Aging Effects in a Lennard-Jones Glass

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Using molecular dynamics simulations we study the out of equilibrium dynamic correlations in a model glass-forming liquid. The system is quenched from a high temperature to a temperature below its glass transition temperature and the decay of the two-time intermediate scattering function $C(t_w, t + t_w)$ is monitored for several values of the waiting time $t_w$ after the quench. We find that $C(t_w, t + t_w)$ shows a strong dependence on the waiting time, i.e. aging, depends on the temperature before the quench and, similar to the case of spin glasses, can be scaled onto a master curve.

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Thanks to a remarkable combination of experimental, theoretical and numerical work, in the last few years considerable progress has been made in the understanding of the dynamical properties of disordered systems such as spin glasses [1]. In particular, the importance of the so called aging phenomenon, i.e. the out of equilibrium evolution of a system quenched into a glassy state, has been realized. This phenomenon, which is well known experimentally in structural (e.g. polymer) glasses, was shown to display some universal scaling features, common to spin and structural glasses. Subsequently, several theoretical interpretations of the phenomenon were put forward, involving either phenomenological “trap” [2] or “coarsening” [3] models, or the solution of dynamical equations for disordered systems in the mean-field limit [4]. Interestingly, the dynamical equations describing these models turn out
to have a structure which is extremely similar to the structure of the so called mode-coupling
equations, that were developed by Götze, Sjögren and coworkers in order to describe the
glass transition singularity in structural glass-formers [5]. Again, this similarity at the formal
level points towards a possible connection between the slow dynamics in structural and spin
glasses, a possibility that has recently attracted much interest [6,7]. In this work, we investi-
gate the nonequilibrium dynamics of a simple structural glass-former, seeking for evidence
of an “aging” behavior similar to what is observed in spin glasses. Although the method
we use (Molecular Dynamics (MD) simulations) is limited to relatively short time scales,
typically $10^{-8}$s, and high quenching rates, it has proven to be very useful in assessing the
applicability of mode coupling theory to structural glass-formers [8]. Hence we believe that
the universal features of nonequilibrium slow dynamics, if they exist, should already appear
at such short time scales.

The model glass-former we study in this work is a binary mixture of particles interacting
through Lennard-Jones potentials. This system has been studied extensively by one of us
[9], and we refer to these papers for a detailed description of the model and of its equilibrium
properties. For the present purpose, it will be sufficient to say that the equilibrium
dynamics of the model has been shown to be well described -on the time scale of MD simulations- by
“ideal” mode coupling theories (MCT) [5], with a critical temperature (in reduced Lennard-
Jones units) $T_c \simeq 0.435$ [9].

Our aim here is to study the nonequilibrium properties of this well characterized model.
Our strategy is the following: Starting from an equilibrium system at some initial tempera-
ture $T_i > T_c$, we instantaneously “quench” the system by rescaling particles velocities to a
final temperature $T_f$. The system is subsequently allowed to evolve at constant temperature
for $5 \cdot 10^6$ time steps, which corresponds to $10^5$ reduced Lennard-Jones time units (typically
$10^{-8}$s for a real system). This procedure is then repeated for several independent starting
configurations (typically 10) in order to improve the statistics of the results.

The evolution of the system towards equilibrium can in principle be monitored by using
“one-time” observables, such as the energy or the pressure. Unfortunately these observables
are rather insensitive to the very slow evolution of the system that takes place after the quench. After a fast “equilibration” period of several thousand LJ time units, they essentially level off, as can be see in the time dependence of the potential energy $e_{pot}$ (see inset of Fig. 1). A naive conclusion would be that the system is at equilibrium. This is, however, not correct, since a careful examination of the data shows that, for $T_i = 5.0$ and $0.8$, $e_{pot}$ shows a power-law dependence on time (Fig. 1), with an exponent around 0.144, and that such a functional form is also compatible with the data of $T_i = 0.466$ at long times. Since the exponent is small, the data is also compatible with a logarithmic dependence on time, but since it was recently shown that for a soft sphere system $e_{pot}(t)$ shows a power-law dependence [7], this functional form seems to be more appealing. Thus we find that this “one-time” quantity shows indeed only a small sensitivity on the nonequilibrium evolution of the system, which is in agreement with the theoretical prediction [4] and was also found, e.g., in Ref. [10].

The nonequilibrium dynamics is much better characterized by the study of two-time correlations functions, of the form $C_A(t_w, t+t_w) = \langle A^*(t_w)A(t_w+t) \rangle$, where $A$ is a microscopic observable, and $t_w$ is the “waiting time”, i.e. the time elapsed after the quench, which takes place at $t = 0$. The brackets refer here to an equilibrium average over the initial configurations, at temperature $T_i$. In this work, we focus on the case where $A = \exp(i\mathbf{q}\cdot\mathbf{r}_i(t))$, where $\mathbf{r}_i$ is the position of atom $i$ and $\mathbf{q}$ is a wave-vector. Hence the correlation function we compute is simply the nonequilibrium generalization of the usual incoherent scattering function:

$$C_q(t_w, t_w + t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \exp \left( i \mathbf{q} \cdot (\mathbf{r}_i(t_w + t) - \mathbf{r}_i(t_w)) \right) \right\rangle .$$

Figure 2 displays such correlations functions, for $T_i = 5.0$ and $T_f = 0.4$. The evolution of the curves as $t_w$ increases clearly shows that the system does not reach equilibrium within the time window explored in the simulation. A striking fact is that if one attempts to extract a “relaxation time” $t_r$ from $C_q(t_w, t_w + t)$, this relaxation time will be a rapidly increasing function of $t_w$. The larger the waiting time, the longer it takes the system to forget the initial configuration. This behavior is quite typical of “aging” phenomena [4]. Although
the time scale explored here is quite atypical in the study of such phenomena, the basic observation is similar to what can be seen experimentally on much longer time scales.

Correlation functions such as those displayed in Fig. 2 depend on a number of parameters that can be varied independently. \( q, t_w, \) and \( t \) are explicit arguments in Eq. (1), but the initial and final temperature are also implicitly present. \( T_i \) determines the ensemble average, and \( T_f \) the dynamics after the quench. In the following, we concentrate on the results obtained for a value of \( q \) that corresponds to the main peak in the structure factor of the fluid, \( q = 7.2 \) (in Lennard-Jones units) \[9\]. We also focus on quenches to a final temperature \( T_f = 0.4 \). At this temperature, the relaxation time of the system, estimated by extrapolating equilibrium data from higher temperatures using a Vogel-Fulcher law, will be of order \( \tau_e(T = 0.4) \sim 10^7 \) time units, much larger than our simulation times \[9\]. We have also performed similar calculations for other wave-vectors and other values of \( T_f \), but the results do not differ in any essential way from those presented here \[11\].

In order to rationalize the results obtained for various values of the remaining parameters \( (T_i, t \) and \( t_w) \), we use the popular and intuitive picture \[12\] that describes the whole system as a point evolving within a complex multidimensional (free) energy landscape. The system starts with a high average kinetic energy corresponding to the temperature \( T_i \). It is subsequently quenched instantaneously, so that it will be “trapped” (by entropic or energetic barriers) in a configuration typical of temperature \( T_i \). The following nonequilibrium evolution will bring the system closer to configurations characteristic of \( T_f \), which might or might not be reached on the time scale of the simulation.

Based on this type of picture, we can attempt to get some insight into the nonequilibrium dynamics for systems quenched to the same \( T_f \), starting from different values of \( T_i \). For clarity, let us consider the case were we have two initial temperatures, \( T_{i1} = 5.0 \) and \( T_{i2} = 0.8 \), and \( T_f = 0.4 \). If the evolution of the system is seen as a slow evolution of the system towards parts of the configuration space that correspond to lower free energies (deeper valleys), we can reasonably expect that the system on its way from \( T_{i1} \) to \( T_f \) will visit valleys typical for \( T_{i2} \). Hence, we expect that the relaxation curves corresponding to \( T_{i1} \) will, after some
waiting time $t_{(1,2)}$, essentially coincide with those obtained with a starting temperature $T_{i2}$. A reasonable assumption is that the time lag $t_{(1,2)}$ will be roughly of the order of magnitude of the relaxation time $\tau_e(T_{i2})$ for an equilibrated system at temperature $T_{i2}$. In terms of the two time correlations, this suggests a relation of the form $C_q^{(2)}(t_w, t + t_w) \simeq C_q^{(1)}(t_w + t_{(1,2)}, t + t_w + t_{(1,2)})$. (Here the superscript corresponds to the value of the starting temperature). This conjecture is tested in Fig. 3, and is seen to be reasonably well borne out by the numerical data in that the curve for $T_i = 0.8 (\tau_e \approx 100 \ [9])$ for $t_w = 10$ is very similar to the curve for $T_i=5.0, t_w = 160$. The natural consequence of this behavior is that for a given starting temperature $T_i$, we expect “aging” phenomena to take place only for waiting times that exceed the equilibrium relaxation time $\tau_e(T_i)$, whereas for $t_w < \tau_e(T_i)$ the relaxation behavior is almost independent of $t_w$. In other words, it takes the system a time of order $\tau_e(T_i)$ to realize that the quench has created a nonequilibrium situation. In fact, we have observed that for an initial temperature $T_i = 0.466$, for which $\tau_e \sim 10^5$, aging effects such as those depicted by Fig. 2 are very weak on the time scale of the simulation [11].

This situation could seem somewhat discouraging, in the sense that it implies that the observation of interesting effects will require either large values of the temperature jumps $T_i - T_f$, or simulations on time scales much larger than $10^5$ time units. The question that immediately arises if we consider large temperature jumps is to which extent the aging effects will display the universal behavior observed in real experiments, where the typical parameters of the quench are very different. Experimentally, the most striking observation, which is also predicted by several theoretical models, is that the curves corresponding to different values of the waiting time can be rescaled in the form

$$C_q(t_w, t + t_w) = C_q^{st}(t) + C_q^{ag} \left( \frac{h(t + t_w)}{h(t_w)} \right).$$

Here the first term corresponds to a short time dynamics that does not depend on $t_w$, while the second term, or “aging” part, depends only on the ratio $h(t_w + t)/h(t_w)$, were $h$ is an increasing function of $t$. In many cases, $h(t) \simeq t$ (the so called “simple aging” case), or $h(t) \simeq t^\alpha$, so that the aging part is simply a function of $t/t_w$. The existence of
the \( t_w \) independent, short time part is evident from the data shown in Fig. 2. The scaling assumption for long times is tested in Fig. 4 for an initial temperature \( T_i = 5.0 \). Except for the data that corresponds to small values of \( t_w (t_w < 10) \), which -not surprisingly- do not fit the scaling picture, the long time decay of the different curves can be superimposed, indicating the validity of the scaling ansatz. In Fig. 5, the relaxation time \( t_r \) of \( C_q(t_w, t + t_w) \) is displayed as a function of the waiting time. This relaxation time was defined, somewhat arbitrarily, as the time it takes to reach the value \( C_q = 0.45 \), which is the lowest value of \( C_q \) for \( t_w = 39810 \). For \( T_i = 5.0 \) the two times turn out to be roughly proportional, \( t_r \sim t_w^{\alpha} \), \( \alpha \approx 0.88 \) (see Fig. 3), which indicates that the system quenched from this \( T_i \) approximately follows the “simple aging” scaling over the time scales we are able to investigate.

A similar analysis can be carried out for systems quenched from lower temperatures, \( T_i = 0.8 \) and \( T_i = 0.466 \). As we mentioned earlier, aging effects in these systems start being appreciable only for \( t_w > \tau_e(T_i) \) and thus \( t_r \) is essentially constant for \( t_w < \tau_e(T_i) \) (see Fig. 3). For \( t_w > \tau_e(T_i) \), however, \( t_w \) and \( t_r \) are again roughly proportional to each other \( \square \), as can be inferred from the corresponding curves in Fig. 3.

A number of interesting conclusions and perspectives can be drawn from these MD results on the nonequilibrium dynamics of a glass forming liquid. The similarity with comparable studies on spin glasses, in particular the existence of a “universal” \( t/t_w \) scaling in the aging behavior, is striking. This can be seen as an indication that, in spite of very different forms of the Hamiltonians and of the microscopic dynamics, the geometry of phase space, which ultimately determines the long time behavior, is not dissimilar in spin and structural glasses. Because of the short time scales that are investigated in this work, we have carefully examined the role of initial conditions. Their influence can be rationalized by introducing an effective waiting time \( t_w + \tau_e(T_i) \), for a system quenched instantaneously from a temperature at which the equilibrium relaxation time is \( \tau_e(T_i) \). This notion might be useful in understanding annealing experiments. Finally, the obvious extension of this work will be to investigate the behavior of the one-particle response functions under the same conditions and on the same time scales as was done in this work. This would allow to investigate
possible violations of the fluctuation dissipation theorem during the aging process, and will be the subject of future work [11].

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FIGURES

FIG. 1. Potential energy of the system as a function of time for different values of $T_i$ (inset). Main figure: $e_{pot} + 7.17$ versus $t$, demonstrating that the time dependence of $e_{pot}$ is compatible with a power-law.

FIG. 2. $C_q(t_w, t + t_w)$ versus $t$ for $t_w = 0, 10, 100, 1000, 10000$ and $39810$ (from left to right); $T_i = 5.0, T_f = 0.4, q = 7.2$.

FIG. 3. $C_q(t_w, t + t_w)$ for $T_f = 0.4$ and two different values of $T_i$. Thin lines: $T_i = 0.8, \tau_e(0.8) \approx 100$ time units, $t_w = 0, 10, 100, 1000, 10000$ and $39810$ (from left to right). Dotted line: $T_i = 5.0, t_w = 160$.

FIG. 4. The data of Fig. 2, rescaled in such a way that all curves coincide for $C_q = 0.45$.

FIG. 5. Relaxation time $t_r$ of $C_q(t_w, t + t_w)$ versus $t_w$ for $T_f = 0.4$ and three values of the initial temperature $T_i$. The dashed line is a power-law with an exponent 0.882.
$e_{pot} + 7.17$

$T_i = 5.0$

$T_i = 0.8$

$T_i = 0.466$

$e_{pot}$

$t$

$10^1$

$10^2$

$10^3$

$10^4$

$10^5$
\[ C_q(t_w, t+t_w) \]

Graph showing the function \( C_q(t_w, t+t_w) \) over a range of values for \( t \) and \( t_w \) with \( t_w = 0 \) and \( t_w = 39810 \).
$C_q(t_w, t + t_w)$

$t_w = 39810$

$t_w = 0$
$C_q(t_w, t + t_w)$

$t_w = 0$

$t_w = 39810$
$T_i = 0.466$

$T_i = 5.0$

$T_i = 0.8$