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. [S0031-9007(97)03374-7]

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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 [1,2]. 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" [3] or "coarsening" [4] models, or the solution of dynamical equations for disordered systems in the mean-field limit [5]. Interestingly, the dynamical equations describing these models turn out to have a structure which is very 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 [6]. 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 [7,8]. In this work, we investigate the nonequilibrium dynamics of a simple structural glass former, seeking 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 [9]. 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 [10], 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 the "ideal" mode coupling theory (MCT) [6], with a critical temperature (in reduced Lennard-Jones units) $T_c \simeq 0.435$ [10].

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 temperature $T_i > T_c$, 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 5×10^6 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 ten) in order to improve the statistics of the results. The number of particles was 1000 and the temperature of the system was controlled by coupling it every 50 time steps to a stochastic heat bath.

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 seen in the time dependence of the potential energy e_{pot} (see inset of Fig. 1). (Note that in all figures the quantities are given in reduced Lennard-Jones units.) 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 are also compatible with a logarithmic dependence on

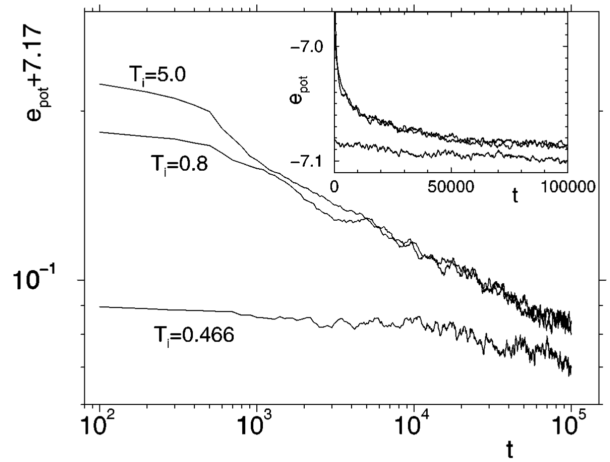

FIG. 1. Potential energy of the system as a function of time for different values of T_i (inset) and $T_f = 0.4$. Main figure: $e_{\mathrm{pot}} + 7.17$ versus t, demonstrating that the time dependence of e_{pot} is compatible with a power law.

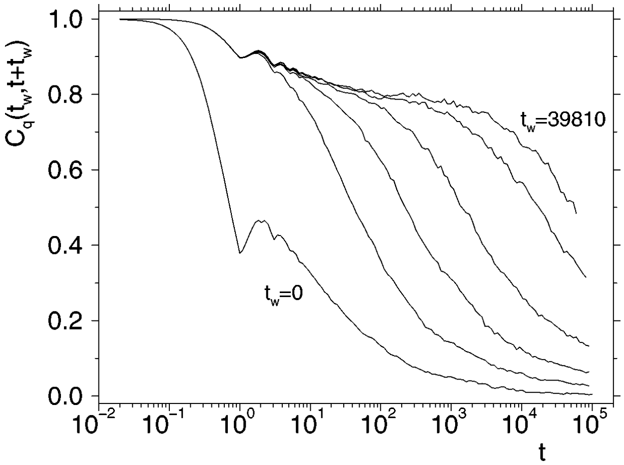

FIG. 2. $C_q(t_w, t + t_w)$ versus t for $t_w = 0$, 10, 100, 1000, 10 000, and 39 810 (from left to right); $T_i = 5.0$, $T_f = 0.4$, and $q = 7.2$.

time. However, since recently it was demonstrated that for a soft sphere system $e_{\mathrm{pot}}(t)$ shows a power-law dependence [8], 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 [5] and was also found, e.g., in Ref. [11].

We also note that the exponent found in Ref. [8] is significantly larger (0.7) than the one found here (0.144). Since a soft sphere system and a Lennard-Jones system have very similar potentials it is somewhat improbable that this difference in the exponent is just due to the different potential. A more likely cause is the fact that in Ref. [8] a Monte Carlo dynamics was used as opposed to the MD used here. Thus this might indicate that the microscopic dynamics has a significant influence on the aging process.

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

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

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. Qualitatively similar results were also found by Parisi [8]. 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 [5]. 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.

In this figure we also observe that at $t \approx 1$ the correlation functions show a quite strong (damped) oscillation. It is very unlikely that the cause for this feature is the finite size effect that has been observed in this [10] and, more pronounced, in other systems (see, e.g., Ref. [12]) since for this system this finite size effect should occur at around $t \approx 15$ [10] (and are not observed here because the effect is so small). It is also implausible that the oscillation is due to the dynamical feature called the boson peak, since no hint for such a peak was found in this system [10]. The most probable reason is that the oscillations are due to an effect called "quench echoes," which is a dynamical feature that occurs in systems that are quenched periodically (as is the case in the present simulation), and which was described nicely in a paper by Nagel *et al.* [13]. We will elaborate more on this point in Ref. [14].

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) [10]. 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 [10]. 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 [14].

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 [15] 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 where 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 in a "rugged energy landscape" picture, or larger domain size in a "domain growth" picture), 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 $T_i = 0.8$ ($\tau_e \approx 100$ [10]) 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 [14].

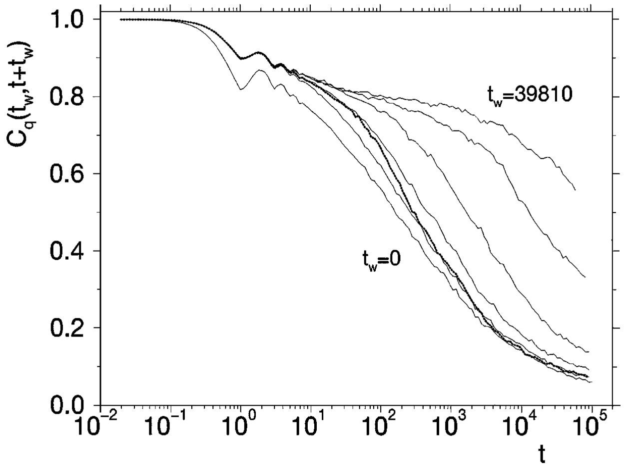

FIG. 3. $C_q(t_w, t + t_w)$ for $T_f = 0.4$ and two different values of T_i. Thin lines: $T_i = 0.8$, $\tau_e(0.8) \approx 100$ time units, $t_w = 0$, 10, 100, 1000, 10 000, and 39 810 (from left to right). Bold dotted line: $T_i = 5.0$, $t_w = 160$.

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 what 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 (see, e.g., Refs. [1,5] and references therein) and was also found in simulations of spin glasses [2], is that the curves corresponding to different values of the waiting time can be rescaled in the form

$$C_q(t_w, t + t_w) = C_q^{st}(t) + C_q^{ag}\left[\frac{h(t + t_w)}{h(t_w)}\right]. \qquad (2)$$

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 $h(t + t_w)/h(t_w)$, 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 correspond 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 $t_w = 39\,810$. 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. 5), 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.

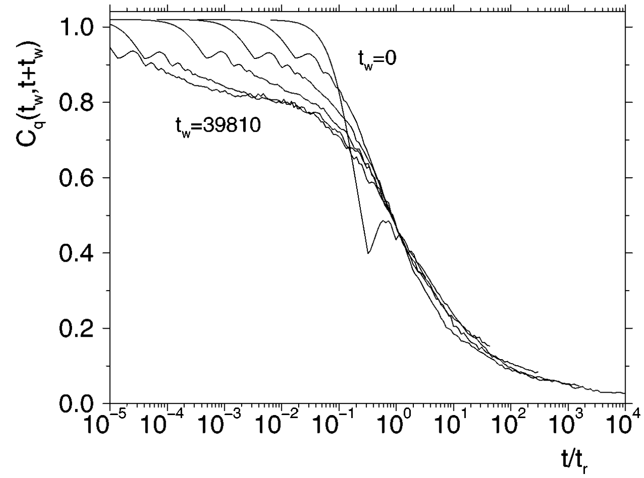

FIG. 4. The data of Fig. 2, rescaled in such a way that all curves coincide for $C_q = 0.45$.

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. 5). For $t_w > \tau_e(T_i)$, however, t_w and t_r are again roughly proportional to each other [14], as can be inferred from the corresponding curves in Fig. 5.

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 one to investigate possible violations of the fluctuation dissipation theorem during the aging process, and will be the subject of future work [14].

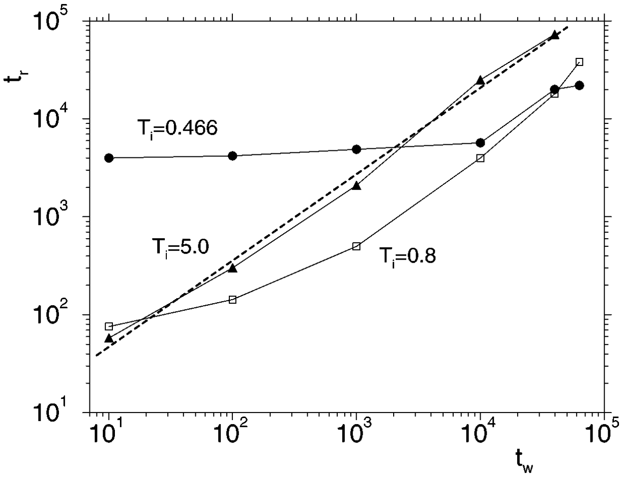

FIG. 5. Relaxation time t_r of $C_q(t_w, t + t_w)$ versus t_w for $T_f = 0.4$ and three values of the initial temperature T_i. The dashed line is a power law with an exponent 0.882.

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