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Fluctuation-dissipation ratio in an aging Lennard-Jones glass

J.-L. BARRAT[1] and W. KOB[2]

[1] *Département de Physique des Matériaux, Université Claude Bernard and CNRS 69622 Villeurbanne Cedex, France*
[2] *Institut für Physik, Johannes Gutenberg-Universität Staudinger Weg 7, D-55099 Mainz, Germany.*

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Abstract. – By using extensive molecular dynamics simulations, we have determined the violation of the fluctuation-dissipation theorem in a Lennard-Jones liquid quenched to low temperatures. For this we have calculated $X(C)$, the ratio between a one-particle time-correlation function C and the associated response function. Our results are best fitted by assuming that $X(C)$ is a discontinuous, piecewise constant function. This is similar to what is found in spin systems with one-step replica symmetry breaking. This strengthens the conjecture of a similarity between the phase space structure of structural glasses and such spin systems.

Obtaining information on the phase space structure of glassy systems is a very difficult challenge. By definition, relaxation times in a glass are so long as to preclude equilibration within an experimental (or numerical) time scale, except perhaps for very small systems [1,2]. Exploration of phase space in these systems is necessarily incomplete, and the results from any experimental investigation cannot be expected to be representative of a well-defined statistical ensemble. Hence, although many conjectures have been formulated concerning the structure of phase space in glassy systems [3], very little is actually known.

A promising route, that might to some extent bypass this intrinsic difficulty, is the idea that relevant information on phase space structure is encoded in the nonequilibrium dynamics of glassy systems. This idea was actively developed in the field of spin glasses [4-6], but its extension to the field of structural glasses is more recent [7-10]. Among the important quantities that can be investigated in a nonequilibrium system is the so-called fluctuation-dissipation ratio X, defined in the following way. Consider an observable A whose normalized autocorrelation function will be denoted by C, and let R be the response function of A to a field H conjugate to A. Then, for a system in equilibrium at temperature T, $C(t)$ is related

to the response function $R(t)$ of the system to H by the usual fluctuation dissipation theorem (FDT), $R(t) = -\frac{1}{k_{\rm B}T}\frac{{\rm d}C}{{\rm d}t}$. In a system that is out of equilibrium (*e.g.*, a system that has been quenched at $t = 0$ to a low temperature) the property of time translation invariance is lost, and C and R become functions of two time variables, *e.g.* $C(t', t) = \langle A(t')A(t)\rangle$. A formal way of generalizing the usual FDT consists in writing, for $t' > t$

$$R(t', t) = \frac{1}{k_{\rm B}T} X(t', t) \frac{\partial C(t', t)}{\partial t}\,, \tag{1}$$

which in this form is merely a definition of X. The importance of this "FDT violation factor" $X(t', t)$ was recognized in the context of mean-field theories of spin glasses [11], where it appears that $X(t', t)$ has the properties discussed below. For this discussion it is useful to consider the situation in which the system is driven out of equilibrium at time $t = 0$, then aged for a waiting time $t_{\rm w}$ after which the measurement of the time correlation functions $C(t_{\rm w} + \tau, t_{\rm w})$ are started. For mean-field models exhibiting glassy behavior it has been shown that in the limit of long times, $t_{\rm w}, \tau \to \infty$, $X(t_{\rm w} + \tau, t_{\rm w})$ is a function of the correlation function C only, *i.e.*

$$X(t_{\rm w} + \tau, t_{\rm w}) = x(C(t_{\rm w} + \tau, t_{\rm w}))\,, \tag{2}$$

where x is now a function of one variable. In this asymptotic limit two regimes can be distinguished. If $t_{\rm w}$ is kept fixed, $C(t_{\rm w} + \tau, t_{\rm w})$ eventually becomes a function of τ only. The limiting value of this function for $\tau \to \infty$ is the Edwards-Anderson parameter associated with observable A, which is usually denoted by $q_{\rm EA}$. Obviously $q_{\rm EA}$ vanishes for an equilibrium system, and differs from zero in a nonergodic system. For $1 > C > q_{\rm EA}$, we have $x(C) = 1$, meaning that the FDT holds. This means that for time differences that are small compared to the waiting time $t_{\rm w}$, the response of the system is similar to that of an equilibrium system, in spite of the fact that only a restricted part of phase space is explored. Nonequilibrium, or "aging" features, show up in a different limit, namely for $\tau > t_{\rm w}$. In this limit, the correlation function depends on both $t_{\rm w}$ and τ in a nontrivial way, typically $C(t_{\rm w} + \tau, t_{\rm w}) = F(h(t_{\rm w} + \tau)/h(\tau))$, where $h(x)$ is a monotonically increasing function. In this "aging" regime, $C < q_{\rm EA}$, and $x(C) < 1$. The system starts to sample a larger portion of phase space, but this sampling is an out-of-equilibrium process, and does not obey the equilibrium FDT.

An important property of $x(C)$, again discovered in the context of mean-field spin glasses, is that the general structure of this function is identical to that of the function $x_{\rm stat}(q)$ obtained by inverting the integral of the Parisi function $q_{\rm stat}(x)$. The latter reflects the probability distribution of overlaps between replicas of the same system, and does not involve any dynamical consideration [12]. At present, the similarity between these two functions has escaped physical understanding, although a formal justification has recently been proposed [13]. This similarity between the two functions is, nevertheless, believed to be a general feature. If this is the case, the implication is that the study of a dynamical quantity such as $x(C)$ provides indirect information on the structure of phase space. So far $x(C)$ was determined for the 3d Edwards-Anderson model [14], for ferromagnetic coarsening [15], for p-spin models in 3 dimensions [16], for the 3d Ising spin glass [17] and a string in a disordered medium [18], confirming in each case the general features of mean-field predictions. In this letter, we show that an accurate determination of $x(C)$ for a structural glass model is indeed possible, using standard simulation techniques.

The system we study is a 80:20 mixture of 1000 Lennard-Jones particles, with interaction parameters that prevent crystallization [19]. In the following, we shall use as length, energy and time units the standard Lennard-Jones units σ_{AA} (particle diameter), ϵ_{AA} (interaction energy), and $\tau = (m_A\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$, where m_A is the particle mass and the subscript A

refers to the majority species [19]. The system has been described in detail elsewhere, and its equilibrium (high temperature) properties have been fully characterized. At the reduced density $\rho = 1.2$, a "computer glass transition" is found in the vicinity of $T = 0.435$ and the slowing down of the dynamics seems to be described well by mode-coupling theory [19]. A first study of the aging behavior of the correlation functions at low temperatures has also been published recently [7, 20].

In order to obtain a fluctuation-dissipation ratio, we need to compute C and R for the same observable. Previous work [7] focused on the aging behavior of the incoherent scattering function for the wave vector $\mathbf{k}$:

$$C_k(t_\mathrm{w}+\tau, t_\mathrm{w}) = \frac{1}{N}\sum_j e^{i\mathbf{k}\cdot(\mathbf{r}_j(t_\mathrm{w}+\tau)-\mathbf{r}_j(t_\mathrm{w}))}. \tag{3}$$

In order to compute the associated response function, we use the following numerical approach. A fictive "charge" $\epsilon = \pm 1$ is assigned randomly to each particle. An additional term of the form $\sum_j \epsilon_j V(\mathbf{r}_j)$, where $V(\mathbf{r}) = V_0 \cos(\mathbf{k}\cdot\mathbf{r})$ is a small ($V_0 < k_\mathrm{B}T$) external potential, is then added to the Hamiltonian. It is then easy to show that, *if one averages over several realizations of the random charge distribution*, the time-correlation function of the observable $A_k = \sum_j \epsilon_j \exp[i\mathbf{k}\cdot r_j(t)]$ is the incoherent scattering function. The procedure to generate the response function associated to C_k is thus straightforward: For a given realisation of the random charge distribution, the system is equilibrated at a high temperature ($T = 5.0$), and quenched at $t = 0$ to the desired final temperature T_f. The evolution is followed with the field off until a waiting time t_w, then the field is switched on and the response $A_k(t_\mathrm{w}+\tau, t_\mathrm{w})$ is monitored. The same procedure is repeated for several (7 to 10) realisations of the charge distribution, in order to get the response function. The quantity we obtain by this procedure is then an integrated response function $M(t_\mathrm{w}+\tau, t_\mathrm{w})$, defined as

$$\langle A_k(t_\mathrm{w}+\tau, t_\mathrm{w})\rangle = V_0 \int_{t_\mathrm{w}}^{t_\mathrm{w}+\tau} R(t_\mathrm{w}+\tau, t)\mathrm{d}t \tag{4}$$

$$= V_0 M(t_\mathrm{w}+\tau, t_\mathrm{w}). \tag{5}$$

This procedure was carried out for three different values of the final temperature T_f, namely $T_\mathrm{f} = 0.4, T_\mathrm{f} = 0.3$ and $T_\mathrm{f} = 0.1$. The amplitude of the external potential was chosen in such a way that a linear response is obtained at each temperature. For $T_\mathrm{f} = 0.4$, $V_0 = 0.2$ while for $T_\mathrm{f} = 0.1$, $V_0 = 0.05$. The wave vector was $k = 7.25$, the location of the main peak in the structure factor. The runs had a length of $5 \cdot 10^6$ time steps, corresponding to 100000 time units.

Typical data for the integrated response and for the correlation function is shown in fig. 1, for $T_\mathrm{f} = 0.4$ and $k = 7.25$. The way by which the correlation function and the integrated response are related to each other can be understood well by means of a parametric plot of M *vs.* C, as shown in fig. 2 for different values of t_w and two different T_f. If the generalized fluctuation theorem holds, it is easily checked that M can be written as a function of C, with

$$M(C) = -\frac{1}{k_\mathrm{B}T}\int_C^1 x(c)\mathrm{d}c\,. \tag{6}$$

From fig. 2, it is clearly seen that the usual FDT with $x = 1$ is very well verified for short times, *i.e.* values of C close to 1, in that the curves are linear and have slope -1. For longer times a break in the curves is observed, *i.e.* the FDT is violated. Some transient effects are perceptible for the shorter waiting time, but they tend to disappear with increasing t_w. This violation is compatible with the ansatz (2), since the parametric curves obtained for different waiting times superimpose satisfactorily.

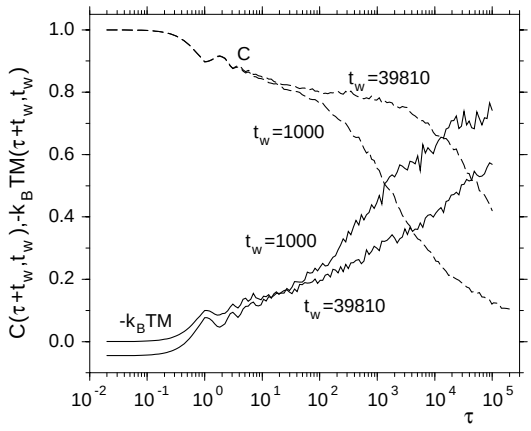

Fig. 1. – Correlation function $C(t_\mathrm{w}+\tau,t_\mathrm{w})$ (dashed lines) and integrated response function $M(t_\mathrm{w}+\tau,t_\mathrm{w})$ (solid lines) for $T_\mathrm{f}=0.4$, $k=7.25$, and two different waiting times.

For the regime in which the FDT is violated, the $M(C)$ curve can have different forms [5,6]: Domain growth models predict that $M(C)$ is a constant, whereas mean-field models predict a linear dependence, for the case of "one step" replica symmetry breaking (RSB), and a more general dependence for the case of continous replica symmetry breaking.

As can be seen from fig. 2, a good fit to the resulting M *vs.* C curve is obtained with a piecewise linear function, which corresponds to a piecewise constant $x(C)$:

$$x(C)=1 \text{ for } C>q_b, \quad x(C)=m<1 \text{ for } C<q_b, \tag{7}$$

where q_b is the value of C at which the mentioned break in the curves is observed. Such a dependence has, *e.g.*, been found for mean-field "p-spin" models [5]. Thus our results give

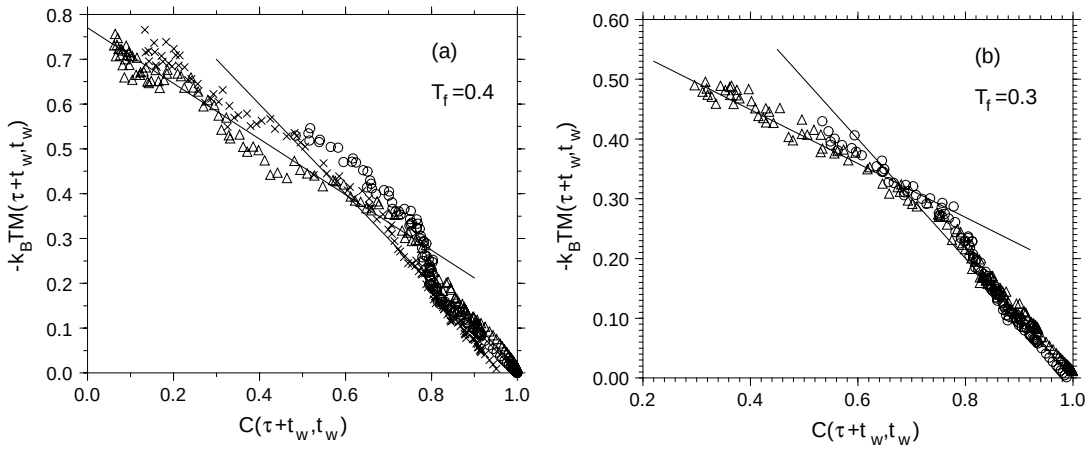

Fig. 2. – Parametric plot of the integrated response function $M(t_\mathrm{w}+\tau,t_\mathrm{w})$ and the correlation function $C(t_\mathrm{w}+\tau,t_\mathrm{w})$ for $k=7.25$. a) $T_\mathrm{f}=0.4$, triangles: $t_\mathrm{w}=100$, crosses: $t_\mathrm{w}=1000$, circles: $t_\mathrm{w}=39810$. The two straight lines have slopes -1.0 and 0.62. b) $T_\mathrm{f}=0.3$, triangles: $t_\mathrm{w}=1000$, circles: $t_\mathrm{w}=10000$. The straight lines have slopes -1.0 and -0.45.

support to the hypothesis first formulated by Kirkpatrick and coworkers [21] and revived by Parisi [10], that structural glasses belong to the same "universality class" as mean-field p-spin models.

Under the assumption that our results correspond to such a "one-step RSB" behaviour, we can read off from fig. 2 $m \simeq 0.62$ and $q_b \simeq 0.6$. The latter value is clearly smaller than the plateau value for the correlation function in fig. 1, $q_{\mathrm{EA}} \simeq 0.8$. This means that the FDT appears to hold even for times at which the system is no longer time translationally invariant, a feature which is not predicted by current theories of aging.

Finally, the dependence of x on the final temperature can be investigated. To explore this dependence we have also done simulations at $T_{\mathrm{f}} = 0.3$ and $T_{\mathrm{f}} = 0.1$. In all cases, we find that the M *vs.* C plot can be fitted well by two straight lines. Our results for m as a function of T are thus given by: $T_{\mathrm{f}} = 0.4$, $m = 0.62 \pm 0.05$; $T_{\mathrm{f}} = 0.3$, $m = 0.45 \pm 0.05$; $T_{\mathrm{f}} = 0.1$, $m = 0.2 \pm 0.1$ Within the accuracy of our data these values of m are compatible with a linear dependence on T_{f}, quite similar to that found by Parisi [9] for a soft-sphere system. Such a linear dependance ($m(T_{\mathrm{f}}) \sim T_{\mathrm{f}}$) corresponds to a constant "fluctuation-dissipation effective temperature" $T_{\mathrm{eff}} = T_{\mathrm{f}}/m$. The later concept, introduced in [22], could help rationalize the older "fictive temperature" idea.

We mention that, in his analysis of the fluctuation-dissipation relation, taking as an observable the mean-squared displacement, Parisi found that $m(T_{\mathrm{f}})$ can be approximated by $m(T_{\mathrm{f}}) = T_{\mathrm{f}}/T_{\mathrm{c}}$ for $T_{\mathrm{f}} < T_{\mathrm{c}}$, where T_{c} is the "mode coupling critical temperature" of the system under study. In our case, $T_{\mathrm{c}} \simeq 0.435$ [19], so that our data is in contradiction with such a simple dependence of m on T. Our results are much more similar to the ones found by Alvarez *et al.* for the p-spin model in that these authors found for a temperature a bit below T_{c} a value of m which is significantly smaller than 1. The reason for this difference might be related to the much smaller waiting times used in ref. [9, 23]. In any case, it is not clear why the mode coupling critical temperature should play a particular role in the present analysis. If the same type of simulations were carried out at a temperature slightly above T_{c}, we would expect that interrupted aging would be observed, so that at short t_{w} a violation of FDT occurs. As t_{w} increases, equilibrium will progressively be approached, and the M *vs.* C plot will approach a straight line with slope -1. Hence the main difference between $T > T_{\mathrm{c}}$ and $T < T_{\mathrm{c}}$ will be that for $T > T_{\mathrm{c}}$ the M *vs.* C plot depends on t_{w}, as has been shown for the Sherrington-Kirkpatrick model in three dimensions [14]. However, for T close to, but above, T_{c} this t_{w} dependence will be so weak that it can be neglected for all practical purposes. In terms of the "effective temperature" $T_{\mathrm{eff}} = T_{\mathrm{f}}/m$, our system falls out of equilibrium above T_{c}, so that we can expect T_{eff} to be larger than T_{c}—which is indeed the case.

In summary, we have shown that the fluctuation-dissipation ratio of a supercooled liquid out of equilibrium can be computed with good accuracy from MD simulations. Several nontrivial features predicted by the theory of mean-field spin glasses, beginning with the existence of a waiting time independent function $x(C)$, seem to be present also in the model structural glass we study. Our data is compatible with a stepwise constant $x(C)$, which would correspond to a phase space structure similar to that of spin systems undergoing one step replica symmetry breaking. This means that phase space is divided by high barriers into different valleys each of which has the same statistical properties. (The case of continuous replica symmetry breaking corresponds to a case that the valleys are organized in a hierarchical way.) In any case, finding a nonzero value of m seems to be a clear indication that a "domain growth" picture is not applicable to our model. A quantitative comparison between theoretical predictions and simulation results, similar to the work carried out for testing mode coupling theory, would be required in order to fully clarify the situation with respect to nonequilibrium dynamics. However, such calculations are currently not yet feasible.

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