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Temperature-dependent mechanisms of homogeneous crystal nucleation in quenched Lennard-Jones liquids: Molecular dynamics simulations

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We have observed homogeneous crystal nucleation in Lennard-Jones liquid by molecular dynamics simulations. A clear nucleation time delay has been observed at $T=0.677T_m$ and $T=0.629T_m$ indicating the presence of a barrier, in contrast to recent reports [Trudu *et al.*, Phys. Rev. Lett. **97**, 105701 (2006)]. The structure of nuclei observed in the previous results and in the present work is evidence of transient-time dominated nucleation, not of a spinodal. Very rapid nucleation is observed at $T=0.484T_m$, indicating either a low (but finite) barrier or possibly a spinodal transformation. No spinodal effect has been observed in similar simulations of crystal nucleation in aluminum at any temperature [Aga *et al.*, Phys. Rev. Lett. **96**, 245701 (2006)], suggesting that different *qualitative* behaviors may be possible in what would seem to be similar potentials.

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Understanding the nature of crystallization from supercooled liquids is of fundamental importance, and also of practical importance in terms of predicting and designing material properties. This is especially for bulk metallic glasses, which require avoiding nucleation during quench before a glass transition is reached. In glasses, the stability of the disordered state is of particular interest. Though there have been extensive experimental and theoretical investigations, many issues in crystal nucleation remain unclear. Without a nucleation center, homogeneous nucleation is the primary process. The usual description of classical nucleation theory requires spontaneous fluctuations in the metastable liquid to form a nucleus that overcomes the free-energy barrier and form a stable solid phase.

Using mean-field theory, Klein *et al.*[1] suggested that at deep undercoolings, the nucleation mechanism is controlled by the *instability* of liquids with spinodal-like behaviors in certain limits. In later papers,[2–4] they observed evidence of spinodal (barrierless) nucleation in deep quenched Lennard-Jones liquid. Using an umbrella sampling method, the homogeneous nucleation barrier ΔG^* was found to decrease with temperature and predicted to vanish near $T/T_m=0.46$. Using the metadynamics method, Trudu *et al.*[5] obtained the free-energy barriers in the range of temperatures between 0.7 and $0.8T_m$, and extrapolated that ΔG^* vanishes at a significantly higher (normalized) temperature of $T/T_m=0.64$. However, Bartell and Wu[6] argued that the presence of a spinodal mechanism so close to the melting temperature was unlikely, and showed that in a simulated selenium hexafluoride system, a spinodal was not encountered at supercoolings even considerably deeper than $T/T_m=0.6$. They pointed out that rather than implying the Lennard-Jones had a spinodal, in Klein's paper the nucleation process of Lennard-Jones was affected by a "pseudospinodal" (i.e., a very small barrier on the order of k_BT that is rapidly crossed). Whether a spinodal in freezing one-component systems can be reached is still an open question that requires more careful and convincing studies. Moreover, the generality of the results are also unclear: if there is a spinodal in the Lennard-Jones system, does this imply one in other single-component systems?

The aim of this paper is to study homogeneous nucleation in supercooled Lennard-Jones liquids using molecular dynamics (MD) simulations. We find that nucleation in moderate and deep undercoolings clearly exhibit different behaviors. In moderate undercoolings, a clear long-time lag between quench and nucleation suggests that there is no spinodal at the reduced temperatures close to Trudu's.[5] In deep undercoolings, the diffuse solid structure and rapid nucleation imply a very low free-energy barrier consistent with spinodal effect predicted by Klein *et al.*[1]

The system studied here consists of 32 000 particles interacting via the modified Lennard-Jones potential by Broughton and Gilmer,[7] which is truncated at 2.5σ and shifted to obtain a continuous potential. This is chosen to match the potential where interfacial free energies have been calculated.[8,9] The melting temperature is $0.62\varepsilon/k_B$ at a pressure of $P=0.0\varepsilon/\sigma^3$. Periodic boundary conditions are employed during the simulation. We cool the liquid from slightly above melting temperature T_m by rescaling the atom velocities. The system evolves at the condition of constant temperature and volume while the pressure is close to zero. A time step of 0.001τ is used in all of the simulations, where $\tau=(m\sigma^2/\varepsilon)^{1/2}$. For each temperature, the system runs for 50 0000–1 000 000 time steps. The configurations are recorded every 500 time steps for tracing the crystallization process.

To help identify the nucleation and growth progress, we monitor the number of crystalline atoms and the number and sizes of crystal clusters. There are numerous methods to distinguish "solidlike" and "liquidlike" particles.[10–14] Honeycutt and Anderson (HA) (Ref. 15) developed a pair analysis technique based on the geometry of the neighbors to study the local structure. This method has proven to be successful in amorphous systems and is used in the present work. Only close-packed atoms are identified as solid in these simulations. A cluster is defined as two or more solid atoms that are nearest neighbors. The atoms with face-centered-cubic (FCC) and hexagonal-close-packed (HCP) local structures

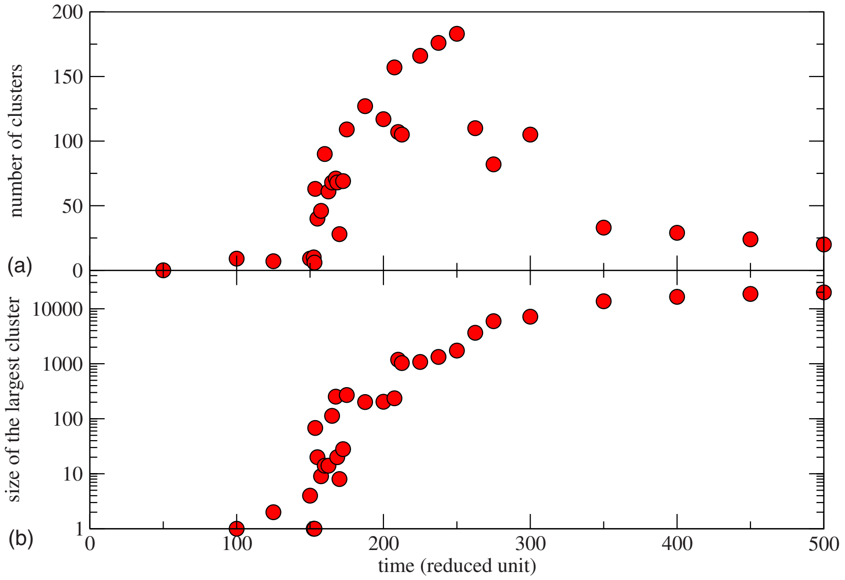

FIG. 1. (Color online) (a) Representative trend of clusters vs time at $T=0.677T_m$. Every size of clusters is included. A clear time lag before the rapid growth of clusters is observed in the plot. The onset time is around 153.5τ. (b) The size of the largest cluster vs time. Note that the y axis is on a logarithmic scale.

are marked by different colors in subsequent figures. We have observed a mixture of FCC and HCP atoms, indicating nearly random close-packed solid regions, consistent with a low stacking fault energy.

In Trudu *et al.*,[5] the linear extrapolation of metadynamics data predicted that the spinodal occurs at $T/T_m=0.64$. We perform our simulation at $T/T_m=0.677$, close to their value, and examine the formation of clusters which are identified by the HA pair analysis method. Three independent simulations are operated at this temperature. The number of clusters is recorded during the process. Figure 1(a) presents the representative trend of clusters vs time. In this plot, there are no solid atoms found during the first 100τ and no more than ten clusters before 153.5τ. A sudden jump from 6 to 63 clusters is observed at $t=153.5\tau$. The number of clusters roughly keeps increasing in the next 100τ and drops off after $t=250\tau$ due to the coarsening and coalescence of different grains. At the end of the simulation ($t=500\tau$), about 2/3 of the system is crystallized in one main cluster. These results are striking: during the first 150τ of simulation, there are essentially no solid atoms; in the next 150τ, most of the 32 000 atoms become crystalline. *This long-time delay followed by rapid growth is completely counter to spinodal behavior.*

To further demonstrate that the behavior is inconsistent with a barrierless transformation, we show the time dependence of the largest cluster size in Fig. 1(b). The size of the largest cluster fluctuates around 100–200 atoms during the time interval of 165 to 207.5τ before rising monotonically. The growth and shrinking process during the time frame suggests the competition between the interfacial energy and the driving force, which is the typical nucleation mode in classical nucleation theory. Using Monte Carlo simulations, Wang *et al.*[2] found that the nucleation droplet contained more than 250 atoms at the same reduced undercooling T/T_m (though at a higher liquid density, changing both the melting temperature and the driving forces for nucleation). Due to the limitation of our statistical data, we are not able to accurately estimate the critical nucleus from the simulations, but the long-time cluster size fluctuations near 100–200 atoms suggest that the critical size is larger than (or near to) 200 atoms.

By comparing the MD simulation configurations at different temperatures, Trudu *et al.*[5] argued that the solid regions occurring during the nucleation and growth process had a branched fractal character at $T/T_m=0.65$ (Fig. 4 of Ref. 5) which is characteristic of spinodal behavior. Figure 2 shows our series of snapshots at $T/T_m=0.677$ revealing the nucle-

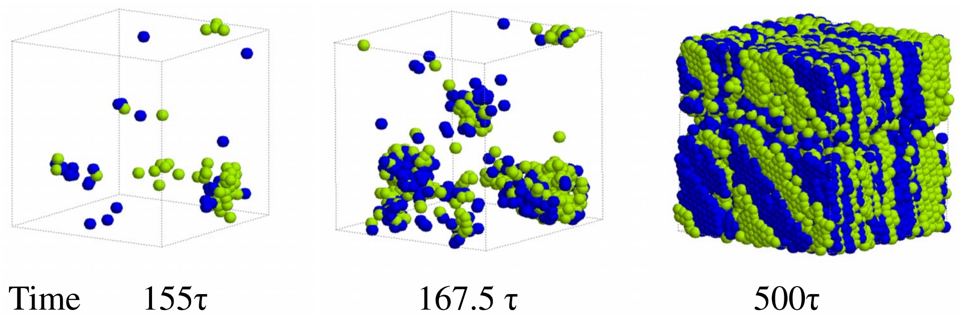

FIG. 2. (Color online) Snapshots at $T/T_m=0.677$. Only close-packed atoms are shown in the pictures. The HA method identifies FCC atoms (green or light gray) and HCP atoms (blue or dark gray). We show the arguable diffuse and fractural nuclei at 155τ which become compact and spherical at later stages.

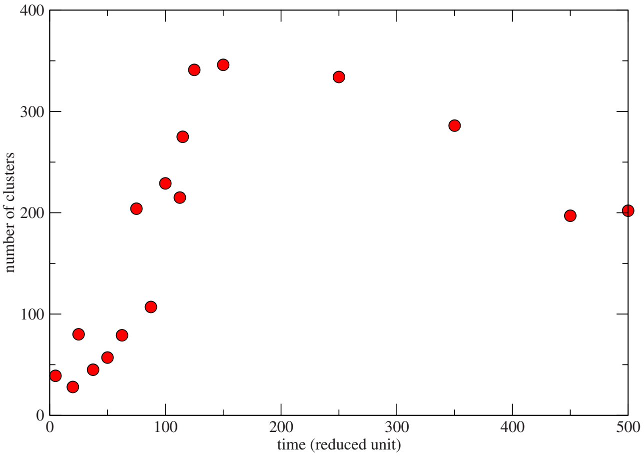

FIG. 3. (Color online) Representative trend of clusters vs time at $T=0.484T_m$. The clusters appear essentially instantaneously after quench, which is different from the observations at higher temperatures.

ation process. At 155τ, there are nuclei with broad surfaces which look similar to that of Ref. 5. These nuclei evolve into multiple compact clusters at 167.5τ and big crystallites at 500τ that finally take up the whole system with many stacking faults. While these are arguably diffuse and fractal-like, we do not believe that this provides evidence of a spinodal. Instead, we interpret this as the rapid formation of crystal nuclei after a transient time, consistent with time-dependent nucleation theory. The time delay before 153.5τ is consistent with a transient time, a period between the quench and nucleation during which the solidlike cluster concentrations increase to their steady-state values at the current temperature. The absence of a spherical nucleus is likely due to the fact that the interface is rough.[9] Experimentally, time-dependent nucleation is known to be important in describing nucleation from glasses.[16] We have previously shown that this delay time in nucleation can be predicted and compared quantitatively with MD simulations.[17] Similar behaviors are also observed at $T/T_m=0.629$, lower than Trudu *et al.*'s predicted spinodal. Thus, the real-space images shown in Fig. 2 or in Fig. 4 of Ref. 5 are not evidence of a spinodal or a pseudospinodal but only reveal the early rapid stage of classical nucleation after the transient time.

To examine the possible existence of a spinodal at lower temperatures, we present simulations at $T/T_m=0.484$. In these runs, the clusters appear nearly immediately after quench (Fig. 3), which is quite different from the observations at $T/T_m=0.677$. The potential energy of this system decreases immediately from the beginning of the simulations due to the phase transition. A series of snapshots at $T=0.484T_m$ is shown in Fig. 4. The solid atoms are distributed evenly through the system without well-defined cores or clearly differentiated surfaces. The rapid appearance of solid atoms and immediate growth throughout the system suggests that the free-energy barrier is rather low or absent. At the end of the simulation, many fine grains have been formed. Wang *et al.*[2] had similar qualitative observations at $T/T_m=0.46$ where the spinodal was predicted by umbrella sampling method, but they found the barrier did not actually vanish by further Monte Carlo simulations. Since rapid nucleation should occur once the amplitude of thermal fluctuations is comparable to the height of barrier, our observation does not necessarily correspond to a spinodal. However, it is clear that classical nucleation theory, which assumes a compact approximately spherically symmetric critical nucleus with a well-defined solid core is not applicable to deep quenches. Furthermore, the transient time predicted by time-dependent nucleation theory for $T/T_m=0.484$ is nearly as long as for $T/T_m=0.677$ but no clear time delay occurs during the simulation. The different behaviors suggest different mechanisms at lower temperature. All of the independent simulations at the same temperature support this statement. However, our simulations cannot distinguish between a true spinodal with no barrier to nucleation, and a small barrier that is crossed very quickly (a pseudospinodal). Note that within classical nucleation theory, the energy barrier and nucleus size become arbitrarily small at small undercoolings due to the large driving force for nucleation, though the nucleation *rate* does not vanish (due to the rapidly decreasing diffusion rate with decreasing temperature).

We note that the comparison with the work of Wang[2] cannot be quantitatively compared either with the present simulations or with those of Trudu,[5] as Wang's work is performed at significantly higher pressures and at constant density (resulting in a melting temperature nearly double that of ours). However, the critical free energy for nucleation shown in Fig. 1 of Ref. 2 shows that linearly extrapolating the high-temperature values to zero will significantly overestimate the spinodal temperature, suggesting that this is the cause of the inaccurate prediction of Ref. 5. Certainly, it would be useful to perform a careful comparison of calculations made with

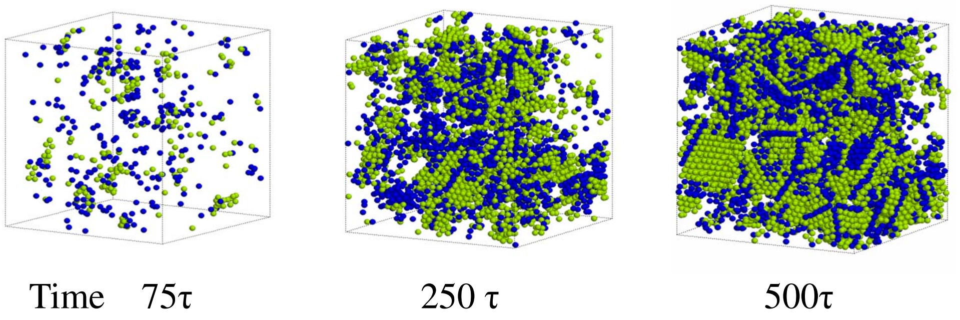

FIG. 4. (Color online) Snapshots at $T/T_m=0.484$. Only close-packed atoms are shown in the pictures. The HA method identifies FCC atoms (green or light gray) and HCP atoms (blue or dark gray). The nuclei have no well-defined cores or clearly differentiated surfaces.

the metadynamics approach of Ref. 5 with the umbrella sampling approach of Ref. 2 under more similar conditions. In terms of melting temperature and pressure, our simulation conditions are similar to those of Trudu *et al.*[5]

In our previous work, careful investigations on homogenous nucleation in undercooling liquids were performed for a model of aluminum.[17] At all temperatures where crystal formation was observed, the potential energy of the system displayed a clear drop after the quench due to the release of latent heat. This drop only occurred after a significant delay, indicating that the liquid was not "unstable" as expected for a spinodal, but instead it was metastable. The time lag before the drop was accurately predicted by time-dependent nucleation theory. At low temperatures, the time lag *increased* with decreasing temperature, consistent with calculations using the classical theory. These results indicated there was no spinodal in the model Al system. Considering that aluminum is similar to Lennard-Jones in many respects, why they behave differently at deep undercoolings is still unknown. This may be due to the presence of a spinodal in the Lennard-Jones system that is absent in Al, indicating that the Lennard-Jones system is not "universal," or may simply be a *quantitative* difference between the two systems, with a much lower barrier for the Lennard-Jones system. Similarly, Bartell and Wu[6] argue that Trudu's system is not a spinodal. However, their analysis is on a molecular system, which may be different due to the anisotropy of interactions between the molecules and the possibility of orientational order.

To summarize, we have shown that in the Lennard-Jones system, there is no spinodal at $T/T_m=0.677$ and $T/T_m=0.629$ even though individual snapshot pictures could be interpreted as having a spinodal-like structure. This is in direct contrast to the work of Trudu *et al.*[5] A significant time lag before nucleation at this temperature is interpreted as the transient time by time-dependent nucleation theory. At $T/T_m=0.484$, the observation of immediate crystallization after quench suggests a different nucleation mechanism at deep undercooling. The diffuse clusters in the early stage of the nucleation and the final crystalline microstructure are consistent with the prediction of spinodal theory. Comparing with aluminum system, we raise the question on whether the Lennard-Jones potential is a universal model for FCC systems.

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