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Short-range ordering in the supercooled states of a dimer system

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Detailed analyses have been carried out on the molecular dynamics simulations on the short-range ordering of the quenched states below melting temperature for a system of nearly spherical rigid dimer molecules under constant high pressure. We present evidence of preserving local ordering that prevents the system from having long-range translational ordering. The effect provides the cause for the formation of the amorphous solid, which is more stable than the corresponding supercooled states at the same temperature.
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The local structural properties in the supercooled liquid and amorphous solid, obtained via fast quenching below the melting point, have been shown to provide important information for understanding the phenomena related to these nonequilibrium states [1,2]. It has been suspected that the conflict between the local close-packing arrangement and the global space-filling placement plays a role in the formation of these disordered states. A geometric consideration of sphere packing helps to illustrate the effect. It has been pointed out by Frank and Kasper [3] that twelve spheres, arranged at the vertices of a regular icosahedron, give the most efficiently closely packed structure around a common center sphere, with each of the outer spheres being surrounded by five other spheres. Such a locally favored structure, however, could not extend to fill up all of space [2]. Indeed, a hierarchy based on the building blocks of spherical geometry is unstable against the long-wavelength orientational fluctuations in flat space [4]. The supercooled state is considered as a state of balance between the local and global preferences and is characterized by a sea of molecules, most of which are connected by fivefold coordinations to their neighbors, mingled with some sixfold or fourfold disclinations. In the equilibrium state, such local structures yield to form a globally ordered crystal where sixfold and fourfold symmetry dominate. The effect of ''geometric frustration'' has recently been suspected to be responsible for the formation of new amorphous states [5,6], which is more stable than glassy states at the same temperatures. While such new types of amorphous states may not be unusual in systems of complex molecules [7], it is worthwhile to examine a system the local geometry of which slightly deviates from the spherical symmetry. In this study, we analyze systematically the short-range orientational as well as translational orders in the quenched states of a dimer system. We examine how the frustration involved in a system with nonspherical local geometries could lead to the formation of amorphous states. It is found that the building blocks based on the detailed geometries of the individual molecules form the basis for the formation of stable structure. The result can still be understood in terms of the concept of geometric frustration.

The model system considered in this study consists of 500 rigid dimers in a cubic space, subject to minimum image periodic boundary condition [8]. The molecules interact with each other via a site-site Lennard-Jones potential, $4\epsilon((\sigma/r)^{12}-(\sigma/r)^{6})$, which mimics certain diatomic molecules with properly chosen bond length b [9]. In our simulation, we choose a small $b(=0.329\sigma$ [10]). We carried out constant-pressure–constant-enthalpy (NPH) molecular dynamics simulations on the system, using the extended system method [8]. The translational motion of individual molecules is described by a modified version of Newton's equation for its center of masses. The rotational motion of each rigid molecule is dictated by the torques generated by the interactions between pairs of atomic sites and is tracked by the time evolution of the transformation matrices between the body frame and the lab frame [8]. The equations of motion were integrated via Gear's algorithms in a time step of 0.002τ and with an interaction cutoff distance 2.3σ. (In this paper, we use the reduced units defined in terms of the interaction strength ϵ and length σ of the Lennard-Jones potential). The supercooled dimer system considered in this study was quenched in a stepwise manner. With an abrupt lowering of instant temperature by an amount of $\Delta T=0.025$ (the temperature unit is σ/κ_B) at the beginning of each stage, the system then evolved for 80 time units (τ), under an isobaric process at pressure $P=3.7$ (the pressure unit is ϵ/σ^3). At each stage, the temperature was controlled, by externally rescaling the kinetic energy of the molecules, to the desired temperature for the first 20τ, followed by a strict NPH simulation. It was found the spatial correlation became stable by the next 20τ and the data were then collected for the last 40τ of the stage. The solid curve in Fig. 1 shows the fitting of the simulated data (squares) for the density as a function of temperature, obtained in such procedure. Under a pressure as high as $P=3.7$ [11], the curve was found to be weakly quadratic. The results have been compared with the data for a system of a larger size containing 1372 molecules (circles in Fig. 1), obtained under the same static and dynamic conditions. It was further tested against different, but similar orders or higher rates, of quenching or heating (denoted by diamonds in Fig. 1). We conclude that the quenching procedure effectively filtered to obtain a macroscopic state at each temperature, which is stable against fast dynamic decaying. In Ref. [12], for the examination of the change of spatial correlation function in lowering the temperature, it was found that there was a structural crossover regime around $T=0.8$ (see Fig. 2 in Ref. [12]). The diffusion constant cor-

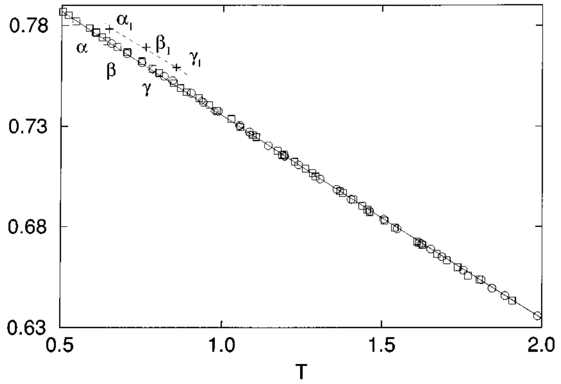

FIG. 1. Density vs temperature. The squares represent data for a 500-molecule system. The circles are for a 1372 system. Each system was quenched by a stepwise lowering of temperature at a rate of changing temperature $\Delta T = 0.025$ every 80 time units (τ), under an isobaric process at pressure $P = 3.7$ in reduced units. The points α_1, β_1, and γ_1 (denoted by plus symbols) correspond to amorphous solid evolved from supercooled liquid states at α, β, and γ (denoted by thick squares), respectively, after a phase-transition-like catastrophic process (see text). The solid line is a quadratic curve fitted to the squares. The diamonds were obtained via heating at similar orders or higher rates.

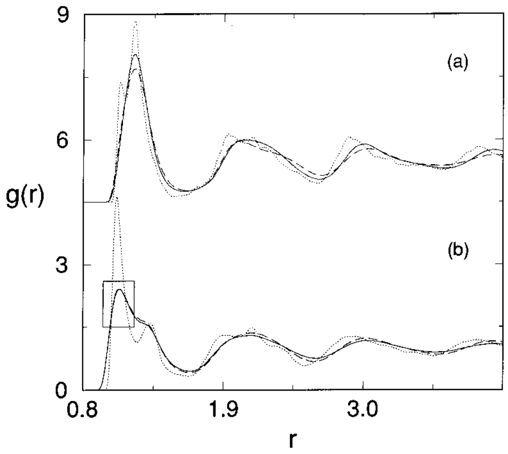

FIG. 2. Radial correlation functions between pairs of centers (a) and pairs of sites (b) for dimer molecules. The figure shows the comparison between the results for states on the supercooled branch (broken lines, at $T = 0.75$) and those for the amorphous solid states (solid lines, at $T = 0.76$). The dashed lines denote the results for the thermally suppressed later state at an equivalent $T = 0.049$. Note the virtually identical first site shells (enclosed by a box) for states on the supercooled branch and the counterpart on the solid branch at almost the same temperature.

respondingly was found to fit to the Vogel-Fulcher law, diverging at even lower temperature, which is similar as the liquid-to-glass phenomena found in real glass-forming systems [13]. It is worth noting that the glasslike states at the low-temperature part of the supercooled branch in our system of nearly spherical molecules are dominated by much shorter time scales than those for real glass formers. The latter were considered as ''frozen liquid'' by conventional wisdom.

With periodic boundary conditions, the supercooled states below a certain temperature (close to 1.0), whether they be above or below the structural crossover regime, would undergo a catastrophic nucleation at long times (on the order of a few hundreds to a few thousands τ, depending on the temperature) to form states that are more stable and better packed. In Fig. 1, α_1, β_1, and γ_1 are three such states obtained via nucleation from the supercooled states α, β, and γ, respectively. These states are virtually frozen and solidlike such that the molecules can change their positions only by hopping, in contrast to the more or less diffusive motion in the supercooled states. Thus we obtained the second branch of states, denoted by the broken curve in Fig. 1. (A continuous process along the curve that would require sufficient time to allow for structural relaxation in these solidlike states was not carried out in our simulation.) In the following, we are going to show that, in addition to the difference in the nature of molecular diffusion, the states on the solid branch are characterized by better longer-range translational correlation than those on the supercooled branch. Such enhanced translational correlation, however, fails to sustain a long-range ordering. These better packed amorphous solid states, on the other hand, bear the same ordering in the nearest neighbor shell of atomic sites as that for the less stable supercooled-branch states at the same temperature (see below). This provides an interesting case that preserves the local arrangement favored by liquid. It is likely that the formation of such solidlike states can be understood as a result of the compromise between the local geometry and the global placement.

Structural information was collected for both the radial and angular distribution with respect to a center molecule or a center site. Of particular interest is the comparison between the data for two states at the same temperature and on the two different branches as discussed above. We present data (Figs. 2, 3, and 4) for a typical case of two such states, one in the supercooled branch at $T = 0.75$ (broken lines) and the other in the solid branch at approximately the same temperature $T = 0.76$ (solid lines). In order to examine for the possible presence of longer-range ordering, we also present data for the latter state with thermal motion suppressed to an equivalent temperature $T = 0.049$ (dashed lines). (Such a state is *not* a true stable state obtained by evolution.) Figure 2 shows the radial correlation functions between centers of molecules and between atomic sites

$$g(r) = \langle \delta(r_{ij} - r)/4\pi r^2 \rangle, \qquad (1)$$

where r_{ij} is the distance between the molecule (site) j to the center molecule (site) i. We can roughly regard each oscillation between two successive major minima in Fig. 2 as defining a shell of neighbors to a center molecule or site. For each shell, we calculate the angular correlation functions

$$f(\theta) = \langle \delta(\theta^i_{jk} - \theta)/\sin\theta \rangle, \qquad (2)$$

where θ^i_{jk} is the angle between the relative positions of two molecules (or sites) j and k on a specified shell to the center molecule (or site) i. Figure 3 shows the angular correlation functions for the nearest neighbor shells for the centers [Fig. 3(a)] and for the sites [Figs. 3(b) and 3(c)]. The functions for the second and the third coordination shells are shown in Figs. 4(a) and 4(b), respectively, where the data for the cen-

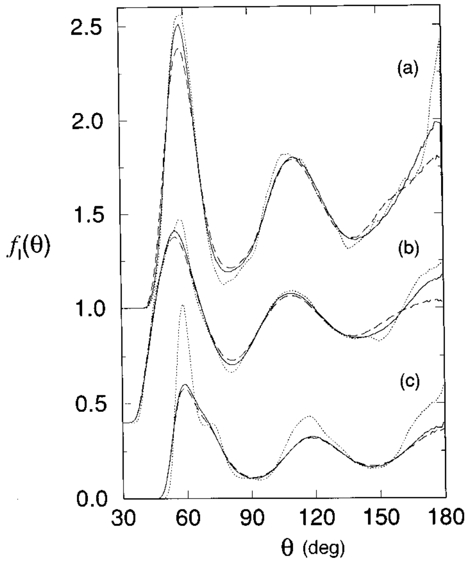

FIG. 3. Angular correlation functions for centers of masses in the nearest neighbor shell of a center molecule (a) and the corresponding functions for sites around a center site (b), plotted for states considered in Fig. 2. A molecule or atomic site is considered as in the first neighboring shell of a center molecule (or site) if it is at a distance within the first major minimum of its corresponding radial correlation function. We use the same notation to denote the curves for three different states considered in Fig. 2. We also present data (c) excluding the small shoulder of the main peak in Fig. 2.

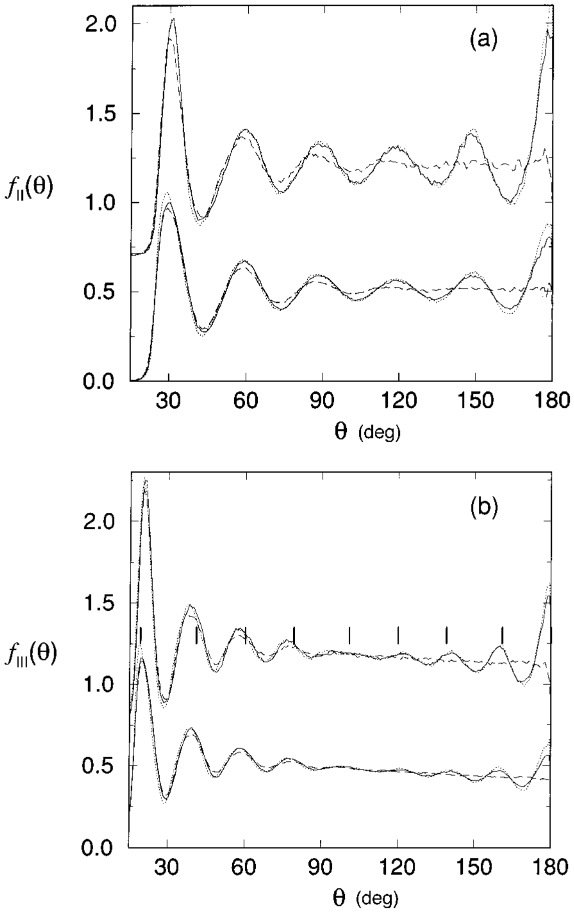

FIG. 4. Angular correlation functions, for the second (a) and the third near neighbor shells (b), determined by Fig. 2 (see text) for the center of molecules (upper curves in each plot) and atomic sites (lower curves in each plot), respectively. The figure shows the comparison between the results for states on the supercooled branch (broken lines, $T = 0.75$) and those for the amorphous solid states (solid lines, $T = 0.76$). The dashed lines denote the results for the thermally suppressed later state at an equivalent $T = 0.049$. In (b), the vertical thick line segments mark the expected location of the peaks for the third shell of an ideal planar triangular lattice structure.

ters of molecules are presented in the upper part and those for the atomic sites in the lower part of each plot.

From the observation of the radial correlation function $g(r)$, an enhanced correlation was found for the solidlike state characterized by the emerging subpeaks in the first two shells, if the thermal motion is suppressed (Fig. 2). Such a signature of ordering, however, does not persist beyond the third shell, indicating a long-range translational correlation that is still weak. An interesting observation was the almost-identical nearest site shell between states of the supercooled branch and of the solid branch at the same temperatures (the portion enclosed by a rectangular block in Fig. 2). The results indicate that certain nearest neighbor correlations between sites may be preserved for the amorphous solid state as compared with the supercooled liquid state at the same temperature. More detailed information was obtained by examining the angular correlation over the neighboring shells surrounding a center molecule and the correlation for atomic sites in the corresponding nearest neighbor shell of a center site. Since the partner site for each nearest neighbor site sits at a distance slightly further away from the center site, a subshell shoulder can be identified next to the true nearest neighbor site shell (Fig. 2). We present the angular correlation for the cases, both including [Fig. 3(b)] and excluding [Fig. 3(c)] contributions from this subshell. In Fig. 3(c), the angular correlations of the first site shell are virtually identical between a state on the supercooled branch and that on the solid branch at the same temperature. There is, however, an obvious difference between these two states if we consider the site shell with the shoulder subshell included [Fig. 3(b)]. A difference exists also for the shell of molecule centers [Fig. 3(a)]. Thus, in our dimer system, a kind of invariant structure that preserves *only* the nearest site-site correlation is present in the states on supercooled branch and its counterpart on the amorphous branch at the same temperature.

While the ordering within the nearest neighboring shell depends much on the linear geometry of individual molecules and does not show any simple symmetry (Fig. 3), it is interesting to find that the angular correlation between pairs on the second shell displays planar sixfold symmetry [Fig. 4(a)]. The positions of the peaks for the centers are virtually identical to those for the sites, indicating the effect of the detailed molecular structure has become invisible in this and further shells. The angular correlations for a state on the supercooled branch decays to zero at larger angles in contrast to the significant correlations at all angles for the corresponding state on the solid branch at the same temperature. This difference is also true for the third shell [Fig. 4(b)]. As can be seen, the locations of those peaks in the third shell start to deviate from an ideal sixfold symmetric structure. [The latter

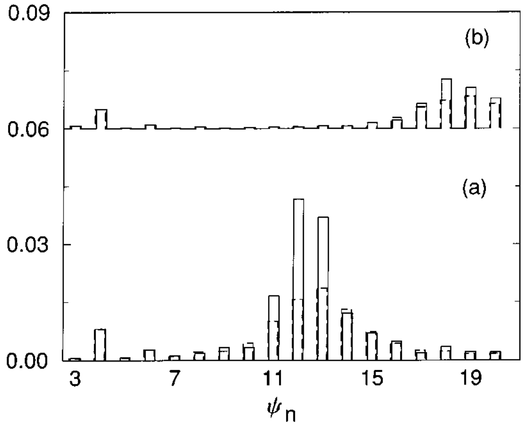

FIG. 5. Parameter ψ_n vs n defined for the second (a) and the third (b) coordination shells of molecule centers. The figure shows the comparison between the results for states on the supercooled branch (broken lines, $T=0.75$) and those for the amorphous solid states (solid lines, $T=0.76$).

is marked by the thick vertical line segments in Fig. 4(b).] This deviation accounts for the absence of long-range translational correlation, which results in amorphous structures. Further information that confirms a quasi-six-fold structure being present over short distance has been obtained by considering the quantity,

$$\psi_n=\left\langle \left| \sum_{\theta} e^{in\theta} \right|^2 \Big/ \left| \sum_{\theta} 1 \right|^2 \right\rangle, \qquad (3)$$

where the summation runs over all pairs of centers of molecules extending an angle θ on a specified shell. The peaks near $n=12$ for the second shell [Fig. 5(a)] and $n=18$ for the third shell [Fig. 5(b)] are consistent with the contribution from a triangular planar structure. The presence of the minor peaks at $n=4$, on the other hand, corresponds to a very weak cubic symmetry. Indeed, layered structures were observed in the simulation, which is consistent with the presence of the quasi-six-fold symmetry in orientation. It is worth pointing out that, in the simulation of a system of the size considered in our study, the effects due to periodic boundary condition are not negligible. The formation of well-defined layered structures may be due partly to the effects of boundary conditions. We have checked the results by changing the simulated space from a cube to one with a different linear dimension in one direction from the other two. We found that the conclusion about the short-range ordering is independent of the boundary conditions.

The data presented in this paper support the idea that the amorphous solid state represents a state to satisfy the requirement of global placement. The building blocks to play this game are different from those of the spherical cases. A kind of intermolecular (site) correlation is preserved. The extention is not simply a tile of blocks as in the packing of spheres for which only the contact neighbor spheres count. It is, instead, a building hierarchy in which local frustration extends to destroy the longer-range correlations. Indeed, similar frustration of geometric origin has also been applied to systems of liquid crystals [14] with dominant linear or planar geometries. The existence of intermediate partially ordered states has been proposed. Recent experimental observation [5] of the existence of the transition from glassy state to a second amorphous states, termed ''glacier phase,'' may bear some resemblance to the formation of the state on the solid branch in this work.

In summary, we have carried out a systematic comparison between the short-range structural information for supercooled liquid states and those for better packed amorphous solid states. The presence of identical nearest neighbor site-site correlation indicates a type of local arrangement being preserved in extending the structure to fill the space. The presence of the sixfold symmetry in the intermediate range and the gradual absence of ordering in the subsequent longer range indicate the more complicated effect from the local geometry in tiling the space than in the cases for spherical molecules.

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