Aging and the fluctuation dissipation ratio in a Lennard-Jones fluid

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Abstract. We discuss numerically the relaxation dynamics of a simple structural glass which has been quenched below its (computer) glass transition temperature. We demonstrate that time correlation functions show strong aging effects and compute the fluctuation dissipation ratio of this non-equilibrium system.

1. Introduction

Whenever a system whose relaxation time is large is driven out of equilibrium, it can be expected that its dynamics will show aging effects. This means that observables that in equilibrium are constant become time dependent, and time correlation functions that in equilibrium depend only on time differences will now depend on *two* times. Typical examples for such situations are ferromagnetic coarsening, and the relaxation dynamics of spin and structural glasses [1]. The investigation of such aging phenomena is by no means a new subject [3], but due to new theoretical approaches [1], and to the development of accurate experiments in the field of spin glasses [2], this field has recently become a very active area of research.

For the case of structural glasses, not much is known about the aging dynamics *on a microscopic level*, since the experiments needed to address these questions are unfortunately quite difficult. This is in contrast to computer simulations, since these readily allow one to study the system on a microscopic level and thus give access to all observables of interest. The price of this advantage is that only relatively small timescales and systems can be studied, but it has turned out that these disadvantages are not too serious. In such simulations one usually mimics the experimental set-up, in that the system is prepared in an equilibrium state and is at time zero driven out of equilibrium, e.g. by decreasing the temperature or by applying an external field. Subsequently the system is allowed to relax for a certain waiting time t_w and then one starts to measure its properties, such as the density and the magnetization or a time correlation function. This approach is also the one that we will use in the present work in an attempt of gain a better understanding of the dynamics of structural glasses at low temperatures.

2. The model and details of the simulation

For the investigation of aging effects it is useful to be able to change the waiting time over as many decades as possible and, for a given waiting time, to study the subsequent relaxation

dynamics over a long time. Therefore it is advisable to study aging phenomena for models that are simple enough that they can be simulated over a large time window and are still reasonably realistic, to catch the essential features of structural glasses. One such model is a binary Lennard-Jones mixture whose dynamical properties in its strongly supercooled state have been investigated in great detail [4]. In these studies it has been shown that the dynamics of this system can be quite described well by means of mode-coupling theory [5], with a critical mode-coupling temperature T_c around 0.435 (in reduced energy units). The computer glass transition takes place (depending of course on the cooling rate) in the vicinity of $T = 0.46$.

The particles in this 80:20 mixture interact via a Lennard-Jones potential of the form $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$ where α and β denote the types of particle (which we call 'A' and 'B'). In the following we will use σ_{AA} and ϵ_{AA} as the units of length and energy, and $(m\sigma_{AA}^2/48\epsilon_{AA})^{1/2}$ as the unit of time, where m is the mass of the particles, which is independent of the species. The parameters of the potential are $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$, and $\sigma_{BB} = 0.88$. The total number of particles was 1000, and in order to minimize finite-size effects we used a cubic box of size 9.4 and periodic boundary conditions. The equations of motion have been integrated using the velocity form of the Verlet algorithm with a step size of 0.02.

3. Aging of a 'zero-field-cooled' system

In order to have aging phenomena a non-equilibrium situation has to be generated; this was done as follows. Starting from an equilibrium configuration at a high temperature ($T_i = 5.0$) we quenched the system at time $t = 0$ to a final temperature T_f. This was done by coupling the system periodically (every 50 time steps) to a heat bath. The system was allowed to evolve at the temperature $T_f < T_c$ for the waiting time t_w and subsequently we started the measurement of the time correlation functions. In order to improve the statistics of the result, this procedure was repeated 6–10 times for different initial conditions.

As shown previously in reference [6], quantities that, *in equilibrium*, do not depend on time, such as the total energy of the system, are not very sensitive to the aging process. Much more pronounced non-equilibrium effects are observed for time-dependent quantities, such as the intermediate-scattering function [6, 7] or the mean squared displacement [8]. In the following we will therefore study the dependence on time and t_w of $C_k(t_w + \tau, t_w)$, the generalization of the self-intermediate-scattering function to non-equilibrium situations. This observable is defined by

$$C_k(t_w + \tau, t_w) = \frac{1}{N} \sum_j \exp\left[i\mathbf{k} \cdot (\mathbf{r}_j(t_w + \tau) - \mathbf{r}_j(t_w))\right] \tag{1}$$

where $\mathbf{k}$ is the wavevector and $\mathbf{r}_j(t)$ is the position of particle j at time t. In figure 1 we show the time dependence of $C_k(t_w + \tau, t_w)$ for different waiting times (see the figure caption). The value of k is 7.25, the location of the maximum in the structure factor, and $T_f = 0.4$, i.e. is only 10% below T_c. The main figure shows C_k in a log–linear representation. We see that at short times the curves do not depend on t_w, i.e. no aging effects are observed [9]. For longer times we find, however, very pronounced aging effects in that the curve with waiting time t_w starts to leave the common curve observed at short times and decays towards zero. In reference [6] it was shown that the time at which this pealing off from the envelope curve occurs is of the order of t_w.

In the inset we show the same data on a log–log plot. From this figure it is evident that at long times the relaxation of C_k is described well by a power law with an exponent that is independent of t_w and is around 0.4. Qualitatively similar results are found for other values of
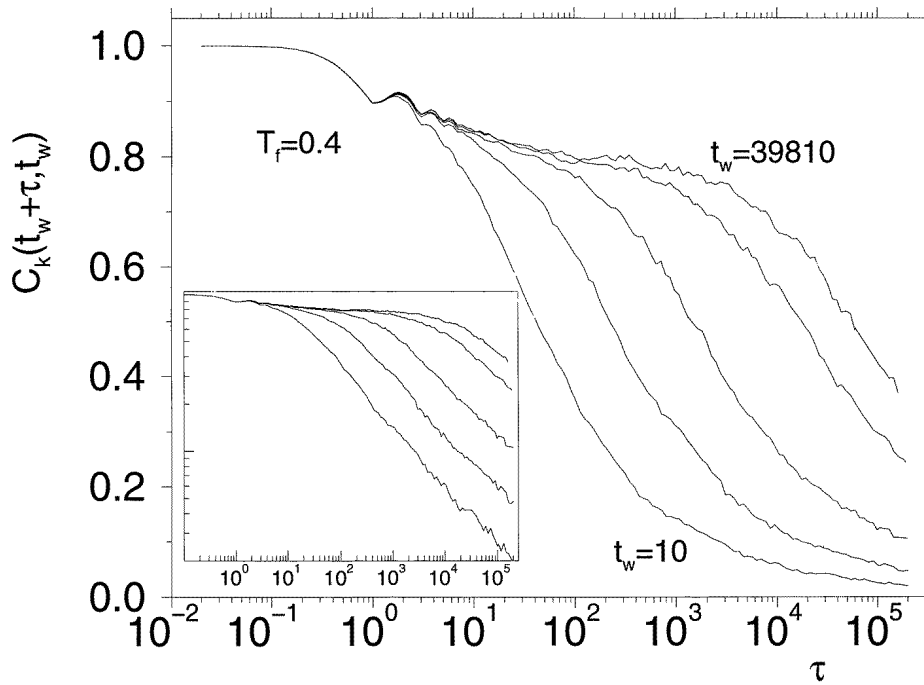
Figure 1. The time dependence of $C_k(t_w + \tau, t_w)$ for different waiting times ($t_w = 10$, 40, 1000, 10 000, 39 810). $T_f = 0.4$. Inset: the same correlation functions in a double-logarithmic representation.

k. For short times we have found that the approach to the plateau is described well by a power law, $C_k(t_w + \tau, t_w) \propto \tau^{-a}$, with an exponent around 0.45, a time dependence that is compatible with the prediction of mean-field theories of aging [1].

The results presented so far have been for the final temperature $T_f = 0.4$, i.e. a temperature that is only about 10% below the critical mode-coupling temperature of the system ($T_c = 0.435$). Similar behaviour was observed for $T_f = 0.3$. For $T_f = 0.1$, however, the relaxation behaviour is qualitatively different. The main difference occurs for long waiting times in the time regime in which the correlation functions decay below the plateau. Here the correlators for $T_f = 0.1$ seem to show an additional plateau, a feature which is not present in the correlators for $T_f = 0.4$. A closer inspection of the curves for the *individual* samples (for $T_f = 0.1$ we have nine different samples) revealed that the reason for this second plateau is given by a quite dramatic (0.1–0.2) and fast decay of the correlation function shortly before the plateau is reached. The time at which this decay occurs depends on the sample but is usually of the order of 10^3–10^4 time units. An analysis of the motion of the particles in the time range in which this sudden drop occurs shows that the decay is related to a very collective movement in which of the order of 10% of the particles move by about 0.1–0.5 units of length in one direction. This observation can be rationalized as follows. After the quench the configuration of the particles is very unfavourable and thus the system relaxes very quickly. If the system is given a bit more time, i.e. for larger waiting times, it has enough time to relax to a state which is no longer that unfavourable (for the given T_f) and hence does not relax that quickly. For intermediate and large t_w it will hence explore for short times τ only than part of the configuration space which corresponds to the motion of the particles within their cages.

However, the system will locally still have quite large stress fields and, given enough time, will yield to these stresses and hence show a rupture-like motion which is the reason for the fast drop in C_k. Since this type of motion is so abrupt, it is unlikely that a mean-field like theory will be able to give a correct description of it, except perhaps in a phenomenological way. (We note that this situation is reminiscent of that of the mode-coupling theory of supercooled liquids, since also in that case the so-called 'hopping processes' strongly affect at low temperatures the very continuous, flow-like motion of the particles [5].)

4. The fluctuation dissipation ratio

A very interesting result of the theories of aging is related to the way in which the usual fluctuation dissipation theorem (FDT), which holds for non-equilibrium systems, is violated. In equilibrium, the autocorrelation function $C_A(t)$ of an observable A is related to the response $R_A(t)$ of A to its conjugate field by the FDT, i.e. $R_A(t) = -(1/k_B T) \, \partial C(t)/\partial t$. For the non-equilibrium situation this relation is no longer valid, but it can be generalized to

$$R_A(t', t) = \frac{1}{k_B T} X_A(t', t) \frac{\partial C_A(t', t)}{\partial t} \tag{2}$$

where $t' \geqslant t$ and $X_A(t', t) \leqslant 1$ is defined by this equation. Hence $T/X_A(t', t)$ can be considered as the temperature for which the usual connection between the time correlation function and the response holds [10]. The concept of such a temperature has been used in the glass literature for a long time, in the form of the 'fictive temperature', but has remained so far an ill defined quantity. In contrast to this, the definition given by equation (2) is from a theoretical *and practical* point of view much clearer and more useful, and hence more appealing.

Instead of calculating the response $R_A(t', t)$ directly, where now A is the one-particle density distribution, we proceeded (basically) as follows. 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 ($V_0 < k_B T$) 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 $A_k = \sum_j \epsilon_j \exp(\mathrm{i}\mathbf{k} \cdot \mathbf{r}_j(t))$ is the incoherent scattering function. The procedure for generating the response function associated with C_k is thus straightforward. For a given realization 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 for a waiting time t_w; then the field is switched on and the response $A_k(t_w + \tau, t_w)$ is monitored. The same procedure is repeated for several (seven to ten) realizations of the charge distribution, in order to get the response function. The quantity that we obtain by this procedure is then an integrated response function $M(t_w + \tau, t_w)$, defined as

$$\langle A_k(t_w + \tau, t_w) \rangle = V_0 \int_{t_w}^{t_w+\tau} R(t_w + \tau, t) \, \mathrm{d}t = V_0 M(t_w + \tau, t_w). \tag{3}$$

This procedure was carried out for three different values of the final temperature T_f, namely $T_f = 0.4$, $T_f = 0.3$ and $T_f = 0.1$. The amplitude of the external potential was chosen in such a way that a linear response is obtained at each temperature. For $T_f = 0.4$, $V_0 = 0.2$, while for $T_f = 0.1$, $V_0 = 0.05$. The wavevector was $k = 7.25$, the location of the main peak in the structure factor. The runs had a length of 5×10^6 time steps, corresponding to $100\,000$ time units.
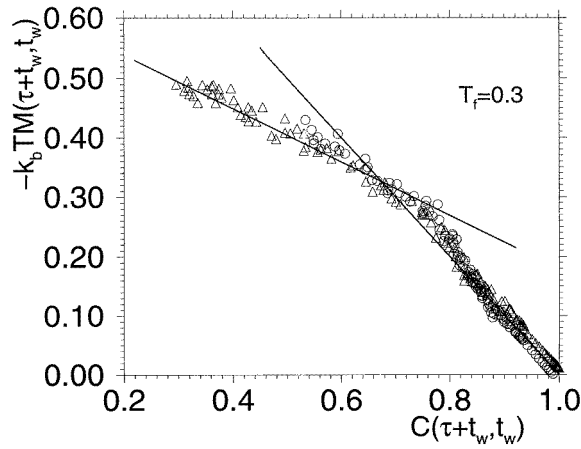
Figure 2. A parametric plot of $k_B T M$ versus C, where M is the integrated response. $T_f = 0.3$, $t_w = 1000$.

It has been argued that for t_w and τ large, $X_k(t_w + \tau, t_w)$ becomes a function of C_k only, i.e. $X_k(t_w + \tau, t_w) = x(C(t_w + \tau, t_w))$, where x is a function of one variable. Using this and equation (2), we obtain

$$M(C) = \frac{1}{k_B T} \int_C^1 x(c)\, \mathrm{d}C \qquad (4)$$

where we used the fact that $C_k(t_w + \tau, t_w) = 1$ for $\tau = 0$. This result suggests that a parametric plot of $k_B T M$ versus C is a useful way to look at the data and in figure 2 we show such a plot. For large values of C, which corresponds to short times, we see that $M(C)$ is essentially a straight line with slope close to -1.0. This means that $x(C)$ has a slope close to -1, i.e. that the FDT holds. With decreasing C, corresponding to increasing time τ, the curve is compatible with a straight line with slope $-m > -1$. Therefore we find that in that region $-x(C) = m < 1$, and hence that the FDT is violated. Note that a linear dependence of M on C in the non-FDT region has also been found for 'p-spin' models [1] and this gives support to the hypotheses [11] that structural glasses are in the same universality class as such models. Finally we mention that the T_f-dependence of the slope m is essentially linear. In particular we find for $T_f = 0.1$, $m = 0.2 \pm 0.1$, and for $T_f = 0.3$ and $T_f = 0.4$, $m = 0.45$ and $m = 0.62$, respectively.

The effective 'fluctuation dissipation temperature' appears therefore to be essentially independent of the actual temperature T_f, and significantly larger than the glass transition temperature. This is somewhat reminiscent of the usual 'fictive temperature' concept. Obviously, it would be quite interesting to test the dependence of this 'fluctuation dissipation temperature' on the cooling rate.

Basically, our data support a picture of phase space and of its exploration that is quite similar to what is found in 'p-spin' mean-field models. Below a certain temperature (the temperature T_c of mode-coupling theory), the system can be in many different and similar states, with large barriers between them. Within one energy minimum, the system is at equilibrium, and the usual FDT holds. The process of exploring phase space beyond one minimum is a non-equilibrium one, and is in some sense performed at a 'fictive temperature' higher than the actual temperature.

Acknowledgments

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