$G^{\mathrm{eq}}(t) = \lim_{t_w \to \infty} G(t, t_w), \qquad C^{\mathrm{eq}}(t) = \lim_{t_w \to \infty} C(t, t_w). \tag{4}$$

It is convenient to define the integrated response:

$$\begin{aligned} R(t, t_w) &= \int_0^t d\tau\, G(t - \tau, t_w + \tau), \\ R^{\mathrm{eq}}(t) &= \lim_{t_w \to \infty} R(t, t_w). \end{aligned} \tag{5}$$

$R(t, t_w)$ is the response of the system at time $t + t_w$ to a field acting for a time t starting at t_w. The usual FDT relation becomes

$$R^{\rm eq}(t) = \beta(C^{\rm eq}(t) - C^{\rm eq}(0)). \tag{6}$$

The off-equilibrium fluctuation-dissipation relation states that the response function and the correlation function satisfy the following relation for large t_w:

$$R(t, t_w) \approx \beta \int_{C(t,t_w)}^{C(0,t_w)} X(C)\, dC . \tag{7}$$

In other words if we plot R versus βC for large t_w the data collapse on the same universal curve and the slope of that curve is $-X(C)$. The function $X(C)$ is system dependent and its form tells us interesting information. The relation in Eq. (7) has been numerically verified in Ref. (8) in the case of three dimensional spin glasses.

We must distinguish two regions:

(1) A short time region where $X(C) = 1$ (the so-called FDT region) and C belongs to the interval I (i.e., $C_1 < C < C_2$).

(2) A large time region [usually $t = O(t_w)$] where $C \notin I$ and $X(C) < 1$. In the same region the correlation function often satisfies an aging relation [i.e., $C(t, t_w)$ depends only on the ratio $s \equiv t/t_w$ in the region where both t and t_w are large: $C(t, t_w) \approx C^a(t/t_w)$].

In the simplest nontrivial case, i.e., one step replica symmetry breaking [6,7], the function $X(C)$ is piecewise constant, i.e.,

$$X(C) = m \quad \text{for } C \in I, \qquad X(C) = 1 \quad \text{for } C \notin I . \tag{8}$$

One step replica symmetry breaking for glasses is the basis of the conjecture of Ref. [9].

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 that $m = 1$ at $T = T_c$ and $m(T)$ is roughly linear in the whole temperature range.

If replica symmetry is broken at one step, the same value of m should be obtained for all the observables. In this case Eq. (8) has a highly predictive power because the value of m may be measured by looking to different quantities.

In this Letter we show that in a binary mixture of soft spheres the function $X(C)$ seems to be given by the one step formula (8) with an approximate linear dependence of m on the temperature. It has already been shown that in this model simple aging is well satisfied and some indications for the validity of Eq. (7) were found [10] by looking to the correlations of the stress energy tensor. Here we study a different and more suitable observable and we find much more accurate results that extend the previous finding.

We consider 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 particles is given by the Hamiltonian:

$$H = \sum_{i<k} \left(\frac{\sigma(i) + \sigma(k)}{|\mathbf{x}_i - \mathbf{x}_k|} \right)^{12}, \tag{9}$$

where the radius (σ) depends on the type of particles. This model has been carefully studied in the past [11–14]. The choice $\sigma_B/\sigma_A = 1.2$ 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, i.e., $[\sigma_A^3 + 2(\sigma_A + \sigma_B)^3 + \sigma_B^3]/4 = 1$.

The thermodynamic quantities depend only on the quantity T^4/ρ, T and ρ being, respectively, the temperature and the density (which we take equal to 1). It is usual to introduce the quantity $\Gamma \equiv \beta^4$. For quenching from $T = \infty$ the glass transition is known to happen around $\Gamma_c = 1.45$ [12].

Our simulations are done using a Monte Carlo algorithm. We start by placing the particles at random and we quench the system by putting it at final temperature (i.e., infinite cooling rate). 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, i.e., $N = 66$. Previous studies have shown that such a small sample is quite adequate to show interesting off-equilibrium behavior in the time window we consider in this Letter [15]. As a check we have also done some other simulations at $N = 130$.

The main quantity on which we will concentrate our attention is the diffusion of the particles:

$$\Delta(t, t_w) \equiv \frac{\sum_{i=1,N} \langle |\mathbf{x}_i(t_w) - \mathbf{x}_i(t_w + t)|^2 \rangle}{N} . \tag{10}$$

The usual diffusion constant is given by $D = \lim_{t\to\infty} \Delta(t, t_w)/t$.

The other quantity we measure is the response to a force. At time t_w we add to the Hamiltonian the term $\epsilon \mathbf{f} \cdot \mathbf{x}_k$, where f is the vector of squared length equal to d and we measure the response

$$R(t_w, t) = \left\langle \frac{\partial \mathbf{f} \cdot \mathbf{x}_k(t_w + t)}{\partial \epsilon} \right\rangle \bigg|_{\epsilon=0} \approx \left\langle \frac{\mathbf{f} \cdot \mathbf{x}_k(t_w + t)}{\epsilon} \right\rangle \tag{11}$$

for sufficiently small ϵ.

The usual fluctuation theorem tells that at equilibrium $\beta \Delta^{\rm eq}(t) = R^{\rm eq}(t)$. This relation holds even though $\Delta(t, t_w)$ is not the product of two observables, one at time t_w, the other at time $t_w + t$. However, it can be written as

$$\Delta(t, t_w) \equiv \frac{\sum_{i=1,N} \langle \mathbf{x}_i(t_w)^2 + \mathbf{x}_i(t_w + t)^2 - 2\mathbf{x}_i(t_w) \cdot \mathbf{x}_i(t_w + t) \rangle}{N}, \tag{12}$$

and a detailed analysis [16] shows that the fluctuation-dissipation theorem is valid also in this case.

In the following we will look for the validity in the low temperature region of the generalized relation $\beta X(\Delta) = \partial R/\partial\Delta$. This relation (with $X \neq 1$) can be valid only in the region where the diffusion constant D is equal to zero. Strictly speaking also in the glassy region $D \neq 0$, because diffusion may always happen by interchanging two nearby particles (D is different from zero also in a crystal); however, if the times are not too large the value of D is so small in the glassy phase that this process may be neglected in a first approximation.

For $N = 66$ we average over 250 samples in absence of the force and on 1000 samples in presence of the force. We have done simulations for $\Gamma = 1.4, 1.5, \ldots, 2.0$. To decrease the error on the determination of R we follow (as suggested in Ref. [17]) the method of computing in the same simulation the response function for different particles [18]. In other words we add to the Hamiltonian the term $\epsilon \sum_{k=1,N} \mathbf{f}_k \cdot \mathbf{x}_k$, where the $\mathbf{f}$ are random Gaussian vectors of average squared length equal to d. The quantity R is the average over the variables $\mathbf{f}$ of

$$\frac{\sum_{k=1,N} \langle \mathbf{f}_k \cdot \mathbf{x}_k(t_w + t) \rangle}{N\epsilon} . \tag{13}$$

The value of ϵ should be sufficiently small in order to avoid nonlinear effects: we have done extensive tests for $\epsilon = 0.1$ and $\epsilon = 0.2$. We found that $\epsilon = 0.2$ is in the linear region, but we have followed the more conservative option $\epsilon = 0.1$. (The choice of ϵ must be done carefully: when ϵ decreases the systematic errors decrease, but the statistical errors on the ratio increase). We do not observe any systematic shift.

In Fig. 1 we show the dependence of Δ and R on the ratio $s \equiv t/t_w$ in the low temperature region, i.e., at $\Gamma = 1.7$ for $t_w = 2048$. They coincide in the small s region, where FDT holds, but they differ for $s > 0.1$.

In Fig. 2 we show R versus $\beta\Delta$ at $t_w = 2048$ and $t_w = 8192$ for $\Gamma = 1.6$ and $t \leq 4t_w$ at $N = 66$. We also show the data for $t_w = 2048$ at $N = 130$. We do not observe any significant systematic shift in this plot among three data sets. We distinguish two linear regions with different slope as expected from one step replica symmetry breaking. The slope in the first region is compatible with 1, as expected from the FDT theorem, while the slope in the second region is near 0.62. Also the data at different temperatures for all values of $\Gamma \geq 1.5$ show a similar behavior. The value of R in the region where the FDT relation does not hold can be very well fitted by a linear function of Δ as can be seen in Fig. 2. The region where a linear fit (with $m < 1$) is quite good corresponds to $t/t_w > 0.2$. The fitted value of $m \equiv \partial R/\partial(\beta\Delta)$ is displayed in Fig. 3 using the data at $t_w = 2048$. When m becomes equal to 1, the fluctuation-dissipation theorem holds in the whole region and this is what happens at higher temperatures. The straight line is the prediction of the approximation $m(T) = T/T_c$, using $\Gamma_c = 1.45$.

The value of m we find at $\Gamma = 1.8$ (i.e., $m = 0.33 \pm 0.04$) is compatible with the value ($m = 0.25 \pm 0.1$) of Ref. [10] extracted from the fluctuation of the stress energy tensor. The method described in this Letter is much more accurate for two reasons: (a) The quantities which we consider become larger when we enter the OFDR region: they increase (not decrease) as function of time. (b) The correlation quantity we measure is an intensive quantity which becomes self-averaging in the limit of infinite volume.

It is amusing to notice that the simple aging relation $\Delta(t_w, t_w) =$ const for large t_w implies that the particles move in average by a constant amount in each interval of time $2^K < t < 2^{K+1}$ [19]. If we assume that the movements in each time interval are uncorrelated, it

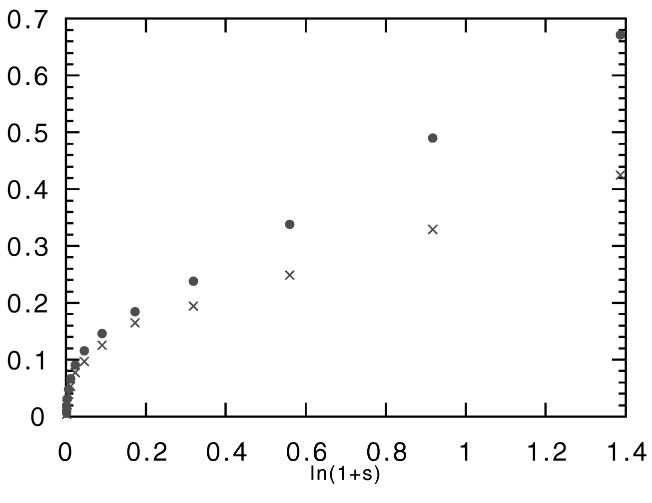

FIG. 1. $\beta\Delta$ (points) and R (crosses) as function the ratio $\ln(1 + s) \equiv \ln(1 + t/t_w)$ at $\Gamma = 1.7$ for $t_w = 2048$.

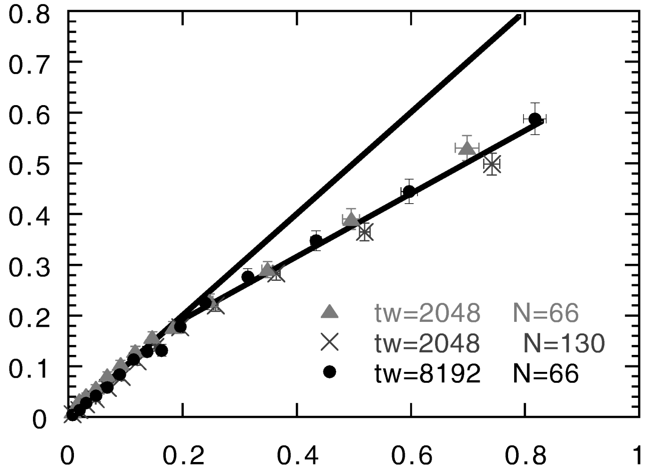

FIG. 2. R versus $\beta\Delta$ at $\Gamma = 1.6$ for $t_w = 8192$ and $t_w = 2048$ at $N = 66$ and for $t_w = 2048$ at $N = 130$. The two straight lines have slope 1 and 0.62, respectively.

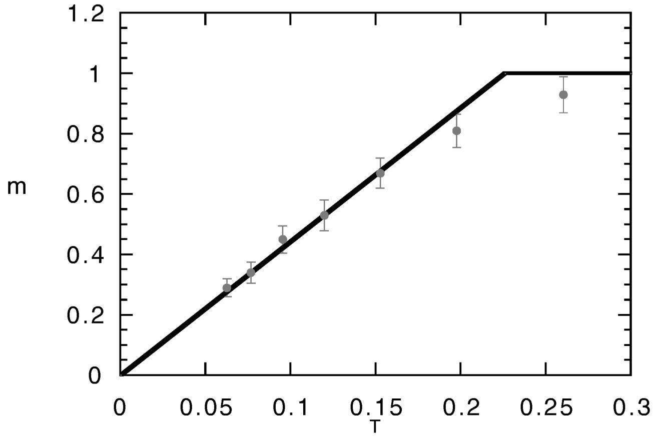

FIG. 3. The quantity $m \equiv \frac{\partial R}{\partial(\beta\Delta)}$ as $t_w = 2048$ as function of the temperature. The straight line is the prediction of the approximation $m(T) = T/T_c$.

follows that in the glassy phase $\Delta(t, t_w) \propto \ln(t/t_w) +$ const for large t/t_w. In Fig. 4 we show the data for $t_w = 1$, i.e., the average distance squared for each particle from the initial position. The data seem to display a very nice logarithmic behavior. The same argument would imply that $\Delta(t, t_w)$ should be a linear function of $\ln(1 + t/t_w)$. This is what happens outside the FDT region (i.e., $t/t_w > 0.2$), as can be seen from Fig. 1.

All the results are in very good agreement with the theoretical expectations based on our knowledge extracted from the mean field theory for generalized spin glass models. The approximation $m(T) = T/T_c$ seems to work with an embarrassing precision. We can conclude that the ideas developed for generalized spin glasses have a much wider range of application than the models from which they have been extracted. It is likely that they reflect quite general properties of the phase space and therefore can be applied in cases which are very different from the original ones. In a recent work [20] some thermodynamic predictions have been obtained for the behavior of glassy systems, like the present ones, under the assumption that they obey the laws derived for generalized spin glasses. The present Letter confirms that assumption.

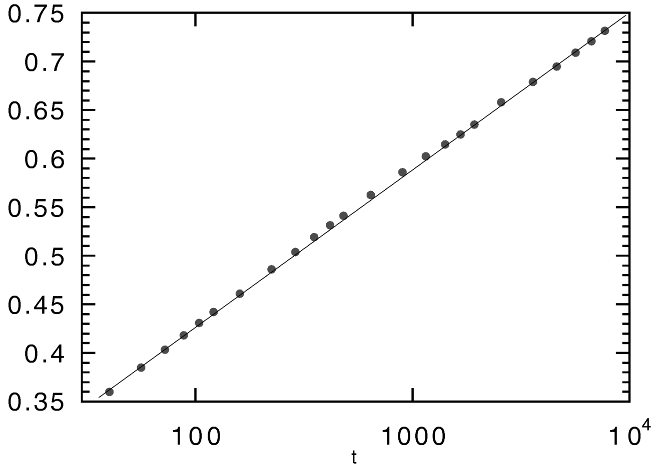

FIG. 4. The average distance squared from the initial configuration [i.e., $\Delta(t, 1)$] as function of the time in a logarithmic scale for $\Gamma = 1.6$.

The most urgent theoretical task now would be to develop an analytic theory for glasses in the low temperature region from which one could compute the function $m(T)$. This goal should not be out of reach: a first step in this direction can be found in [21].

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