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Abstract

Using *ab initio* molecular dynamics simulations, we find direct evidence that icosahedral clusters have a strong tendency to aggregate in Zr1−xCux liquids. Remarkably, the dynamic arrest effect is much more significant in aggregated icosahedral clusters than in nonaggregated ones by a factor of 2 or more. Simulations using a lattice model demonstrate that the dynamic arrest effect resulting from the aggregation of icosahedral clusters may be a fundamental characteristic of the glass transition. Our studies provide an atomistic structural mechanism for dynamic arrest and glass formation.

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Dynamic arrest and glass formation induced by self-aggregation of icosahedral clusters in Zr$_{1-x}$Cu$_x$ alloys

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Using *ab initio* molecular dynamics simulations, we find direct evidence that icosahedral clusters have a strong tendency to aggregate in Zr$_{1-x}$Cu$_x$ liquids. Remarkably, the dynamic arrest effect is much more significant in aggregated icosahedral clusters than in nonaggregated ones by a factor of 2 or more. Simulations using a lattice model demonstrate that the dynamic arrest effect resulting from the aggregation of icosahedral clusters may be a fundamental characteristic of the glass transition. Our studies provide an atomistic structural mechanism for dynamic arrest and glass formation.

I. INTRODUCTION

The mechanism that leads to slow dynamics and glass formation in metallic alloy systems has been an important topic in materials science. It has been recognized that the glass transition is a dynamical phase transition in trajectory space rather than an equilibrium phase transition in configuration space.[1] In many metallic alloys, the liquid-glass transition has been attributed to the geometrical frustration caused by icosahedral short-range order (ISRO).[2–4] Understanding how the frustrated geometry leads to dynamic arrest and glass formation is therefore highly desired.

Extensive theoretical models, such as mode coupling theory and the facilitated lattice model, have been developed to study the dynamical properties of glass-forming systems (see Ref. 5 for a review). However, these models are highly schematic and lack structural details that can be related back to specific materials. Recent molecular dynamics (MD) simulations have identified ISRO as the slowest moving clusters in deeply undercooled Zr$_{1-x}$Cu$_x$ liquids,[6–8] but it was not possible to probe the appearance of glassy dynamics in the system because of the short duration of the simulations.

In this paper, we employ *ab initio* MD simulations to examine the spatial correlations among locally ordered clusters in high-temperature Zr$_{1-x}$Cu$_x$ metallic liquids. We find that atoms with ISRO have a much stronger tendency to aggregate than other types of local order. Moreover, the aggregation of ISRO clusters significantly enhances the slowing effect of ISRO clusters on the local dynamics of the system. We believe that the enhancement of dynamic arrest with aggregation provides a positive feedback mechanism for driving the system into the glass transition in the Zr-Cu system. We incorporate the aggregation-induced dynamic arrest mechanism observed in the *ab initio* MD simulations into a lattice model and demonstrate how glassy dynamics develops as the system is cooled from the liquid state.

II. SAMPLE MODELS

Liquid samples of Zr$_{1-x}$Cu$_x$ with $x = 0.33$, 0.50, 0.57, 0.65, 0.72, and 0.80, which represent various eutectic,

peritectic, or congruent melting behaviors in the binary phase diagram[9] and cover generally the high glass-forming range in this system, were generated using *ab initio* MD simulations at 1500, 1300, and 1100 K, respectively. The simulations were performed using a plane-wave basis with the projector augmented-wave (PAW) method for core-valence electron interactions[10,11] and the Perdew-Wang exchange and correlation functional,[12] as implemented in VASP.[13] The cutoff energy of the plane-wave basis is 273 eV.

Only the Γ point is used to sample the Brillouin zone. The simulations are carried out in the *NVT* ensemble with Nosé thermostats and a MD time step of 3 fs. A unit cell containing 100 atoms with periodic boundary conditions is used for each simulation. Our test simulations with 200 atoms have shown similar results.

III. SPATIAL CORRELATION OF LOCAL ORDERS

The local structures in the liquid samples were analyzed by the Voronoi tessellation method.[14,15] Figure 1(a) illustrates the populations of the 14 most abundant Voronoi clusters observed in Zr$_{35}$Cu$_{65}$ (the best glass former) at 1300 K. In contrast to the glass structure,[16] the icosahedral cluster type is not the most populous in high-temperature liquid states.[17] In order to determine whether the moderate level of ISRO present in the high-temperature liquid exhibits any structural signature associated with a precursor to glass formation, we go beyond short-range order (SRO) and examine the spatial correlations between the specific Voronoi clusters, using the nearest-neighbor correlation matrix of the clusters as defined in our previous paper.[16] By this definition, if cluster types i and j are distributed randomly, $C_{ij} = 0$. $C_{ij} > 0$ indicates that the central atoms of these two cluster types tend to be nearest neighbors, while $C_{ij} < 0$ indicates that they avoid being nearest neighbors.

Figure 1(b) shows the spatial correlation matrix of the major Voronoi clusters. The most important feature of this map is the strongest self-correlation for the icosahedral clusters (Voronoi index ⟨0,0,12,0⟩). Moveover, this tendency toward icosahedral self-aggregation is rather general as it is found in all of the Zr-Cu samples that we simulated. In addition
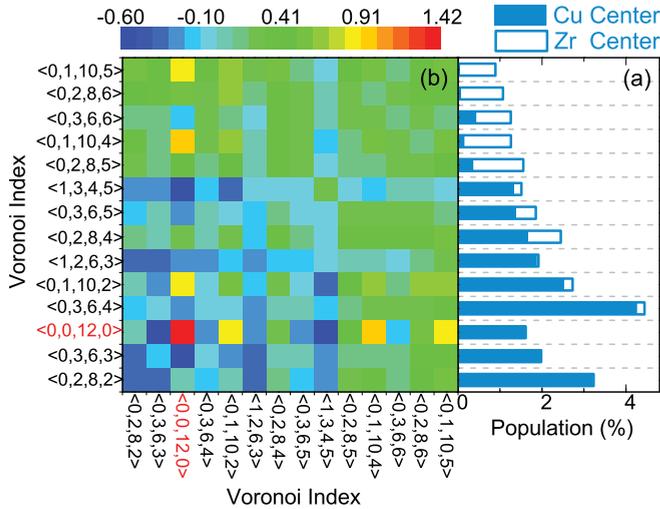
FIG. 1. (Color online) (a) Population and (b) spatial correlation of the 14 most abundant Voronoi clusters in liquid $Zr_{35}Cu_{65}$ at 1300 K. The MD samples with 200 atoms provide almost the same results.

to a strong self-aggregation tendency, the $\langle 0,0,12,0 \rangle$ clusters exhibit remarkable spatial correlation with other pentagon-rich clusters. The characteristics of the spatial correlation map of the high-temperature liquid are notably similar to that of the glass,[16] although the populations of various types of Voronoi clusters are quite different in the two cases. This correlation behavior indicates that, although the high-temperature liquids exhibit fast dynamics, clearly identifiable nonrandom spatial correlations of local orders are already present and may play a major role in the eventual glass transition.

IV. AGGREGATION CAUSED DYNAMIC ARREST EFFECT

The aggregation of icosahedral clusters has dramatic consequences on the dynamics of the system. Figure 2 shows the mean square displacements (MSD) as the function of
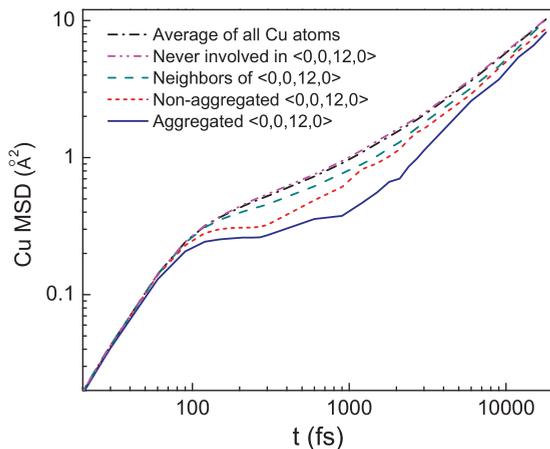

FIG. 2. (Color online) Comparison of the MSDs (in logarithmic scale) of the centered Cu atoms in various types of clusters (as indicated) with the average MSD of all Cu atoms in liquid $Zr_{35}Cu_{65}$ at 1300 K.

time for Cu atoms initially at different environments, in comparison with the averaged values of all Cu atoms in the sample. In the ballistic regime ($t < 60$ fs), there is almost no difference between MSDs for icosahedra-related Cu atoms and non-icosahedra-related Cu atoms. Beyond the ballistic regime, the icosahedra-related Cu atoms clearly exhibit lower mobility than the average, in agreement with Ref. 18. Moreover, the aggregation of icosahedral clusters dramatically enhance this effect. In contrast, the MSD of non-icosahedra-involved Cu is very close to that of the average. We note that the appearance of a long plateau in the MSD versus time is a signature of glassy dynamics. In the present case, although the whole system is in the liquid state much above the glass transition temperature, we already observe a tendency toward glassy behavior in the vicinity of aggregated icosahedral clusters when they appear in the liquid.

The lifetime of the various types of clusters in the liquid is also an important indicator of the relative stability between different cluster types. The cluster lifetime is measured as the time period during which the cluster maintains its Voronoi index. For comparison, we average over all the different kinds of Voronoi clusters, weighted by their respective populations to define a "liquid lifetime." Figure 3(a) shows the average lifetime of nonaggregated and aggregated $\langle 0,0,12,0 \rangle$ clusters in liquid samples of different compositions at 1300 K, in comparison with the "liquid lifetime." The nonaggregated $\langle 0,0,12,0 \rangle$ cluster lifetime is twice that of the liquid lifetime, and the aggregated $\langle 0,0,12,0 \rangle$ cluster lifetime is twice again that of the nonaggregated cluster. This observation indicates that the aggregation of $\langle 0,0,12,0 \rangle$ clusters significantly enhances the stability of local ISRO. Furthermore, Fig. 3(b) shows that $\langle 0,0,12,0 \rangle$ clusters also tend to increase the
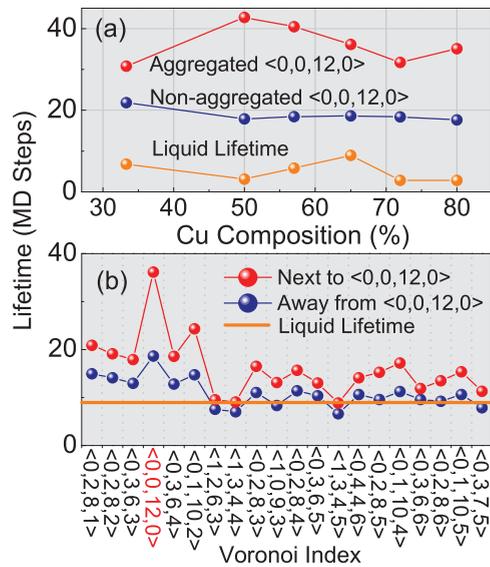

FIG. 3. (Color online) (a) Lifetime of nonaggregated and aggregated $\langle 0,0,12,0 \rangle$ and the liquid lifetime at different compositions of $Zr_{1-x}Cu_x$ at 1300 K. (b) Lifetime of the 20 most abundant Voronoi clusters in the forms of neighboring and not neighboring $\langle 0,0,12,0 \rangle$ in $Zr_{35}Cu_{65}$ at 1300 K. Once a $\langle 0,0,12,0 \rangle$ cluster has a $\langle 0,0,12,0 \rangle$ neighbor during its existence, it is defined as an aggregated $\langle 0,0,12,0 \rangle$, otherwise, it is a nonaggregated $\langle 0,0,12,0 \rangle$.

lifetimes of all their neighboring cluster types, with the most significant effect being observed for the $\langle 0,0,12,0 \rangle$ type itself. The lifetime elongation caused by neighboring $\langle 0,0,12,0 \rangle$ clusters results in a general dynamical slowdown, which becomes more pronounced as the temperature is decreased.

To assess the development of ISRO ($\langle 0,0,12,0 \rangle$) upon quenching, we have further cooled the $Zr_{35}Cu_{65}$ alloy to 300 K at the rate of 1×10^{13} K/s. Our results show that the fraction of ISRO increases to 7%, and becomes dominant. This result is consistent with reported MD simulations using the empirical potential based on the embedded atom method (EAM),[6,19] even though our cooling rates were orders of magnitude faster than those used in the EAM-MD simulations. In addition, our reverse Monte Carlo calculations also produced a structure with a large population ($>7\%$) of ISRO clusters in the $Zr_{35}Cu_{65}$ glass.[16] These results, obtained from different cooling rates and simulation methods, provide compelling evidence to confirm that ISRO does develop dynamically, as the most abundant cluster type in the $Zr_{35}Cu_{65}$ glass.

To examine more closely the effect of the ISRO-aggregation-induced dynamic arrest mechanism of the system, we incorporated the essential physics of this mechanism into a two-dimensional (2D) triangular-lattice model and verified in detail the onset of glassy dynamics through kinetic Monte Carlo (KMC) simulations. This is a two-state model, where the state at each lattice site n_i assumes a value of either 1 or 0, representing an icosahedral or nonicosahedral first-shell environment, respectively. The dynamics of the system are treated by describing the probability of state "flipping" as $\sim \exp(-\Delta f_i / k_B T)$, where Δf_i is the free-energy barrier for the forward or backward transitions. Assuming that there is a single activated transition state, we define the barrier as

$$\Delta f_i = \begin{cases} c_0 + c_1 T + c_2 T^2 & (i = 0), \\ g_0 + g_1 m_{\mathrm{II}}(m_{\mathrm{II}} - \alpha) & (i = 1). \end{cases}$$

We note here that, given the diversity of cluster types that may comprise the nonicosahedral states ($n_i = 0$), the entropy contribution must be considered. Therefore, we require a temperature-dependent Δf_0 and approximate it with a quadratic form. For the icosahedral state, however, the entropy contribution should be much smaller than that in the nonicosahedral state, so a temperature-independent form is chosen. Here, the parameter g_0 denotes the potential energy of ISRO with respect to the transition state, and the second term reflects the energy associated with ISRO aggregation. The parameters g_1 and α are introduced to account for the influence of the first-shell environment on the *in situ* local site energy, where m_{II} counts the number of icosahedral nearest neighbors around a specific icosahedral site, and α is the value of m_{II} yielding an energetic minimum. The increase of energy with larger values of m_{II} reflects the geometric frustration caused by the non-space-filling nature of ISRO. The coefficient g_1 then becomes a scaling parameter, affecting the probability of ISRO aggregation.

With the present model and appropriate parameters,[20] we have performed KMC simulations to study the evolution of ISRO upon cooling, with the initial configuration at 1800 K consisting of only nonicosahedral states. As shown in
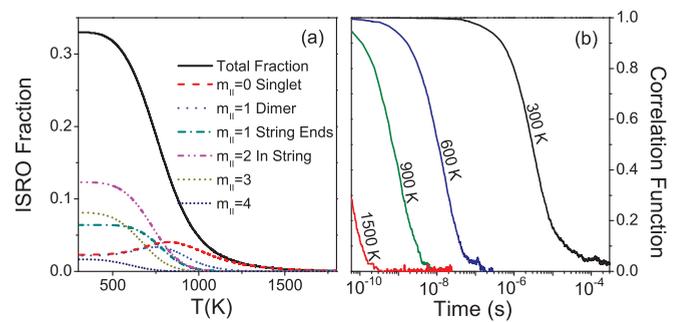

FIG. 4. (Color online) (a) Development of ISRO at a cooling rate of 4.91×10^{10} K/s. This cooling rate is comparable to those employed in typical EAM-MD simulations (Ref. 19). (b) Autocorrelation functions vs time at different temperatures. Initial configurations are obtained from the cooling process with the above cooling rate.

Fig. 4(a), the temperature-dependent behavior of icosahedral order is in good consistency with EAM-MD simulation results.[6] Moreover, as the temperature decreases, the configuration of $m_{\mathrm{II}} = 2$ develops rapidly and is most abundant at 300 K. This indicates a strong tendency toward the aggregation of icoshedral sites into a stringlike morphology, in good agreement with our previous paper.[16] It should be noted that the final ISRO fraction and morphology depend on the cooling rate.

An analysis of the dynamic properties from our model shows that the dynamic arrest induced by ISRO aggregation naturally leads to nonexponential relaxation of the autocorrelation function at low temperatures. The fundamental correlation function of the system at a given temperature is defined as[21] $A(t) = \langle \delta n_i(t) \delta n_i(0) \rangle_N / \langle \delta n_i(0)^2 \rangle_N$, where $\delta n_i = n_i - \langle n_i \rangle_N$ is the fluctuation from average. ($\langle \cdots \rangle_N$ denotes an average for N sites.) As shown in Fig. 4(b), the decay of the autocorrelation function is exponential at 1500 K, and gradually becomes nonexponential at lower temperatures. The transition from exponential to nonexponential relaxation characterizes the glass formation in this model system, in agreement with the behavior observed in facilitated lattice models.[21,22] The evolution and self-aggregation of ISRO in the system during cooling is illustrated in Fig. 5. As the temperature decreases from 1500 to 300 K, the strong ISRO aggregation tendency leads to packing in a spinodal-like morphology. The development of such a structure during cooling gives rise to nonexponential relaxation and the corresponding overall dynamic arrest associated with glass formation. Our model brings together the effects of geometric frustration caused by the non-space-filling nature of ISRO as well as the dynamical stabilization and kinetic *slowdown* associated with the development of medium-range order and morphology through an aggregation mechanism. The aggregation-induced dynamic arrest provides a positive-feedback pathway, leading to glass transition in a class of metallic glass systems.

The spontaneous aggregation plus the non-space-filling fact of icosahedra would not cause a critical-like behavior as what we are familiar with in crystallization. In contrast, nucleation of the crystal phase has to overcome a barrier with respect to embryo size, and therefore becomes competitive only at longer time scales where larger-volume fluctuations are important. Accordingly, it would be very interesting to include the crystal
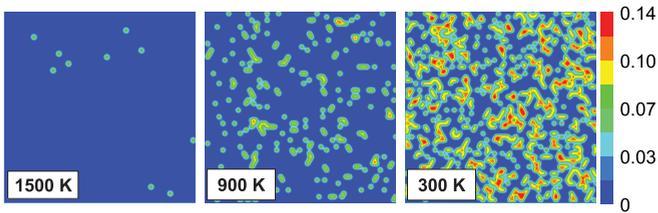
FIG. 5. (Color online) Morphology of ISRO packing density in the 2D lattice.

phase nucleation in our model in future work to investigate the competition between the non-space-filling ISRO growth and crystallization at different cooling rates.

V. CONCLUSION

In summary, we discover strong self-aggregation of ISRO in high-temperature $Zr_{1-x}Cu_x$ liquids. We provide direct evidence showing that the aggregation of ISRO significantly drives the system into dynamic arrest and nonergodicity.

Because of the non-space-filling characteristics of ISRO, its aggregation results in a stringlike network which expands the kinetic slowdown through a large portion of the system. When this network percolates, the dynamics in the entire system is arrested, leading to a glass transition. This mechanism for glass transition is illustrated by a lattice model which takes into account the effect of strong ISRO aggregation. Overall, our simulation results for different scales indicate that in $Zr_{1-x}Cu_x$ systems, this unique aggregation effect is the critical factor in the self-organization of ISRO and the slow dynamics that impede crystallization processes, ultimately leading to glass formation upon rapid cooling.

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