Two Time Scales and Violation of the Fluctuation-Dissipation Theorem in a Finite Dimensional Model for Structural Glasses

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We study the breakdown of fluctuation-dissipation relations between time-dependent density-density correlations and associated responses following a quench in the chemical potential in the frustrated Ising lattice gas. The corresponding slow dynamics is characterized by two well-separated time scales characterized by a constant value of the fluctuation-dissipation ratio. This result is particularly relevant since activated processes dominate the long-time dynamics of the system.

In recent years considerable progress has been achieved in the theoretical description of the glassy state of matter. A scenario for the observed slow dynamics of glass forming materials has emerged through detailed analysis of mean field (MF) spin glass models [1]. The equations describing the off-equilibrium dynamics of these MF spin glasses simplify, above the transition, to the single equation for the mode coupling theory for supercooled liquids [2]. These approaches have been successful in explaining history dependence or aging effects and the nature of the two characteristic relaxations in glasses, the short time or β relaxation and the structural long time α relaxation. In the α relaxation the system falls out of local equilibrium, as a consequence fluctuation-dissipation theorem (FDT) breaks down and can be replaced by the more general relation

$$R(t, t_w) = \frac{X(t, t_w)}{T} \frac{\partial C(t, t_w)}{\partial t_w}, \qquad (1)$$

where $C(t, t_w)$ is a two times correlation function and $R(t, t_w)$ with $t > t_w$ is the associated response. T is the heat bath temperature and $X(t, t_w)$ is a function that measures the departure from FDT: at equilibrium $X = 1$ and the usual FDT is recovered, while in the out of equilibrium regime $X < 1$. In MF approximation [3] the function X, called "fluctuation-dissipation ratio" (FDR), turns out to depend on both times only through $C(t, t_w)$. Moreover, in MF models of glasses X is a constant (when different from 1). This scenario reflects the existence of only two well-separated time scales, the equilibrium or FDT scale and a longer one where the system is out of equilibrium. The ratio T/X has been interpreted as an effective temperature, and it has been demonstrated that it is exactly the temperature that a thermometer would measure if it would be coupled to the slowly relaxing modes of the system [4]. Recently the first experimental determination of the FDR has been done in glycerol [5].

This scenario, while appealing, is essentially based on an analogy between the physics of some MF spin glasses and the behavior of real structure glasses (being the formal connection valid only in the high temperature region). At this point it seems crucial to test the link between MF theories and realistic models in the glassy phase. In particular, we still do not know which will be the role of activated processes in realistic models. Activated processes are absent in completely connected models in the thermodynamic limit, while on the contrary they dominate the relaxation dynamics below the glass transition temperature T_g in real glasses.

The goal of the present Letter is to go beyond the MF-like description of structural glasses by considering a finite dimensional model, the frustrated Ising lattice gas (FILG) [6,7], which presents most of the relevant features of glass forming materials, in particular, activated processes at low temperatures. Here we analyze the violation of FDT in the FILG in three dimensions through Monte Carlo simulations. The (very precise) results confirm the qualitative scenario of MF models of a constant FDR with large separation of time scales and set the stage for a detailed investigation of activated processes in realistic models of glasses.

The FILG is defined by the Hamiltonian

$$H = -J \sum_{\langle ij \rangle} (\varepsilon_{ij} \sigma_i \sigma_j - 1) n_i n_j - \mu \sum_i n_i. \quad (2)$$

At each site of the lattice there are two different dynamical variables: local density (occupation) variables $n_i = 0, 1$ ($i = 1 \dots N$) and internal degrees of freedom $\sigma_i = \pm 1$. The usually complex spatial structure of the molecules of glass forming liquids, which can assume several spatial orientations, is in part responsible for the geometric constraints on their mobility. Here we are in the simplest case of two possible orientations, and the steric effects imposed on a particle by its neighbors are felt as restrictions on its orientation due to the quenched random variables $\varepsilon_{ij} = \pm 1$. The first term of the Hamiltonian implies that when $J \to \infty$ any frustrated loop in the lattice will have at least one hole and then the density will be $\rho < 1$, preventing the system from reaching the close packed configuration. The system will then present "geometric frustration."

Finally, μ represents a chemical potential ruling the system density (at fixed volume).

The system presents a slow "aging" dynamics after a quench from a small value of μ characteristic of the liquid phase to a large μ corresponding to the glassy phase [7], what is equivalent to a sudden compression. In the present numerical experiments we always let the system evolve after a quench in μ with J and T fixed. The origin of the times is set on the quench time. After the quench the density slowly relaxes up to a critical value near $\rho_c \approx 0.675$ (further details will be given in [8]). After a waiting time t_w we fix the density to the value $\rho = \rho(t_w)$ (for technical reasons explained below) and a small random perturbation ($\mu_i = \pm 1$) is applied [9]:

$$H'(t) = H(t) - \epsilon(t) \sum_i \mu_i n_i(t). \qquad (3)$$

In all our numerical experiments the field is switched on at time t_w and kept fixed for later times, that is, $\epsilon(t) = \epsilon \theta(t - t_w)$. Then we measure the density-density autocorrelation function

$$C(t, t_w) = \frac{1}{N\rho} \sum_i \overline{\langle n_i(t) n_i(t_w) \rangle}, \qquad (4)$$

where $\langle \cdot \rangle$ and $\overline{}$ are the averages over thermal histories and disorder realizations [10]. At the same time we measure the associated response function integrated over the time and divided by the perturbing field intensity, which defines the off-equilibrium compressibility

$$\kappa(t, t_w) = \frac{1}{\epsilon} \int_{-\infty}^t R(t, s)\epsilon(s)\, ds = \int_{t_w}^t R(t, s)\, ds, \qquad (5)$$

where, as usual, the response is defined as

$$R(t, t') = \frac{1}{N\rho} \sum_i \frac{\partial \overline{\langle n_i(t) \rangle}}{\partial \epsilon(t')}. \qquad (6)$$

In the large times limit ($t, t_w \to \infty$), $X(t, t_w)$ depends on both times only through the correlation $C(t, t_w)$. Then integrating Eq. (1) from t_w to t we obtain a useful relation linking the correlation and the compressibility in the out of equilibrium regime

$$T\kappa(t, t_w) = \int_{C(t, t_w)}^1 X(C)\, dC. \qquad (7)$$

This is the key relation used in order to extract the FDR.

In our case the perturbing term in the Hamiltonian, shown in Eq. (3), gives to the integrated response the following form:

$$\kappa(t, t_w) = \frac{1}{N\rho} \left(\sum_i [\overline{\langle \mu_i n_i(t) \rangle}]_{\mathrm{av}} - \sum_i [\overline{\langle \mu_i n_i(t_w) \rangle}]_{\mathrm{av}} \right), \qquad (8)$$

where $[\cdot]_{\mathrm{av}}$ is the average over the random μ_i realizations [10]. The second term can be ignored because the μ_i are random and completely uncorrelated from the configuration at time t_w.

Performing a parametric plot of the compressibility (or the integrated response) versus the correlation is a useful way of getting information about the different dynamical regimes present in the model and, in particular, the time scales of the system. In fact, from Eq. (7) it is easy to see that, plotting $T\kappa(t, t_w)$ vs $C(t, t_w)$, the FDR can be simply obtained as minus the derivative of the curve, i.e.,

$$X(C') = - \frac{\partial [T\kappa(t, t_w)]}{\partial C(t, t_w)} \bigg|_{C(t, t_w) = C'}. \qquad (9)$$

There is already a considerable literature on this kind of analysis in systems with and without quench disorder [11]. Particularly relevant to the present discussion are Refs. [12], where a constant FDR was found in model glasses with interactions of the Lennard-Jones type and in a purely kinetic lattice gas. The FILG has the advantage of being a Hamiltonian lattice model with short range interactions and, in this sense, it is more realistic than purely kinetic models and more accessible analytically and computationally than Lennard-Jones systems. Moreover, it is a valid on-lattice model for structural glasses and it may be simple enough to apply statistical mechanics techniques.

We have simulated the FILG in 3D for linear sizes $L = 30$ and 60. Fixing the coupling constant $J = 1$ and a temperature $T = 0.1$ the system presents a glass transition around $\mu = 0.5$ [6].

In all our numerical experiments we have prepared the system in an initial state with low density, characteristic of the liquid phase, and then, at time zero, we have performed a sudden quench in μ to a value deep in the glass phase (the data presented here refer to $\mu = 1$). As already explained above, after a time t_w a perturbation in the form of a random small chemical potential has been applied and the density-density autocorrelation, Eq. (4), and the corresponding integrated response, Eq. (8), have been recorded. At time t_w the density has been fixed to the value $\rho = \rho(t_w)$ for the following reason: the perturbing term in the Hamiltonian [see Eq. (3)] favors roughly half of the sites (those with $\mu_i = 1$) to be filled and the remaining half to be empty. When the perturbation is switched on, the first half starts to be more filled than the second one and this increases the integrated response, as it should. On very long times, however, because the density reached at time t_w is still a bit below the asymptotic value, the number of particles continues growing and new particles are added with higher probability on the sites with $\mu_i = -1$, which are emptier. Then the response becomes negative because of systematic errors. We avoid the negative responses fixing the density at time t_w. In the limit $t_w \to \infty$ we recover the right behavior in any case; however, with our choice the extrapolation is safer.

In all our simulations we have verified that the strength of the perturbation $\epsilon = 0.02$ is small enough in order to be in the linear response regime. We have also checked that the system thermalizes at temperatures $T \geq 0.3$ (being

always $\mu = 1$) and satisfies FDT. Further details will be given in [8].

In Fig. 1 we show the main result of this Letter: a parametric plot of the integrated response versus the density autocorrelation for different waiting times. The behavior of the curves is exactly the one predicted by MF theories for a glass former. Two distinct regimes can be perfectly recognized. In the FDT or quasiequilibrium regime, $t - t_w \ll t_w$ (β relaxation), the points lie on the straight line given by

$$T\kappa(t, t_w) = 1 - C(t, t_w). \tag{10}$$

This first time regime corresponds then to a FDR $X(t, t_w) = 1$ independent of t and t_w. In this regime the system is in quasiequilibrium, with the particle moving inside the cages formed by nearly frozen neighbors and the temperature measured from particle fluctuations is that of the heat bath. When $t - t_w \gtrsim t_w$ the system falls out of equilibrium, entering the aging regime, and the data in Fig. 1 depart from the FDT line. From the figure it is clear that the FDR is still a constant, but now $0 < X(t, t_w) < 1$. The constancy of the FDR in the out of equilibrium regime is one of the central predictions of MF approaches. Here we see that this is still valid for a finite dimensional system.

In Fig. 2 we compare the results for the FDR measured on two large systems, whose sizes are $N = 30^3$ and $N = 60^3$. Both curves correspond to $t_w = 10^4$ and no finite size effects are evident. Fitting the data in the out of equilibrium regime to the straight line

$$T\kappa(t, t_w) = X(t_w)[q_{EA}(t_w) - C(t, t_w)]$$
$$+ [1 - q_{EA}(t_w)] \tag{11}$$

allows us to compute the t_w-dependent FDR $X(t_w)$ and the Edwards-Anderson order parameter $q_{EA}(t_w)$. In the large times limit they should converge to the corresponding equilibrium values [13,14].

We report the linear fit in Fig. 2 in order to show how well the data can be fitted with the formula in Eq. (11). As one can see from Fig. 1, the slope $X(t_w)$ changes very little with t_w and it takes the same value (within the error) for the two largest waiting times. The results of our fits give $X = 0.64(3)$ and $q_{EA} = 0.92(1)$. In comparison with other works the correlation range we are exploring may seem quite small. However, it should be kept in mind that we are using nonconnected correlation functions which tend in the large times limit to $\rho^2 \simeq 0.44$. So we are actually spanning half of the allowed range.

In the inset of Fig. 2 we present the same kind of data ($t_w = 10^5, 10^6$) for the Edwards-Anderson (EA) model, which is expected to have more than two time scales. It is clear that in the EA model the slope changes along the curve and a straight line is not able to fit the whole set of data. Moreover, higher temperature data [11] suggest that the slope still has to decrease (in modulus) for smaller correlations, making the linear fit even poorer.

An important difference between the present model and MF approaches should be evident: activated processes present in finite dimensional systems should dominate the asymptotic dynamics and as $t_w \to \infty$ equilibrium dynamics should be restored (a similar behavior can be observed in MF models by considering small systems [15]). However, the time a macroscopic system needs to reach such an equilibrium (thermalization time, t_{eq}) increases very rapidly with the system size and then the use of large sizes (here we have $L = 30$ and 60) prevents the system from reaching equilibrium in accessible time scales. In other words, we expect that the FDR explicitly depends on t_w and it tends to 1 in the limit $t_w \to \infty$. However, in the range
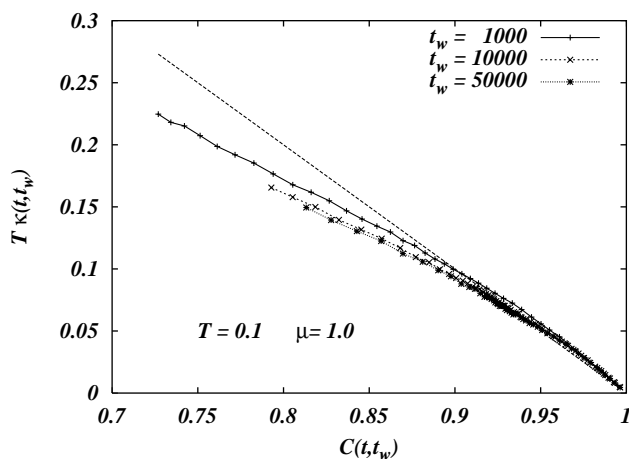

FIG. 1. The plot of the integrated response times the temperature versus the correlation gives clear evidence for the existence of two well-separated time scales, together with a constant FDR in both regimes. The dashed line is $T\kappa = 1 - C$. The errors are of the order of the symbols and have been estimated from sample to sample fluctuations.
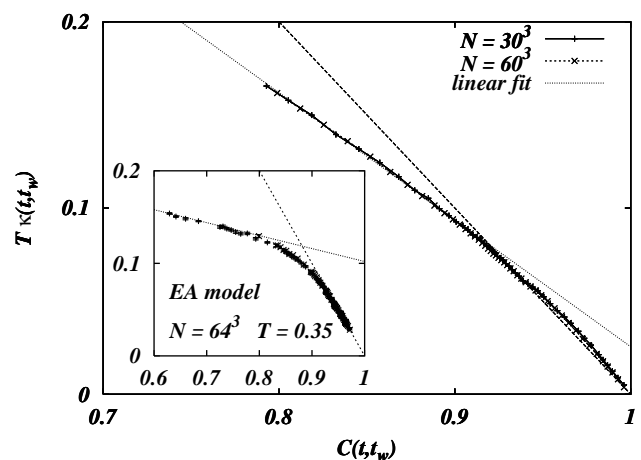

FIG. 2. Same as Fig. 1, now with different volumes in order to show the absence of finite size effects. The linear fit to the data is very good and gives a value for the FDR $X \simeq 0.64$. For the EA model (inset) the linear fit is far from good.
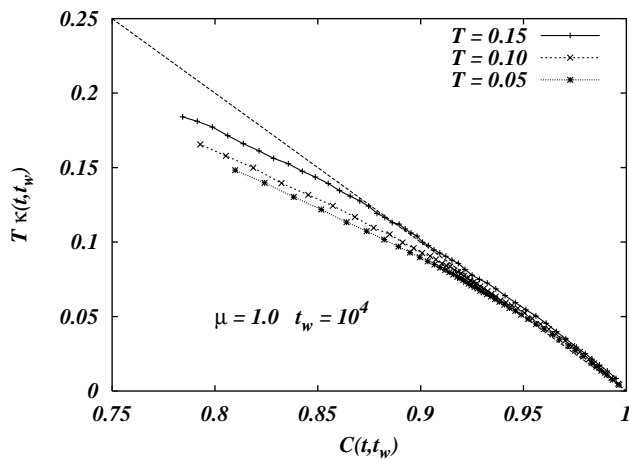
FIG. 3.   Same as Fig. 1 for different temperatures in the glass phase.

$1 \ll t_w \ll t_{eq}$ (where we actually are) the FDR should relax into some very long plateau. It is very remarkable that finite times effects are very well described by MF theories.

In Fig. 3 we show the usual integrated response versus correlation plot for different temperatures, being the chemical potential always equal to $\mu = 1$. We estimated, both from the density measurements and from the FDR, the glassy transition to be located around $T_g \simeq 0.2$. So all the data refer to the glassy phase. The main result to be noted is the good parallelism between all the curves in the aging regime. They can be perfectly fitted with the same value for X and different values for q_{EA}, which increases lowering the temperature. As T approaches T_g from below, FDT is recovered. Also, as $q_{EA}(T)$ decreases, X remains constant within the numerical precision. The exact behavior near the transition, that is, whether X (and q_{EA}) are continuous or not [16], is difficult to establish numerically and will be addressed in a future work.

In summary, we have found that the glassy phase of a realistic model of structural glass presents two well-separated time scales, as found in MF models of spin glasses. The out of equilibrium long-time dynamics can be characterized by a constant value of the fluctuation dissipation ratio X which is, with a very good approximation, independent of temperature in the glass phase. This last observation does not agree with MF predictions. Being a model in 3D, the frustrated lattice gas is an interesting test ground for performing a systematic study of activated processes, a main ingredient absent in MF models.

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