Correlation between structural relaxation and connectivity of icosahedral clusters in CuZr metallic glass-forming liquids

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The correlation between structural relaxation and the medium-range structures formed by icosahedral cluster packing in CuZr supercooled metallic glass-forming liquids was studied via molecular dynamics simulations. We find that compared to the amount of icosahedral clusters, the medium-range structures formed by icosahedral cluster packing play more important and controlling roles in the structural relaxation process of the supercooled liquids. The relaxation times of local structures depend exponentially on the connectivity of local structures. Despite the argument whether there is a specific connection between the static structure and dynamic property of glass formers in particle level, it does exist on larger length scale. Our results demonstrate that dynamical heterogeneity is indeed correlated with the medium-range static atomic structures in the supercooled glass-forming liquids.

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I. INTRODUCTION

Uncovering the structure-dynamics relationship of supercooled metallic glass-forming liquids is a crucial precondition for understanding the nature of glass transition, glass forming ability, and mechanical properties. The gradually established coherent structure during supercooling is the underlying mechanism of the changing liquids state.[1–6] It has been demonstrated that icosahedral short-range order is an important local structure motif for the dynamical slow down in metallic supercooled liquids, the stability of supercooled liquids against crystallization, and formation of metallic glasses (MGs).[7–10] On the other hand, medium-range order (MRO) has also been revealed to be quite important to the structure and dynamical properties in metallic glasses.[11–14] MRO typically covers a few hundreds of atoms, the length scale of β relaxation,[15–17] shear transformation zones,[18–21] and flow units,[22–24] which all have considerable impact on the fundamental relaxation behavior and mechanical properties of MGs.[25–28] However, the MRO and its correlated dynamical behavior in MGs still remains elusive, hampering the understanding of MG properties.

It has been shown that icosahedral clusters exhibit stronger self-aggregation tendency than other types of clusters and form a stringlike icosahedral network, the so-called MRO.[3,9,10] The self-aggregation tendency of icosahedral clusters is rather general in the CuZr metallic glass-forming alloy system.[9,10] These findings encourage us to expect that the medium-range structure formed by the icosahedral cluster packing may be a good spatial structure representative of MRO in MGs, so that we may examine the development of icosahedral MRO and their morphology in the supercooled metallic glass-forming liquids, and investigate its correlation with the structural relaxation and thermal stability of the supercooled liquids. It has been shown that CuZr metallic supercooled liquids with different Cu compositions exhibit different relaxation dynamics, which was found to be correlated with the population of icosahedral clusters.[37] The higher the concentration of icosahedral clusters, the lower the mobility, and vice versa. However, because both the degree of MRO and the population of icosahedral clusters change with Cu concentration,[3,9,10,29] it is not clear what role the MRO, formed by icosahedral cluster packing, played in the relaxation dynamics. To examine it, one should eliminate the effect of different population of icosahedral clusters on relaxation dynamics and single out the effect of MRO on relaxation dynamics.

In this paper, classical molecular dynamics (MD) simulations were performed with LAMMPS package[30] for CuZr metallic glass-forming alloys to examine the effect of icosahedral MRO on the structure relaxation and thermal stability of metallic supercooled liquids. Three samples were generated to possess very similar local structures characterized in terms of Voronoi tessellation[12,31] method. Graph theory was introduced to characterize the MRO formed by icosahedral cluster packing.[32–34] We quantitatively demonstrated that the connectivity of icosahedral clusters and their packing mode (coherent structure), i.e., the icosahedral medium-range order, play a key role in the structural relaxation process of supercooled glass-forming liquids, and the relaxation time depends exponentially on the connectivity k of local structures. This indicates that dynamical heterogeneity is indeed correlated with some medium-range static atomic structures.

The paper is organized as follows. In Sec. II, the detailed model and simulation method were presented. In Sec. III, the local structure feature and structure relaxation were compared in three samples. In Sec. IV, we analyzed the connectivity and node degree of icosahedral cluster packing to get deep insight in the structure relaxation properties. Finally, a conclusion was given in Sec. V.

II. MODEL AND METHOD

In our MD simulation, the model system of $Cu_{50}Zr_{50}$ metallic glass-forming alloy was adopted with a realistic embedded-atom method potential.[35] The system contains 10 000 atoms in a cubic box with periodic boundary conditions. In the process of sample preparation, it was first melted and

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equilibrated at $T = 2000$ K for 2 000 000 MD steps, then cooled down to 1000 K in NPT ensemble with different cooling rates to obtain three independent samples, S0, S1, and S2, respectively. During cooling, the sample size was adjusted to give zero pressure. These samples were then relaxed for 1 000 000 MD steps at $T = 1000$ K. The MD step is 1 fs. The first 5 000 configurations in 50 ps were used for the analysis of structure and dynamical properties.

III. COMPARISON OF LOCAL STRUCTURES AND RELAXATION

First, we compared the structure features of three samples. The local atomic structures in the supercooled liquid samples was analyzed by the Voronoi tessellation method. Figure 1 shows the population of the Voronoi clusters whose fractions are more than 0.01 in three samples. It is clearly seen that the types of the most populated Voronoi clusters are almost the same in three samples. Moreover, for the same type of Voronoi cluster, the fraction in each sample is quite close or even almost the same. This indicates that the local structures are almost the same in three samples. In addition, we identified that these three samples also exhibit the same total pair correlation functions as shown in Fig. 1(d), demonstrating the similar global structures in three samples.

Next, we compared the relaxation dynamics in three samples. To characterize the relaxation dynamics, we investigated the self-intermediate scattering function (SISF) of Cu atoms in three samples,[36–38]

$$\mathbf{F}_s^a(q,t) = \frac{1}{\mathrm{N}_a}\sum_{j=1}^{\mathrm{N}_a}\langle\exp\{i\vec{q}\cdot[\vec{r}_j(t)-\vec{r}_j(0)]\}\rangle, \qquad (1)$$

where N_a denotes the number of atoms of element a. $\vec{r}$ is the position of each atom. q is the wave vector and usually fixed at $q_{\max} = |\vec{q}|$, which corresponds to the first peak of the partial structure factor of element a. In general, the time scale of the relaxation dynamics can be characterized by the α-relaxation time τ_α, which is defined as the time where the SISF decays to e^{-1} of its initial value.[36,37] Figure 2(a) shows the SISF as function of time for S0, S1, and S2, respectively. It can be seen that all SISFs of three samples show a nonexponential decay behavior, revealing the existence of additional secondary relaxation process. In structure scenario, the nonexponential decay of SISF can be envisioned by the rattling motion of a particle in the cage formed by its surrounding neighbors, and the breaking of local atomic clusters.[37,38] As shown in Fig. 2(a) three curves collapse together in a very short-time scale (the ballistic regime). However, in the α relaxation regime, three curves split into very different decay rates, which implies that the cooperative motion of atomic clusters in α relaxation process is quite different in three samples. In addition, we also calculated the mean square displacements (MSD) of all atoms for three samples as shown in Fig. 2(b). It is clearly seen that MSD in α relaxation regime are also different in three samples.

As mentioned above, CuZr metallic supercooled liquids with different compositions have been found to exhibit different relaxation dynamics behavior of SISF, where the different population of icosahedral clusters is found to be responsible for the different decay rates of SISF.[37] Thus the relaxation dynamics in three samples should be the same, since the populations of the local structures are almost the same as shown in Fig. 1, especially the fractions of the icosahedral clusters in three samples are almost the same, 0.034 (S0), 0.031 (S1), and 0.030 (S2). However, Fig. 2 shows quite different decaying rate of SISF in α relaxation regime. This implies that apart from the effect of population of icosahedral clusters on relaxation dynamics, there exists some other effects. It is naturally expected that the connectivity or packing of icosahedral clusters might be different in S0, S1, and S2 which could be the origin of the different relaxation of SISFs in three samples. Therefore we will investigate the connectivity of icosahedral clusters in three samples.

IV. CONNECTIVITY AND NODE DEGREE OF ISRO

To characterize the connectivity of icosahedral clusters in a system, we introduced the graph theory. In this scheme, the central atom of an icosahedral cluster is treated as a node, and two nodes are considered to be connected if they are the nearest neighbors, that is, the corresponding two icosahedral clusters are interpenetrated and share at least five nearest-neighbor atoms (or two icosahedral polyhedra are

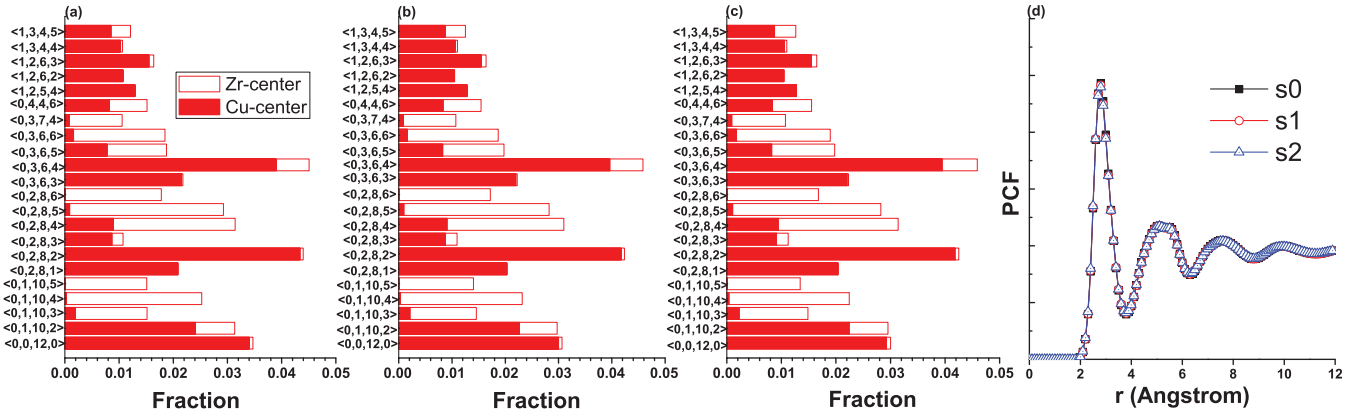

FIG. 1. (Color online) Population of Voronoi polyhedra in liquid $Cu_{50}Zr_{50}$ at 1000 K in samples of S0 (a), S1 (b), and S2 (c), respectively. (d) Total pair correlation functions of three samples at 1000 K.

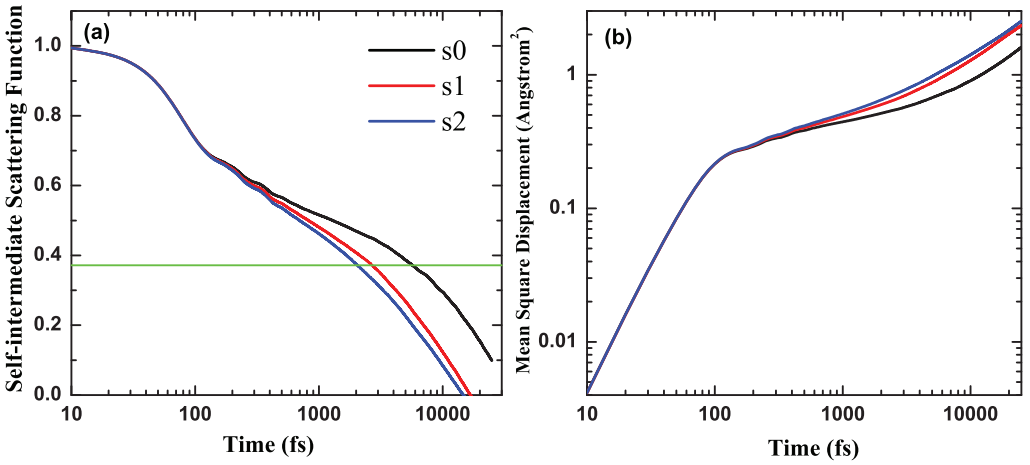

FIG. 2. (Color online) (a) Self-intermediate scattering function (SISF) of Cu for three CuZr supercooled liquids (1000 K). The wave vector is $q_{\max} = |\vec{q}|$, the first peak of the partial structure factor of Cu. The α-relaxation time τ_α is defined as the time when the SISF decays to e^{-1} of its initial value (marked with the green horizontal line). (b) Mean-square displacements of all atoms in three samples.

connected by sharing a pentagon face), so that we may search all connected icosahedral clusters in a system. Based on this scenario, the degree of a node can be defined as the number of nodes connected to it.[32–34,39] The spread of node degree is characterized by a distribution function $P(k)$, which gives the probability that a randomly selected node has exactly k connected neighbor nodes. As shown in Fig. 3, S0 possesses more possibility distribution in large k values, which indicates the icosahedral clusters in S0 are connected more tightly. The average value $\langle k \rangle$ calculated by $\sum kP(k)$ would be a good indicator to show the tightness or connectivity of connected icosahedral clusters. If one examines the average value of k over the annealing time, they show a clear correlation with the α-relaxation times in three samples (see Table in Fig. 3). The larger the value of $\langle k \rangle$, the more tightly and

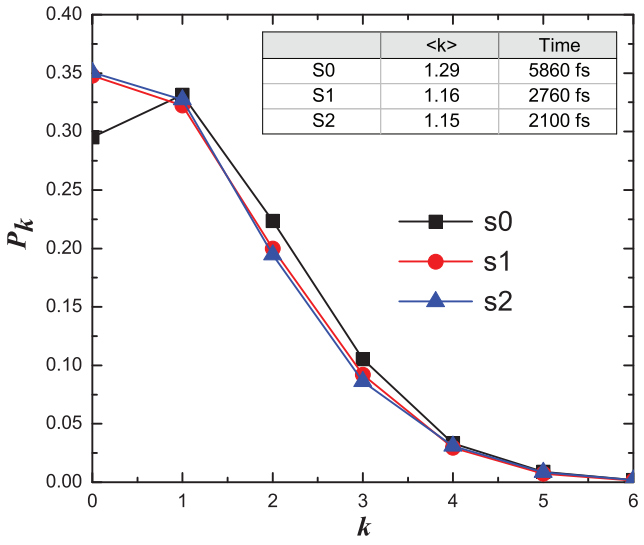

FIG. 3. (Color online) Degree distribution of icosahedral clusters in three samples. The inset table shows the average value of connectivity $\langle k \rangle$ of icosahedral clusters in three samples and the corresponding α-relaxation time τ_α.

compact the icosahedral clusters are connected with each other, and the longer time it takes for the sample to lose memory about its initial state. In this sense, we emphasize that, not only the population of the icosahedral clusters, but more importantly, the MRO formed by the icosahedral cluster packing plays a controlling role in the relaxation dynamics process of supercooled glass-forming liquids. Inspired by previous work,[9,13,14] a self-similar fractal structure would be a good physical picture to describe the icosahedral clusters packing scheme.

To get more detailed relationship information between atomic structural relaxation and the connectivity of icosahedral clusters, we calculated SISFs of the atoms belonging to clusters with different connectivity of k values. The results for sample S0 are shown in Fig. 4(a). The overall behavior of SISFs of the atoms with different k is similar to that of all Cu atoms. However, for the atoms with k larger than 5, SISFs exhibit a plateau, which corresponds to slow β relaxation and indicates that the motion of these atoms is highly confined by their nearest-neighbor atoms, showing a significant cage effect, quite similar to the relaxation behavior of a glass-forming liquid approaching to glass transition. It is clearly demonstrated that even in the supercooled liquid at $T = 1000$ K close to melting temperature, some specific local structures exhibit significant slow β relaxation. Figures 4(b) and 4(c) show the SISFs of atoms with different connectivity of k in S1 and S2, indicating that even in S1 and S2, the relaxation of local structures with different environments is correlated with their connectivity. All these results reveal that the larger the connectivity of icosahedral clusters, the longer the relaxation time $\tau(k)$.

Figure 4(d) explicitly shows that the relaxation time $\tau(k)$ of atoms with different k exhibits a linear relation with the connectivity of k in semi-log plot, indicating an exponential dependence of relaxation time on k, that is, $\tau(k) \sim \exp(k)$. To make k dimensionless in exponential function, it could be scaled with a factor that possesses the same dimension as k. For an icosahedral cluster, the maximum number of node degree is 12, so that it is natural to scale k with 12. On the other hand,

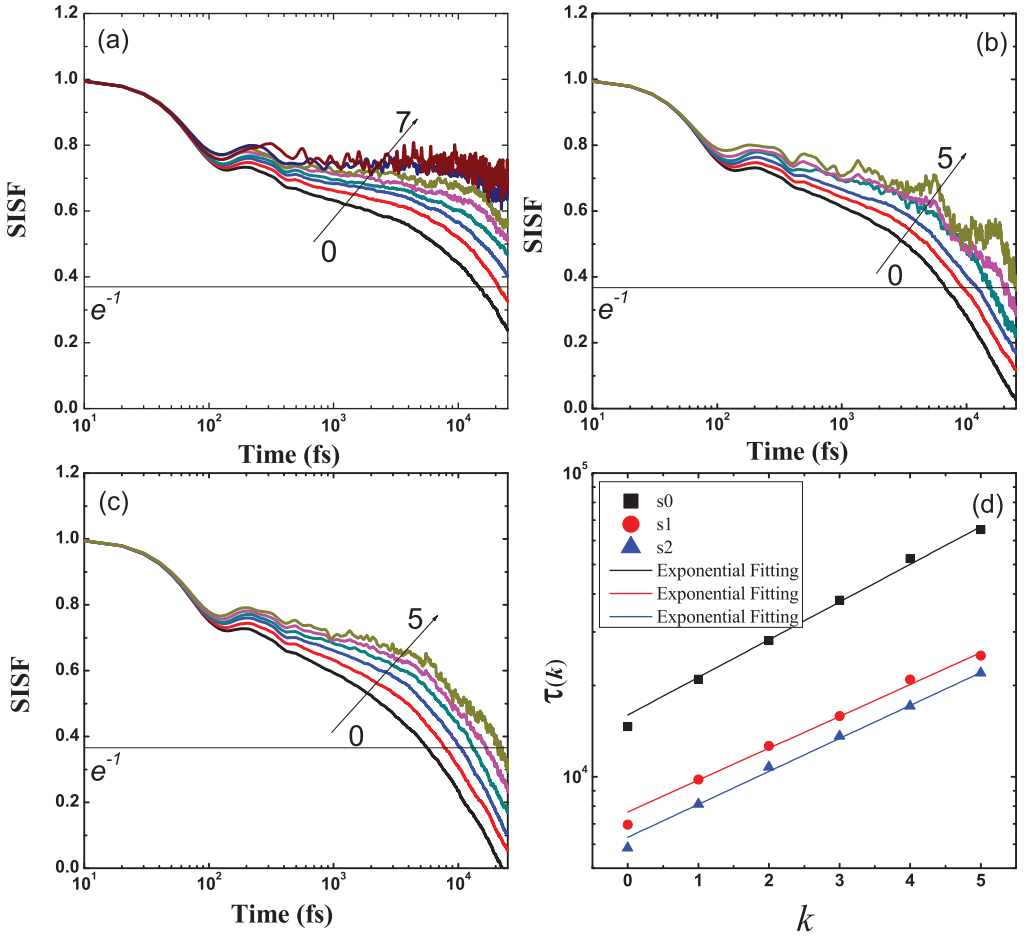

FIG. 4. (Color online) The self-intermediate scattering functions (SISFs) of atoms solely belonging to icosahedral clusters characterized by different degree k for samples S0 (a), S1 (b), and S2 (c). Because of very low population of atoms with k larger than 5, the SISF curves of $k > 5$ in samples S1 and S2 are very noisy and not shown here. (d) k-dependent relaxation time $\tau(k)$ of atoms with different connectivity for three samples. For sample S0, $\tau(k)$ of $k = 2$, 3, 4, and 5 were extracted by extrapolating the SISF curves using the Kohlrausch-Williams-Watts stretched exponential function.

$\tau(k)$ can be scaled with the average relaxation time τ_α which can be measured in experiments. Thus we finally obtained

$$\frac{\tau(k)}{\tau_\alpha} = A \exp\left(R_0 \frac{k}{12}\right), \tag{2}$$

where A and R_0 are free parameters. Apparently, A is a factor between the average relaxation time τ_α and that of isolated icosahedral clusters, and R_0 is an correlation coefficient of the relaxation times and connectivity of k. Therefore A and R_0 vary with samples prepared in different processes. Figure 5 clearly demonstrates that the scaled data of $\tau(k)/\tau_\alpha \sim k/12$ in three samples collapse together, following a linear behavior in semi-log plot, which can be well fitted by Eq. (2) with $A \approx 2.83$ and $R_0 \approx 3.12$. Therefore Eq. (2) is universal and the relaxation time of local structures depends exponentially on their connectivity.

In more general cases, icosahedral clusters are not the only representative structure unit in metallic glass-forming liquids. In some metallic glass-forming liquids, some other types of clusters play important roles in relaxation dynamics, too.[3]

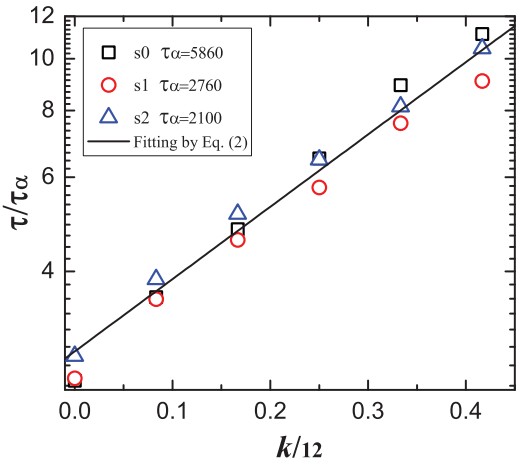

FIG. 5. (Color online) Semi-log plot of scaled relaxation time $\tau(k)/\tau_\alpha$ with scaled node degree $k/12$ in samples S0, S1 and S2. The solid line is fitting curve by using Eq. (2) with fitting parameters A and R_0 are 2.83 and 3.12, respectively.

Therefore, it is necessary to generalize Eq. (2) to more general cases. Based on the above analysis, a more general equation for the relationship between relaxation time and some specific local structures could be expressed as

$$\frac{\tau(k)}{\tau_\alpha} = A \exp\left(R_0 \frac{k}{k_0}\right) \tag{3}$$

to describe the $\tau(k) \sim k$ relationship for various atomic clusters, as well as the icosahedral cluster. In Eq. (3), k_0 is a geometrical factor of a type cluster associated with the total number of faces in the cluster polyhedron. For example, $k_0 = 12$ for icosahedral clusters. Equations (2) and (3) clearly show that the relaxation time of local structures is correlated with their local environments, varying exponentially with the connectivity of a specific local structure unit. This may indicate that the dynamical heterogeneity is closely related to the structural heterogeneity.

V. CONCLUSION

In conclusion, we investigated the structural relaxation and thermal stability of supercooled metallic glass-forming liquids by using MD simulation. The result reveals that the icosahedral medium-range order fundamentally influences the atomic-level structural relaxation and the thermal stability of the supercooled liquids. Even the systems have the same distribution of the local structures, the different connection or packing of the icosahedral clusters will lead to different relaxation behavior of the liquids. In the icosahedral MRO regime, we find that a more tight and compact connectivity of the icosahedral clusters will make the supercooled liquids evolve into another metabasin state more difficultly, thereby the system has a longer lifetime against crystallization. Our results quantitatively confirm that not only the amount of the local icosahedral clusters, but their coherent structure plays more important and controlling role in the relaxation process and the thermal stability of supercooled metallic glass-forming liquids. Correlation between the static structure and dynamic property of glass formers does exist on some larger length scale. Our findings may promote a new structural perspective on the relaxation process and stability of the metallic glass-forming liquids.

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