Direct Observation of Stretched-Exponential Relaxation in Low-Temperature Lennard-Jones Systems Using the Cage Correlation Function

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We report on the direct observation of stretched exponential relaxation in low-temperature monatomic Lennard-Jones systems which were cooled slowly from the liquid phase to form crystals with a large number of defects. We use the cage correlation function [E. Rabani, J. D. Gezelter, and B. J. Berne, J. Chem. Phys. **107**, 6867 (1997)] which measures changes in atomic surroundings to observe the stretched exponential relaxations. We obtain a distribution of hopping rates assuming that the origin of the Kohlrausch-Williams-Watts law is from static disorder in the distribution of barrier heights. [S0031-9007(99)09049-3]

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We have recently developed a method to obtain estimates of the hopping rate between basins for Zwanzig's model of self-diffusion [1], in atomic [2] and molecular liquids [3]. We approached the problem by introducing the *cage correlation function* which measures the rate of change of atomic surroundings in a computer simulation [2]. The hopping rate was associated with the long-time exponential decay of this function. The cage correlation concept has proven itself to be a useful tool in understanding the mechanisms of self-diffusion, and as such was used to test the limits of the Zwanzig model [2,3], which is built on the foundation of Goldstein's activated jump model [4], and also on the rearranging regions model due to Adam and Gibbs [5].

What we report in this Letter is the use of the cage correlation function to study the hopping rate in Lennard-Jones systems that were cooled slowly from the liquid phase and formed crystals with a very large number of defects. These systems are not amorphous, since we can observe long-range translational order within our simulations. However, we are interested in the kinetics of the hopping process at temperatures where the roughness of the potential energy surface is no longer a small perturbation and, for one-component Lennard-Jones systems, this regime corresponds to the defective crystal. Unlike the decay observed in liquids, the cage correlation function shows a long-time *stretched exponential* decay in these "defective crystals." This relaxation behavior is similar to the behavior observed in fragile glass-forming materials [6].

An atom's immediate surroundings are best described by the list of other atoms in the liquid that make up the first solvation shell. When a diffusive barrier crossing involving the atom has occurred, the atom has left its immediate surroundings. Following the barrier crossing, it will have a slightly different group of atoms surrounding it. If one were able to paint identifying numbers on each of the atoms in a simulation, and kept track of the list of numbers that each atom could see at any time, then the barrier crossing event would be evident as a substantial change in this list of neighbors.

The cage correlation function uses a generalized neighbor list to keep track of each atom's neighbors. If the list of an atom's neighbors at time t is identical to the list of neighbors at time 0, the cage correlation function has a value of 1 for that atom. If any of the original neighbors are *missing* at time t, it is assumed that the atom participated in a hopping event, and the cage correlation function is 0. The atom's surroundings can also change due to vibrational motion but, at longer times, the cage will reconstitute itself to include the original members. Only those events which result in irreversible changes to the surroundings will cause the cage to decorrelate at long times. The mathematical formulation of the cage correlation function was given in previous publications [2,3], and is not repeated in this paper. A graphical representation of the cage correlation idea is shown in Fig. 1.

Averaging over all atoms in the simulation, and studying the decay of the cage correlation function, gives us a way to measure the hopping rates directly from relatively short simulations. We have used the cage correlation function to predict the hopping rates in liquids [2,3], and below we discuss the results for this correlation function when the liquid is cooled well below the melting temperature.

We performed molecular dynamics simulations on systems of particles interacting via the Lennard-Jones

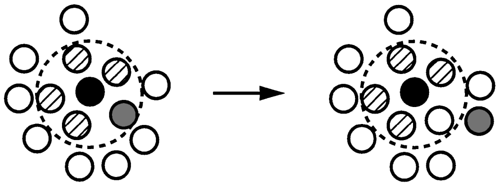

FIG. 1. A sketch of the idea behind the cage correlation function. The black atom's cage radius is denoted by the dotted line. The grey atom was inside the black atom's cage at time 0 (left side), but has exited the cage at time t (right side). The value of the cage correlation function is therefore 0 in the right figure even though four of the original five atoms stayed within the cage radius.

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potential

$$V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - V_{\mathrm{cut}}\,, \qquad (1)$$

with parameters chosen to approximate the interactions between argon atoms ($\epsilon = 0.2381$ kcal/mol, $\sigma = 3.405$ Å) [7]. V_{cut} is the standard Lennard-Jones potential evaluated at the cutoff radius ($r_{\mathrm{cut}} = 3\sigma$), outside of which the potential energy is set to 0. The simulations were carried out with 256 atoms at a reduced density of $\rho^* = 1.0$.

The simulations were started with the atoms in the face-centered-cubic (fcc) lattice, and with velocities sampled from a Maxwell-Boltzmann distribution with a temperature that was 4 times the melting temperature. Following a 100 ps period of equilibration at this temperature, we quenched the liquid system to a temperature just above the melting point ($T^* = 1.25$) with velocity rescaling performed every 100 fs. The trajectory was allowed to stabilize at the new temperature for 100 ps, and following this stabilization we quenched the system in steps of approximately $\Delta T^* = 0.08$ until the system reached $T^* = 0.33$. For each temperature we allowed an equilibration of 100 ps before we performed the next velocity quench. At the reduced temperature $T^* = 0.5$, 0.41, and 0.33, we started collecting data for 7.2 ns runs. This procedure was done separately for each member of an ensemble of 50 trajectories which had different initial configurations.

We calculated the pair distribution function, $g(r)$, for each trajectory (and at each temperature). We used $g(r)$ to classify the configurations, and find that there are two broadly defined types of $g(r)$: One set of configurations is "liquidlike" and has first and second solvation peaks which are characteristic of liquid simulations. These configurations are very unstable (i.e., they often crystallize if allowed to evolve for about 200 ps). The other family of configurations is "defective crystals" which have an additional peak between the first and second solvation peaks. This peak is the signature of the fcc structure, although the peak widths in the perfect crystal (at the same temperature) are narrower in comparison with these configurations.

In the lower panel of Fig. 2 we show $g(r)$ determined from a typical trajectory for a defective crystal. Those trajectories that did not fit this profile were culled from the group of 50 trajectories, leaving us with 15 trajectories for defective crystals. The defective crystal configurations studied here are far from having a perfect fcc structure. Their average potential energy (see the upper panel of Fig. 2) when extrapolated to $T^* = 0$ is higher than the fcc potential energy, and the peaks in $g(r)$ are much broader than those of a perfect fcc structure at the same temperature. By examining several configurations we have observed atomic level defects as well as large-scale fault planes and twists between planes in the local packing arrangement.

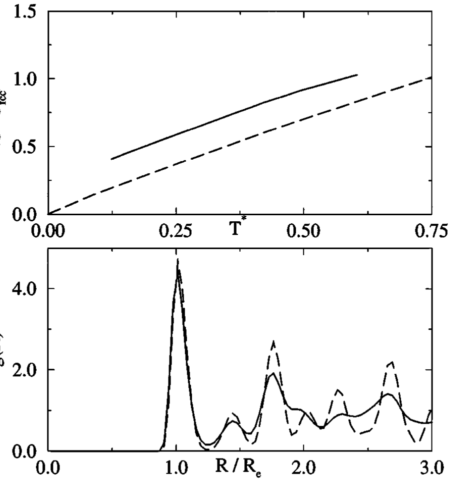

FIG. 2. The lower panel shows the pair distribution function of the defective (solid line) and perfect fcc (dashed line) crystals at $T^* = 0.41$. Distances are reported in units of $R_e = 2^{1/6}\sigma$. In the upper panel, we show the average potential energy per particle (in reduced Lennard-Jones units) for these two crystal systems as a function of temperature.

These 15 defective crystal trajectories are stable on the time scale of our simulations. There is no temperature drift during the runs which would signify a hop to a basin with a very different average potential energy. Also, since we observe self-diffusion on the time scale of the simulation (which is absent for the perfect fcc structure), we can assume that they have not relaxed to the perfect fcc crystal. Furthermore, if we perform the cage correlation function analysis on different segments of the trajectories, we obtain very similar relaxation behavior no matter where our observation begins. We conclude that the dynamics we observed is diffusion via defect migration in highly defective crystals, and is not an annealing process.

The primary result of this paper is the observation that the cage correlation functions in the defective crystals cannot be fit with a simple exponential function at long times, as was done for the liquids [2,3]. The cage correlation functions shown in Fig. 3 were fit with a *stretched* exponential function (Kohlrausch-Williams-Watts law),

$$C_{\mathrm{cage}}(t) = e^{-(\gamma t)^{\beta}}, \qquad (2)$$

with $\beta \approx 1/2$ for all three temperatures shown. Although the value of β has been reported as ≈ 0.8 in Lennard-Jones binary mixtures [8–10], a recent study of *single-component* Lennard-Jones clusters by Angelani *et al.* has reported $\beta \approx 1/2$ for temperatures similar to those that we are reporting here [11]. These other estimates of the value of β have all found that it varies with temperature. Although we have not seen any variation in our estimates of β, the temperature range we have studied is quite small, and β may not vary significantly over this range. Also, our estimates of β are obtained from data that extends to 7 ns. The cage correlation function has decayed

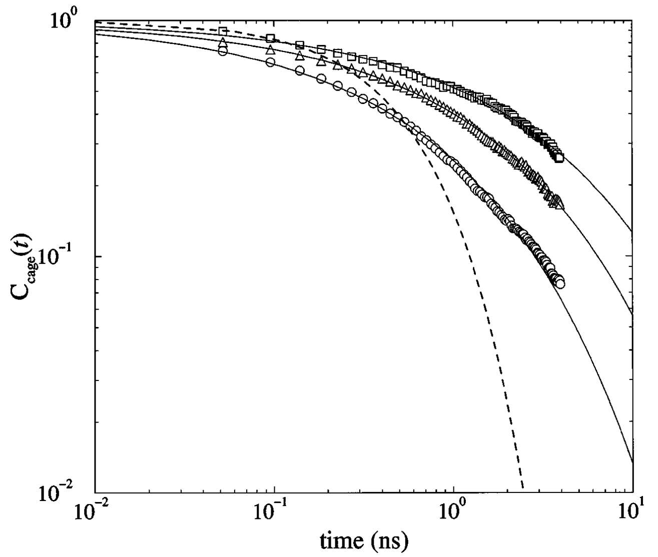

FIG. 3. A log-log plot of the decay of the cage correlation function for near-crystalline Lennard-Jones systems at three different temperatures. The open circles are for $T^* = 0.5$, the open triangles are for $T^* = 0.41$, and the open squares are for $T^* = 0.33$. The dashed curve is an exponential decay with a rate that equals the stretched rate γ at $T^* = 0.5$. Note that the $C_{\text{cage}}(t)$ functions shown here do not decay due to vibrations, as this short-time contribution to the decay has already been subtracted.

by only a single order of magnitude at these times, and estimating stretched exponentials from incomplete decay may result in large errors in β.

Since the cage correlation function is averaged over all atoms in the simulation, it cannot distinguish nonexponential decay that is due to a static distribution of local environments in the system from nonexponential decay that is due to dynamically fluctuating local environments. What the cage correlation function *does* provide is a direct observation of the dynamics of the hopping between basins. In the defective crystal, these hops are not characterized by uniform jumps that give rise to a simple exponential relaxation behavior. We note that the analysis of the van Hove correlation function provides a very similar picture for binary mixture Lennard-Jones glasses [8,10], but it does not directly measure the hopping between basins.

If we make a simplifying assumption that the stretched behavior has only static causes [12], the cage correlation functions that were fit to the Kohlrausch-Williams-Watts law [Eq. (2)] can be used to obtain the distribution of rates by inverting the integrated expression for the correlation function,

$$C_{\text{cage}}(t) = e^{-(\gamma t)^{\beta}} = \int_0^{\infty} dk\, \rho(k) e^{-kt}, \tag{3}$$

where $\rho(k)$ is the distribution of rates. For $\beta = 1/2$, this distribution of rates is known analytically [13],

$$\rho(k) = \frac{1}{2k^{3/2}} \sqrt{\frac{\gamma}{\pi}}\, e^{-\gamma/4k}. \tag{4}$$

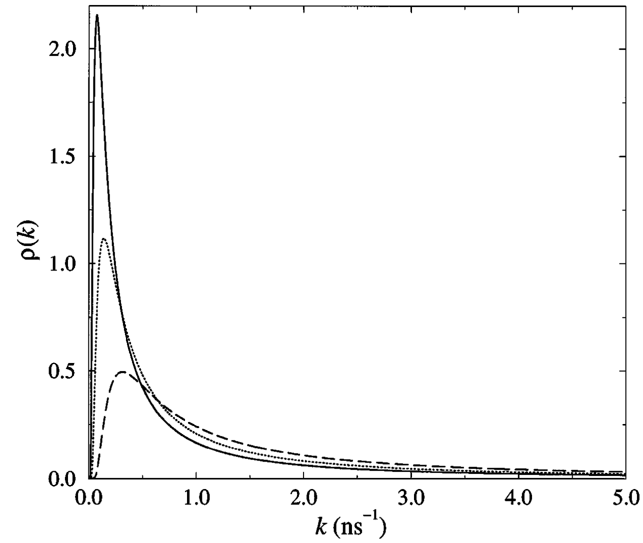

FIG. 4. The distribution of decay rates for three different temperatures assuming a Kohlrausch-Williams-Watts law for the decay of the cage correlation function, and a static mechanism for the nonexponential decay. The solid line is for a temperature of $T^* = 0.33$, the dotted line is for $T^* = 0.41$, and the dashed line is for $T^* = 0.5$.

(The distribution of rates can also be obtained numerically when $\beta \neq 1/2$ [14,15].) The distribution of rates, $\rho(k)$, is shown in Fig. 4 for three different temperatures. In Table I, we show the best-fitting values for γ, assuming the Kohlrausch law with $\beta = 1/2$.

The origin of this value for β in the single-component system is still unexplained. There are dynamic [16–18] and static [18,19] disorder models which predict stretched exponential relaxation with $\beta = 1/2$, but the connection of our work to these models is not yet clear.

The distribution of rates provides a statistical view of the hopping dynamics in the low-temperature Lennard-Jones systems. It is also a useful tool to obtain averaged properties such as the self-diffusion constant. To the extent that the Zwanzig model for self-diffusion is valid for this kind of system [1], we can make the assumption that the nonexponential decay has static origins, and obtain the self-diffusion constant by integrating Zwanzig's expression for the diffusion constant over the distribution

TABLE I. Best fits of the parameters in the Kohlrausch law [Eq. (2)] to the decay of the cage correlation function for three different temperatures of the defective crystals.

Reduced temperature	γ (ns^{-1}) (fit with $\beta = 0.5$)	Full nonlinear fit β	γ (ns^{-1})
0.5	1.9	0.49	1.9
0.41	0.83	0.50	0.83
0.33	0.43	0.49	0.43

TABLE II. Comparison of diffusion constants measured via molecular dynamics with those calculated using Eq. (5). $k_{\max}$ has been set to 0.39 ps^{-1} for all of these calculations, and the diffusion constants reported are in units of Å^2 ns^{-1}.

Reduced temperature	Diffusion constant Einstein relation	 Cage correlation
0.5	0.66	0.74
0.41	0.52	0.42
0.33	0.35	0.24

of hopping rates

$$D = \frac{k_B T}{M} \int_0^{k_{\max}} dk\, \rho(k) \int_0^{\infty} d\omega\, \rho_{\mathrm{vib}}(\omega)\, \frac{k}{k^2 + \omega^2}\,, \tag{5}$$

where $\rho_{\mathrm{vib}}(\omega)$ is the distribution of vibrational frequencies in the basins [3], In the above equation we have introduced a maximum value for the hopping rate, $k_{\max}$, to properly limit the rates to those which are associated with diffusive hopping. Rates higher than this threshold are an artifact of assuming static barrier heights and, beyond a maximum value, are unphysical. (And we strongly caution against interpreting the stretched exponential decay functions too literally at short times.) The agreement between the self-diffusion constant calculated directly from the Einstein relation and from Eq. (5) is reasonable using a single cutoff value of the rate at all temperatures, and the results are given in Table II.

In this Letter we have shown that it is advantageous to use the cage correlation function to study the complex dynamics of low-temperature systems. We have found that, when defective crystals are observed, the cage correlation function decays with a Kohlrausch-Williams-Watts law, with a stretched factor $\beta \approx 1/2$ for all three temperatures studied. To our knowledge, this is the first *direct* observation of the complex hopping dynamics for crystalline defect migration in a molecular dynamics simulation. We also obtained the distribution of hopping rates assuming that the origin of the stretched decay is static, and used this distribution to predict the self-diffusion constant by extending Zwanzig's model to include a distribution of hopping rates. We are currently extending the cage correlation function approach to a simple monatomic system that forms amorphous glasses [20].

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