Geometry of Slow Structural Fluctuations in a Supercooled Binary Alloy

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The liquid structure of a glass-forming binary alloy is studied using molecular dynamics simulations. The analysis employs the geometrical approach of Frank and Kasper to establish that the supercooled liquid contains extended clusters characterized by the same short range order as the crystal. The steep increase in the heat capacity on cooling is directly coupled to the growing fluctuations of the Frank-Kasper clusters. The relaxation of particles in the clusters dominates the slow tail of the self-intermediate scattering function.

If, on supercooling, a liquid accumulates mechanically stable structures with identifiable geometries, then the explanation of many of the anomalous properties of such liquids, including the glass transition itself, becomes straightforward. In 1933, Tammann [1] proposed that glasses were the result of the coagulation of some sort of clusters. Recent simulation studies [2–6] have revived interest in the possibility of accounting for glassy anomalies in terms of the temperature dependence of specific locally favored ordering. A key challenge for any such proposal is to explain how it is that the relevant clusters are stable enough to resist shear yet not capable of translating this stability into growth. Frank's elegant 1952 resolution [7] of this difficulty consisted of pointing out that, in a liquid made up of spherical particles of one size, an icosahedral coordination shell would have a low energy but would be unable to grow extensively without accumulating defects. In this Letter we shall demonstrate an alternate route to stabilizing structural fluctuations against crystal growth, one that does not rely on the stabilization of regular icosahedra, and demonstrate the correlation between the structural and the energy fluctuations.

We consider a model alloy consisting of a equimolar binary mixture of Lennard-Jones particles introduced by Wahnström [8]. The interaction parameters are $\sigma_{AA} = \sigma_{AB}/1.1 = \sigma_{BB}/1.2$, $\varepsilon_{AA} = \varepsilon_{AB} = \varepsilon_{BB}$, and $m_A = m_B/2$. This binary mixture has been studied in the context of the glass transition by a number of groups [3,6,8–10]. Further details concerning the algorithm are provided in the supplementary material [11]. Like all real glass-forming binary alloys, the Wahnström mixture does, eventually, crystallize. Pedersen *et al.* [12] have reported that this liquid will spontaneously crystallize into a crystal structure with A_2B composition. The structure of the crystal is that of $MgZn_2$, which, along with two other A_2B structures: $MgCu_2$ and $MgNi_2$, are known as Laves phases and correspond to the densest packings of a binary mixture of hard spheres with a radius ratio of $\sqrt{(3/2)} \sim 1.22$. The

unit cell, shown in Fig. 1, contains 12 atoms with the smaller A particles (colored green) coordinated in one of two different (irregular) icosahedral polyhedra, both made up of six A and six B particles. The B particles (colored grey) all sit in a 16 vertex coordination polyhedral comprised of 12 A particles and four B particles. The $MgZn_2$ crystal consists of a hexagonal diamond network of B particles (similar to arrangement of oxygens in ice Ih) with each BB pair sharing 6 A neighbors.

Given the complexity of the crystal structure, we direct the reader's attention to the essential feature for the discussion that follows: the unit cell extends beyond the short range (i.e., nearest neighbor) order. This situation is very
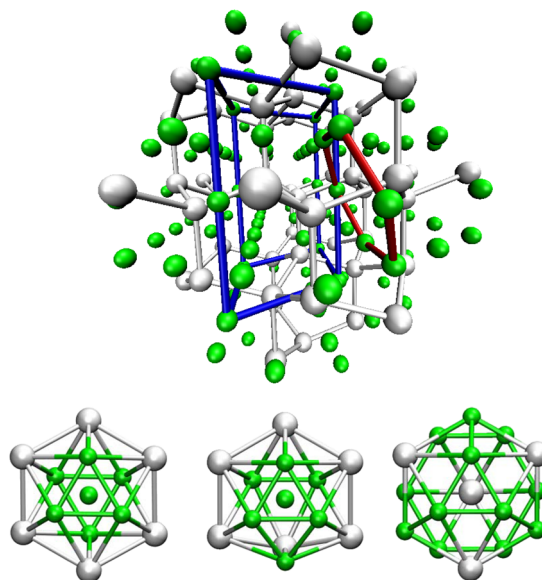

FIG. 1 (color online). Illustration of the unit cell (blue box) of the $MgZn_2$ structure and the three coordination polyhedra found in the crystal. The A (small) particles are green and the B (large) particles are gray (size reduced for visibility). Six A particles of a Frank-Kasper bond are shown connected by red links.

different, for example, from that of simple liquids that form fcc crystals where the length of short range order and that of the crystal unit cell are one and the same. Liquids like the mixture studied here can lower their enthalpy by adopting short range order similar to that found in the crystal without ever having to commit to crystallinity (i.e., the appearance of a unit cell). In the following analysis we present evidence of exactly this phenomenon. Coslovich and Pastore [5] have established that the Wahnström mixture contains A-centered icosahedral coordination polyhedra. The fraction of A particles in the center of such polyhedra grows rapidly on cooling to reach ~25% at $T = 0.623$. We have confirmed these results and established that the most stable coordination is that comprised of six A and six B particles, just as found in the $MgZn_2$ crystal. To extend the description of the amorphous structure, we shall consider the common neighbor analysis, a method that provides information about both short and intermediate order [6,13]. The elementary objects are nearest neighbor pairs plus those particles that are neighbors to both of particles in the "root" pair. This approach was introduced by Honeycutt and Andersen [14] and provides a finite gallery of geometric objects, bipyramids with the root pair in the axial positions and the common neighbors making up the equatorial sites [15], that are robust in the
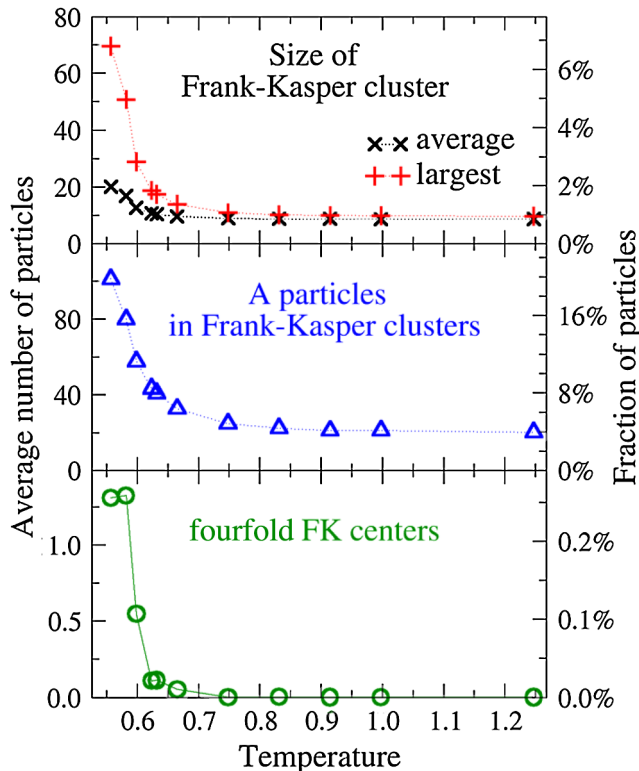
sense that their size and complexity does not scale as the particle size ratio (unlike the coordination polyhedra).

In 1958, Frank and Kasper [16] presented a landmark paper on the enumeration of crystal structures built out of triangulated polyhedra. The Frank-Kasper polyhedra must have 12 fivefold bonds [16], a requirement that means that the sixfold "bonds" are a minority component. In Ref. [16] the pairs with 6 common neighbors were referred to as "backbone bonds" and were used to build up complex crystal structures by starting with the nets of these backbone bonds. Our strategy is to extend this reasoning to the case of the amorphous alloy and look at building up an extended description of the amorphous states by considering clusters of these backbone bonds. We shall refer to a neighbor pair of B particles with six common A neighbors as a Frank-Kasper (FK) bond. As already mentioned, the $MgZn_2$ crystal consists of tetrahedral network of FK bonds. Particles are labeled FK particles if they participate in at least one FK bond. The presence of B particles with 4 FK bonds is a necessary condition for crystallinity. The fraction of A particles involved in FK bonds increases sharply on cooling at $T \sim 0.6$, as shown in Fig. 2. We note that this temperature is very similar to the value of T_c found on fitting $D \sim (T - T_c)^\gamma$ [10] and to the temperature at which a steep drop occurs in the average energy of inherent structures explored by the liquid [9]. The fraction of B particles with 4 FK bonds, a necessary condition for $MgZn_2$ crystallinity (see Fig. 1), stays small throughout the studied temperature range. In Fig. 3 we
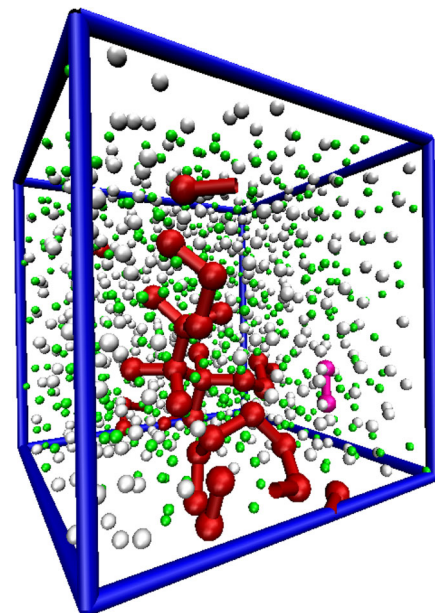

FIG. 2 (color online). The temperature dependence of the average number of B particles of FK clusters (black X's), the average number of B particles of the largest FK cluster (red crosses), the average number of A particles participating in FK bonds (blue triangles) and the average number of B particles with 4 FK bonds (green circles) in inherent structures.

FIG. 3 (color online). A picture of the FK clusters in a supercooled liquid at $T = 0.599$. (The inherent structure used corresponds to time 0.5×10^6 in Fig. 4.) All the FK bonds in a common cluster are depicted as cylinders with the same color. A and B particles are depicted (size reduced for visibility) as green and gray spheres, respectively.

show the spatial distribution of FK bonds in a single configuration at $T = 0.599$.

We find that the inherent structure energy exhibits persistent dips during trajectories of the metastable liquid. In Fig. 4 we show examples of these fluctuations and the associated fluctuations in the size of the largest FK cluster and in the number of B particles with four FK bonds. A strong correlation exists between the transient drop in the inherent structure energy U_{is} and the appearance of large FK clusters. In Fig. 5 we plot the heat capacity C_V, $C_{is}(= \langle \Delta U_{is}^2 \rangle / k_B T^2)$ and C_V-C_{is} as a function of temperature. The apparent divergence in C_V and the breakdown of the Rosenfeld-Tarazona law [17] have been reported previously by Fernández *et al.* [18] for a soft sphere analogue of the Wahnström mixture. We find that the rapid increase in C_V around $T \sim 0.6$ is due entirely to the fluctuations in the inherent structure energy which, in turn, we have shown above to be a direct consequence of the fluctuations in size of the FK clusters.

In Fig. 6 we have plotted the self-intermediate scattering function from the A particles and the contribution to this relaxation function of those A particles initially in FK clusters. Stretched exponential fits to the curves provides
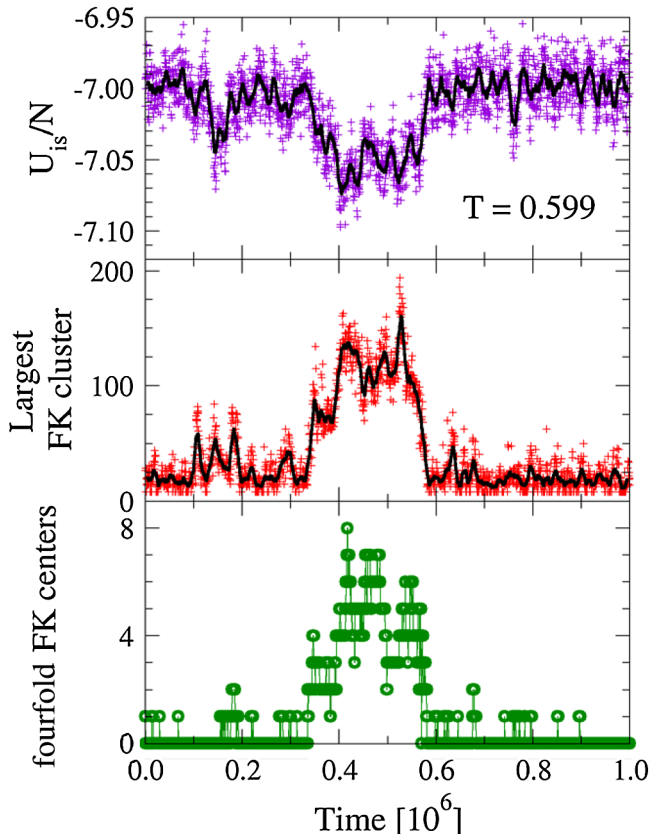
a relaxation time, (700) for the FK contribution that is larger than the corresponding time (150) for the non-FK contribution by a factor that increases from ~4 to 8 on cooling. The stretching exponents are all in the range 0.4–0.5 without any discernible trend. The FK clusters successfully identify the slowest component of the structural relaxation in the supercooled liquid. The related A- centered icosahedral coordination shell also selects for slowly relaxing particles [5].

We conclude that, in the Wahnström mixture, the slow relaxation of the structural fluctuations and the appearance of an abrupt increase in the heat capacity on supercooling are strongly correlated with the appearance of stable clusters whose stability derives from their exploitation of the short range order of the crystal. The clusters are described using the same "backbone" bonds introduced by Frank and Kasper to enumerate the complex structures of alloy crystals. These observations constitute a significant advance in the elucidation of the glass transition *in this mixture*. The kinetic and thermodynamic anomalies that define the glass transition have been associated directly with the development of a specific structure. That the short range order of this structure is the same as that found in the crystal, represents an important break from the tradition of assuming that structure associated with the crystal phase can play no role in the stability of the amorphous phase. A number of groups [3,4,19] have described amorphous models in which overtly crystalline domains are associated with the slow down in structural relaxation. In the Wahnström mixture, we find little sign of the large unit cells that would indicate crystallinity. Configurations of sufficiently low energy to stabilize the amorphous phase are obtained from arranging the short range order found in the crystal into irregular clusters as shown in Fig. 3.
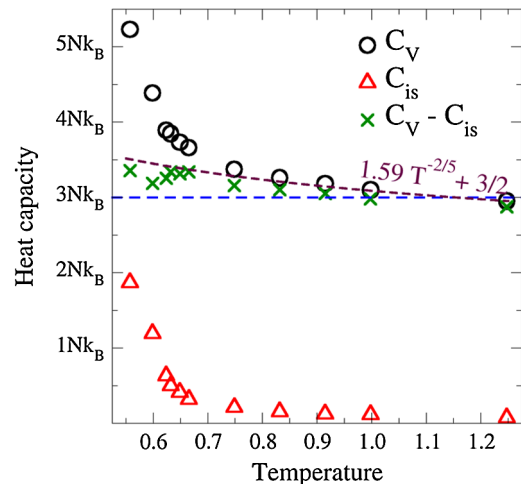

FIG. 4 (color online).   The inherent structure energy per particle U_{is}/N, the number of B particles in the largest FK cluster and the number of B particles with 4 FK bonds (collected using the inherent structures) as a function of time during a simulation run. In each case the points correspond to the actual values and, the solid lines are local averages to indicate the trend.

FIG. 5 (color online).   The heat capacity C_V (black circles) versus temperature along with the contribution from fluctuations in the inherent structure C_{is} (red triangles) and the difference C_V-C_{is} (green X's). A theoretical prediction due to Rosenfeld and Tarazona [17] (dashed line) breaks down at low temperatures.
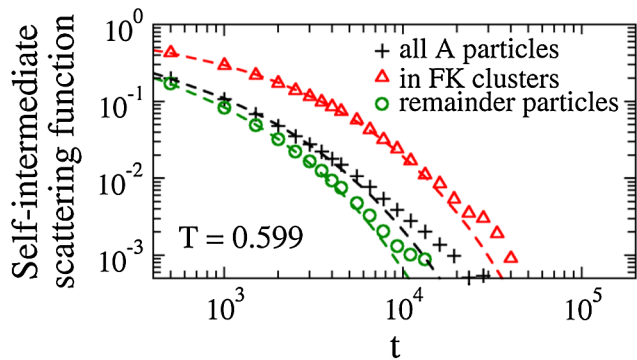
FIG. 6 (color online). Log-log plots of the self-intermediate scattering function $F_s(q = 6.47, t)$ from the A particles (black crosses), the contribution $F_{FK}(t)/F_{FK}(0)$ due to the A particles initially in an FK cluster (red triangles) and $F_{n-FK}(t)/F_{n-FK}(0)$, the contribution due to those A particles *not* in FK clusters at $t = 0$ (green circles) for T 0.599. Dashed lines represent stretched exponential fits to the data.

In the Wahnström mixture, frustration of crystallization does not occur in the coordination shell, as proposed by Frank, but in the multiple possible stable arrangements of crystal-like short range order over intermediate lengths. The possibility of this type of frustration arises as a consequence of the fact that the length of the unit cell extends beyond that of the short range order. Crystal nucleation, therefore, requires fluctuations over intermediate length scales that will involve both structure and composition [20]. How general is the scenario for amorphous stabilization that we have described? We do not know. A chemically ordered A_4B mixture first studied by Kob and Andersen [21], has been shown [5,6,13] to have a short range order in the supercooled liquid dominated by the tricapped triangular prism characteristic of a crystal (the Ni$_3$P structure), but a metastable one—an observation consistent with the results of this Letter. In contrast, our preliminary studies of a molecular glass former consisting of a bent triatomic show little correspondence between the short range order of the liquid and the crystal. What we have established in this Letter is that the structures that stabilize a glass need not be so different to those that stabilize the crystal, suggesting a possible continuity between ordered and disordered solid states.

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