Molecular-Dynamics Investigation of Deeply Quenched Liquids

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Molecular-dynamics simulations of homogeneous crystalline nucleation in systems of 1300 Lennard-Jones particles have been performed as a function of quench depth. The time lag between the time of formation of the critical nucleus and the time of release of latent heat is observed to be a nonmonotonic function of quench depth. The increase of the time lag for deep quenches is interpreted as evidence for critical slowing down and the influence of a "pseudospinodal."

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The method of molecular dynamics has yielded much insight into the properties of supercooled liquids and the nature of homogeneous crystalline nucleation.[1-7] Some of the properties observed in these simulations are difficult to understand by use of classical nucleation theory. For example, although nucleation has been found to occur via the appearance of a critical droplet, there is often a period of time during which the droplet has no effect on the bulk properties of the system.[7] Recently Klein and Leyvraz[8] have suggested that nucleation processes for deep quenches might differ from that predicted by the classical theory and that these anomalous effects might be understood by the assumption that the nucleation process is influenced by the presence of a "pseudospinodal." Their theoretical predictions are based on the use of a mean-field theory and become exact only in the limit of an infinite-range interaction. However, since spinodal effects have been observed in Ising systems with intermediate-range interactions,[9-11] it is possible that a "spinodal" singularity might effect nucleation even for systems with relatively short-range interactions, e.g., the Lennard-Jones potential. If such effects are present in crystalline nucleation, the characteristics of the nucleation process would be expected to depend strongly on the quench depth. For this reason we are motivated to investigate the dependence of nucleation on quench depth in a Lennard-Jones system.

Our molecular-dynamics approach is similar to that of Honeycutt and Andersen.[7] We use Beeman's algorithm[12] to solve Newton's equations of motion for a classical Lennard-Jones system of N particles each of mass m in a cube of side L. The potential is truncated at 2.3σ, and shifted to obtain a continuous potential. (Recall that σ and ϵ are the usual Lennard-Jones parameters.) Periodic boundary conditions and the minimum-image convention are employed. A time step of 0.01τ is used in the simulations, where $\tau=(m\sigma^2/\epsilon)^{1/2}$.

Our configurations are at a number density $\rho^*=(N/L^3)\sigma^3=0.95$ and an initial reduced temperature $T^*=k_BT/\epsilon=1.2$. We choose $N=1300$ for all runs. Since the results of the simulations might depend on the nature of the quench, we note that many quench procedures have been used in the literature. Our procedure is to "quench" the equilibrium-configuration liquid by rescaling the velocity of each particle after every time step, e.g., $\mathbf{v}_i=0.999\mathbf{v}_i$, where $\mathbf{v}_i$ is the velocity of the ith particle. The velocities are rescaled for an interval of $(8\text{-}14)\tau$ (800-1400 time steps), after which the system evolves at constant total energy.

The microscopic information provided by computer simulations allows us to estimate the time of formation of the critical droplet and its size. Since a theoretical criterion for the distinguishing of particles which are in "solidlike" or "liquidlike" configurations does not presently exist, various definitions of solidlike particles have been used. One of the simpler criteria is based on the idea that solidlike particles in a Lennard-Jones system form many triplets which are nearly collinear.[7,13] We adopt a computationally less demanding criterion and assume that particle i is solidlike if r_i^2, the square of its displacement, does not increase with time. Our explicit assumption is that particle i is solidlike if $r_i(2\tau)^2\le\delta$, where $r_i(2\tau)$ is the displacement of particle i during the interval 2τ. We determine δ from the mean square displacement after the system has crystallized and find that $\delta\sim0.02$ for $T^*=0.45$; for other quench depths we assume that $\delta\sim T^*$. Since the nearest-neighbor distance for both the fcc and bcc lattices is $\sim1.15\sigma$, we define two solidlike particles whose mutual separation is less than or equal to 1.15σ to be part of the same cluster.

We monitor the supercooled liquid by measuring the time dependence of T^*, the mean square displacement $\langle R^2 \rangle$, the structure factor $S(\mathbf{k})$, and the pair-correlation function $g(r)$. In order to monitor the nucleation process, we also observe several properties of the clusters. The quantity which provides the most useful information is $S_d(\mathbf{k})$, the structure factor of the largest cluster. $S_d(\mathbf{k})$ is defined as

$$S_d(\mathbf{k}) = \frac{1}{m_d} \left| \sum e^{i\mathbf{k}\cdot\mathbf{r}_j} \right|^2,$$

where the sum is over the m_d particles in the largest cluster. The behavior of $S(\mathbf{k})$ and $S_d(\mathbf{k})$ for certain values of $\mathbf{k}$ indicates whether the particles in the system and in the largest cluster, respectively, are arranged in a disordered or ordered manner.

In Fig. 1 we show results of a typical run during which the system was quenched for 10τ. Since it is possible that a droplet might form during the quench, we measure the time t from the beginning of the quench. The system is not assumed to be in a metastable state until the conclusion of the quench. We see that for $t > 10\tau$, $T^*(t)$ is relatively constant until $\tau \approx 130\tau$ at which time T^* rapidly increases because of the release of latent heat. (Recall that the system evolves at constant energy.) The rapid increase in the maximum value of $S(\mathbf{k})$, the first Bragg peak, also occurs at $t \approx 130\tau$. Hence we can identify a time t_g associated with the release of latent heat and the onset of catastrophic growth. Another criterion for t_g is the time at which $g(r)$ exhibits a well-defined peak at $r \approx 1.6\sigma$, the characteristic second-nearest-neighbor distance of the fcc lattice. These criteria yield consistent estimates of t_g.

We can estimate the time t_d associated with the formation of the critical droplet from the temporal behavior of the first Bragg peak of $S_d(\mathbf{k})$. From Fig. 1(b) we see that this peak increases rapidly shortly after the quench as well as at $t \approx t_g$; the number of particles in the droplet changes at similar times but exhibits larger fluctuations [see Fig. 1(c)]. From these results we conclude that $t_d \approx (15\text{-}20)\tau$ for this run. Note that our result for the time lag $t_{\text{lag}} = t_g - t_d \approx (115\text{-}120)\tau$ is independent of our choice of the zero of t.

For $t_d < t < t_g$, the largest cluster retains its solidlike identity while its size fluctuates because of merger and disassociation processes. We identify this cluster with the critical droplet and find that there are approximately 25 particles in the critical droplet shortly after its formation. (In contrast there is a maximum of ten particles in the largest cluster in the liquid.)

Now that we have confirmed that our definition of the critical droplet and our identification of t_d and t_{lag} yields results consistent with previous work, we use our approach to investigate the dependence of t_{lag} on quench depth. Since the droplet forms shortly after the quench, we are not able to determine the dependence, if any, of t_d on quench depth. For this reason we have $t_d \approx 20\tau$ for all the runs. In Table I we show our results for t_{lag} and T^* for five statistically independent initial configurations of the equilibrated liquid. The quench temperature T^* is estimated shortly after the quench. Note that there are relatively large fluctuations in t_{lag} for a given quench depth. Our most important result is that all the configurations show a similar qualitative dependence of t_{lag} on quench depth. That is, t_{lag} initially decreases for deeper quenches, but for sufficiently deep quenches, t_{lag} is found to be an *increasing* rather than a decreasing

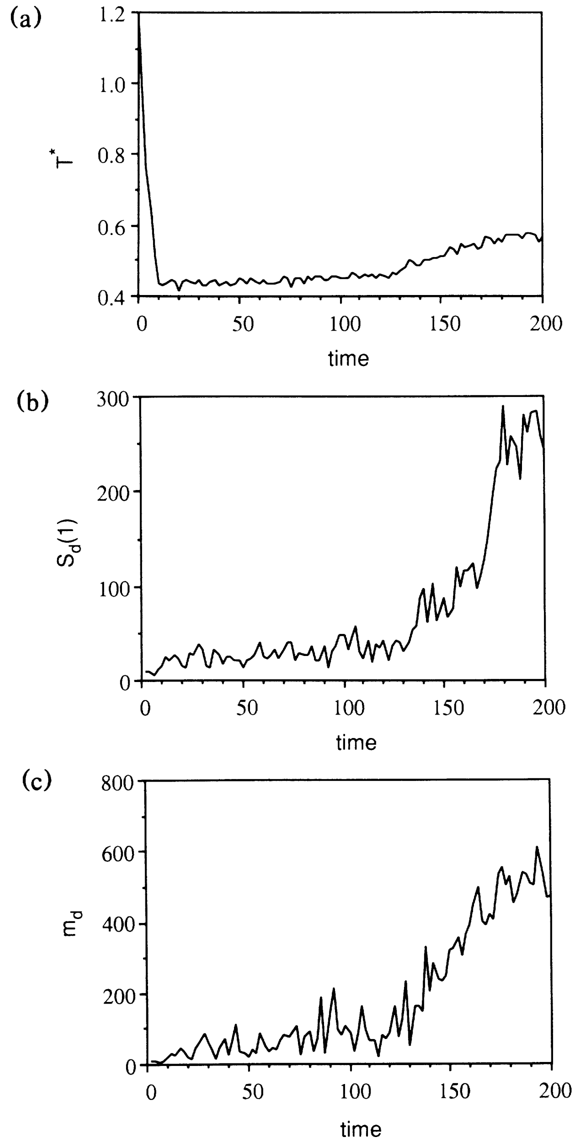

FIG. 1. Typical results for the time evolution of (a) the reduced temperature T^*, (b) the magnitude of the first Bragg peak of the largest cluster $S_d(1)$, and (c) the size of the largest cluster m_d. The quantities were measured at intervals of 2τ. The results correspond to a quench of 10τ from the first initial configuration of the equilibrated liquid.

TABLE I. Summary of results for the time lag t_{lag}, the difference between the time of formation of the critical droplet and the time of onset of catastrophic growth. The values of T^* are averaged over the five different quenches of the liquid. The quench is given by the number of quench steps, with a time step of 0.01τ, and the quench rate determined by the velocity rescaling $\mathbf{v}_i = 0.999\mathbf{v}_i$. Note that all the quenches show the same qualitative behavior—t_{lag} initially decreases as a function of quench depth, but for sufficiently deep quenches, t_{lag} is an increasing function of quench depth.

Quench steps	T^*			t_{lag}		
		Config. 1	Config. 2	Config. 3	Config. 4	Config. 5
825	0.516		300		130	
835	0.516		90			
850	0.506		60		30	
900	0.483	140	100	200	140	100
1000	0.438	120	140	130	140	60
1200	0.360	50	140	40	135	80
1225	0.355			80		
1250	0.344	70		190	180	180
1300	0.326	190		> 200	Glass	
1400	0.299		160	Glass		

function of quench depth. Also note that a small change in the depth of the quench can lead to a large change in the time lag.

The observed dependence of the time lag on quench depth for shallow quenches is consistent with classical nucleation theory. However, the occurrence of a minimum and subsequent increase in the time lag is not. A similar minimum and increase for deep quenches has been observed in simulations of liquid rubidium.[14]

The increase in the time lag for deep quenches can be interpreted as evidence for critical slowing down in the vicinity of the spinodal. This interpretation is consistent with the theoretical predictions of Klein and Leyvraz.[8]

More evidence for the nature of the system during the interval $t_d < t < t_{\text{lag}}$ can be found from the dependence of the self-diffusion constant D on T^*. We determine D from the asymptotic relation $\langle R(t)^2 \rangle \sim 6Dt$. Our results for $D^* = D\tau/\sigma^2$ are summarized in Fig. 2. Note that for deep quenches, a small change in T^* yields a small change in the self-diffusion constant but a large change in the time lag (see Table I). The best linear fit for D^* yields $D^* = -0.0043 + 0.0151T^*$ and consequently $D^* = 0$ at $T_s^* \approx 0.29$. Since one of the characteristics of a spinodal is that the self-diffusion constant be equal to zero, we adopt T_s^* as the effective spinodal temperature.

A possible explanation for the increase in t_{lag} for deeper quenches is that the system is in a glassy rather than a metastable state. However $g(r)$ does not exhibit the characteristic double second peak of a glass (cf. Rahman, Mandell, and McTague[15]). Another possible explanation for the increase in t_{lag} and the decrease in D^* is that this behavior is a signature of an approach to the glass transition. Although this latter interpretation implies that all dynamical processes would slow down significantly near T_s^*, our results for t_d show no significant dependence on T^*. We also determined a "completion time," defined as the time interval between the onset of catastrophic growth and the time at which the Bragg peaks cease to increase rapidly. We find that the completion times does not scale with t_{lag}, but remains essentially constant. On the basis of the observed strong T^* dependence of t_{lag} together with the weak T^* dependence of both t_d and the completion time, we conclude that our spinodal nucleation interpretation is more consistent than an interpretation based on the overall slowing of the dynamics in the vicinity of the glass transition. The applicability of the latter interpretation would indicate that the approach to the glass transition is more subtle than is now understood.

Another signature of the proximity of a spinodal is a

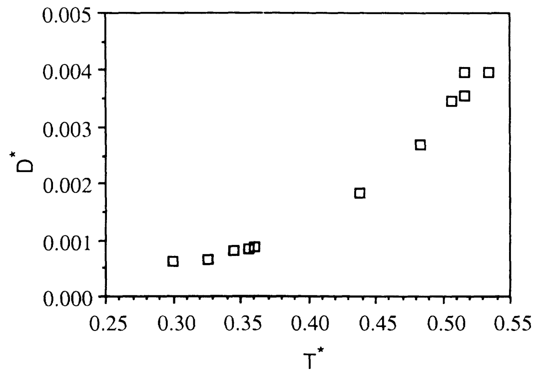

FIG. 2. Temperature dependence of the reduced self-diffusion constant D^*. The results for D^* and T^* are averaged over the five initial configurations. Note that the extrapolation of D^* to lower temperatures yields $D^* = 0$ at the reduced temperature $T_s^* \approx 0.29$.

divergence[16] in the maximum of the static structure factor $S(k)$ at a finite value of k. Although $S(k)$ increases significantly from its value in the equilibrium liquid and exhibits large fluctuations, our results for $S(k)$ do not yield any systematic dependence on T^*. Our interpretation of this behavior is that, in analogy to the behavior near true critical points, the effects of the spinodal are expected to extend over a larger range for dynamical quantities than for static quantities.

Our numerical results are subject to roundoff and truncation errors which might be relatively large because of the duration of our runs and the existence of the structural changes which accompany the crystallization process. In addition, we expect that finite-size effects are important.[7] However our most important result, the quench dependence of the time lag, is qualitative in nature and should be insensitive to these errors. This qualitative behavior and the results of Honeycutt and Andersen[7] are consistent with the ideas of Klein and Leyvraz[8] that the crystalline nucleation process is affected by the proximity of a spinodal. Note that this interpretation does not imply that the Lennard-Jones liquid-solid transition has a true spinodal, i.e., a true critical point. Our point is that there may be an effective spinodal, which affects the nucleation process even though it is physically unreachable for finite-range interactions. If this interpretation is correct, we expect that the effective spinodal will have a greater effect for longer-range interactions. However even if this interpretation is incomplete or incorrect, the quench-depth dependence of the time lag has important consequences for our understanding of crystalline nucleation. Consequently, further theoretical investigations and systematic simulations of crystalline nucleation in larger systems with longer-range interactions will be of much interest.

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