Structural Relaxation in Supercooled Liquids

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Relaxation behavior of structural change at the atomic cluster level in supercooled liquids during isothermal annealing processes is investigated for a model alloy system by using molecular dynamics simulations. The simulation results show that the number density of icosahedral clusters increases with the annealing time. Moreover, the number density of icosahedral clusters, the structural relaxation time, and the atomic diffusivity strongly correlate with the packing density of the supercooled liquids for many kinds of systems of alloying components with a variety of atomic size ratios and heats of mixing. This suggests that the packing density would be a good probe to estimate the stability of supercooled liquid phases and the glass-forming ability of the system.

Keywords: metallic glasses, supercooled liquid, computer simulation, rapid solidification, diffusion

1. Introduction

The bulk metallic glasses\textsuperscript{1,2} are characterized by the existence of a wide range of stable supercooled liquid region in the system. However, the physical origin of the stability of supercooled liquid phases is not clarified completely, although some possible ideas have been suggested,\textsuperscript{3,4} that is, a difficulty of atomic rearrangement due to a low atomic mobility originated from a dense random packing in the liquid phases with a proper combinations of alloying elements, and a necessity of atomic rearrangement on a long-range scale for crystallization due to a difference between the local atomic configurations in the liquid phase and those in the crystalline phase. Therefore, it is very useful if we could make it clear what type of local atomic configuration grows in the supercooled liquid phases of glassy alloy systems by using the computer simulations.

Among miscellaneous simulation methods, the molecular dynamics (MD) simulation is a powerful tool to clarify the structural change in glassy materials at the atomicistic level. However, under the nowadays computer power, the typical time scale that we can handle in the framework is the order of nanoseconds at its maximum. This fact leads us to difficulties in investigating the relaxation behavior of the supercooled liquid phases of real metallic glassy systems, which usually have a much longer relaxation time compared to nanoseconds. Therefore, in this study, we employ a model alloy system, where a typical relaxation time scale in the supercooled liquids of good glass formers is almost within the reach of MD simulations. For the model system, by calculating the atomic mobility and the structural change in the relaxation stage of the supercooled liquids, we clarify the relation of the local atomic structure to the stability of the supercooled liquid phase as well as to the glass-forming ability (GFA) of the system.

2. Computational Methods

2.1 Interatomic potentials

In the MD scheme, we can calculate the atomic trajectories by supposing a functional form of the interatomic potential and by solving the equations of motion numerically. In this study, we employ a model alloy system, where the interaction between the elements $i$ and $j$ is supposed to be described by the 8-4 Lennard-Jones (LJ) potential:

$$V_{ij}(r) = e_{ij}[(r_{ij}/r)^8 - 2(r_{ij}/r)^4],$$

which is proved\textsuperscript{5,6} to be adequate for metallic systems. The potential has the minimum $-e_{ij}$ at the distance $r_{ij}$, which can be considered as the amount of chemical interaction and the atomic size, respectively. We here investigate binary systems and ternary systems composed of elements 1, 2, and 3. For simplicity, when we deal with binary systems, we assume that $r_{11} = 1$, $r_{22} \leq 1$, and $e_{12} = e_{21} = 1$. Then we can vary the concentration $x_2$ of the element 2, the atomic size ratio $r_2 = r_{22}/r_{11}$, and the heat of mixing $\Delta H$ defined as $\Delta H = (e_{11} + e_{22})/2 - e_{12}$ by changing $r_{22}$ and $e_{12}$ independently with preserving $r_{12} = (r_{11} + r_{22})/2$. For ternary systems, we do not use the above restriction on the parameters. All the physical quantities are expressed in the above units throughout this paper.

2.2 Simulation procedures

We consider a system with 4000 atoms under a periodic boundary condition. The equilibrium melting temperature $T_m$ of a monatomic system of the element 1 with $e_{11} = 1$ is around 0.55 in the above-mentioned units. As starting liquid phases, we first prepare binary or ternary mixtures at $T = 0.7$. We then simulate rapid solidification processes or isothermal annealing processes by controlling the temperature and the pressure of the simulation system. The temperature of the system is controlled by scaling the atomic momenta and the pressure of the system is kept zero by using the constant-pressure scheme.\textsuperscript{6} We can examine the phase properties during the simulated process by monitoring the observables such as the atomic volume, the atomic enthalpy, the radial distribution function, and the atomic configuration, as will be exemplified in the next section.

Here we should make a note about the typical order of time scale handled in this MD study. Supposed that the LJ units are identified with a typical mass, atomic radius, and melting point of metallic elements, then the unit of time becomes around $4 \times 10^{-13}$ s and that of cooling rate becomes around $5 \times 10^{15}$ K/s.
3. Results

3.1 Growth of icosahedral order in glass transition

Figure 1 shows the change of the atomic volume of the \((r_2, x_2) = (0.8, 0.5)\) binary system during a rapid cooling process from a liquid phase with a cooling rate \(1 \times 10^{-4}\), which amounts to \(5 \times 10^{11}\) K/s for a typical metallic system. The discontinuity at \(T = 0.28\) in the slope of the temperature dependence of the volume corresponds to a liquid-to-glass transition as marked in the figure by \(T_g\). The glassy nature of the solidified phase, which is depicted in the inset of Fig. 1, is confirmed by calculating the radial distribution and analyzing the atomic configuration.

In the systems where the atomic size difference between the constituent elements is less than 20%, the icosahedral clusters are the most probable candidates for a structural unit in the glassy phases. This point is supported both by the experiments\(^7\) and the simulations.\(^8\) Therefore, we investigate the local symmetry around the individual atoms by using the Voronoi polyhedra analysis,\(^9\) and clarify the cluster structure with paying a special attention to the icosahedral clusters.

In the Voronoi polyhedra analysis, the shape of the Wigner-Seitz cell or the Voronoi polyhedron of each atom represents the local symmetry and is indexed\(^10\) by the set \((n_1, n_2, n_3, n_6)\), where \(n_i\) is the number of the \(i\)-edged faces on the cell surface. We can identify the icosahedral clusters by the atoms that have the Voronoi index \((0, 0, 12, 0)\) and their neighbors. Based on this identification, we can specify the positions of the icosahedral clusters and their spatial distribution. Figure 2 shows an example of a bunch of the icosahedral clusters found in the glassy phase of the \((r_2, x_2) = (0.8, 0.5)\) system. The dark-gray spheres and the light-gray spheres denote the atoms of the element 1 (atomic size: 1.0) and those of the element 2 (atomic size: 0.8), respectively.

![Figure 1](image1.png)  
**Fig. 1** The time evolution of the atomic volume of the \((r_2, x_2) = (0.8, 0.5)\) binary system under rapid solidification with a cooling rate \(1 \times 10^{-4}\). The inset shows a snapshot of the atomic configuration of the solidified phase at \(T = 0.001\), where the atoms of element 1 and 2 are depicted by the dark-gray and the light-gray spheres, respectively.

![Figure 2](image2.png)  
**Fig. 2** A snapshot of a bunch of three interconnected icosahedral clusters found in a glassy phase of the \((r_2, x_2) = (0.8, 0.5)\) system. The dark-gray spheres and the light-gray spheres denote the atoms of the element 1 (atomic size: 1.0) and those of the element 2 (atomic size: 0.8), respectively.

![Figure 3](image3.png)  
**Fig. 3** The temperature dependence of the number \(N_{\text{icos}}\) of the icosahedral clusters in of the \((r_2, x_2) = (0.8, 0.5)\) binary system during rapid solidification with a cooling rate \(1 \times 10^{-4}\).
icosahedral clusters are depicted by the white spheres. Both in the strongly supercooled liquid phases ($T = 0.40$ and 0.35) and the glassy phase ($T = 0.10$), some spatial inhomogeneity exists in the distribution of the icosahedral clusters, which indicates a ‘clustering’ behavior of the icosahedral clusters. This clustering feature of a medium-range scale has also been found in another series of MD simulations\textsuperscript{13} for the Ti–Al amorphous alloys.

### 3.2 Structure evolution in supercooled liquids

In the strongly supercooled liquid phases, a typical time of structural relaxation becomes long and the atomic configuration hardly reaches the fully relaxed state in the rapidly quenching process. Here we shall investigate the relaxation behavior in such supercooled liquids by focusing on the icosahedral ordered structure. Figure 5 shows the time evolution of the atomic enthalpy, the atomic volume, and the number of icosahedral clusters of the supercooled liquids that are isothermally annealed at $T = 0.3$ from initial supercooled liquid states at $T = 0.45$. The closed symbols and the open triangles correspond to the $(r_2, x_2) = (0.82, 0.5)$ system and the $(r_2, x_2) = (0.9, 0.5)$ system, respectively. In the former system, the structural relaxation in the supercooled liquid phase is obviously recognized by the decrease of the enthalpy and the volume, and it is always accompanied with the increase of the number of icosahedral clusters in both systems. Even at the end of the annealing time, the enthalpy of the former system continues to go down and the number of the icosahedral clusters continues to grow, which indicates that the system is still in a structural relaxation period. On the other hand, the latter system seems to reach a quasi-equilibrium state after $t = 500$. Thus we can consider the time dependence $N_{\text{ico}}(t)$ of the number of icosahedral clusters as a probe for the relaxation behavior. We here suppose that the relaxation has an exponential dependence as

$$N_{\text{ico}}(t) = (N_{\text{ico}}(0) - N_{\text{ico}}^0) e^{-t/t_0} + N_{\text{ico}}^0,$$  \hspace{1cm} (2)

where $t_0$ is the relaxation time and $N_{\text{ico}}^0$ is the equilibrium number of the icosahedral clusters. By fitting the simulation data to eq. (2), we can estimate the relaxation time $t_0$ and the equilibrium number $N_{\text{ico}}^0$ of the icosahedral clusters in the supercooled liquids.

When we define the packing density of liquid phases by the volume fraction of atoms that are taken as spheres with their LJ radii, we can find\textsuperscript{14} a strong correlation between the packing density of the supercooled liquid phase and its stability. In this context, we shall clarify the relation between the packing density $\rho$ and the number $N_{\text{ico}}^0$ of the icosahedral clusters in the supercooled liquids, as well as the relation between the packing density and the relaxation time $t_0$. We calculate $\rho, N_{\text{ico}}^0$, and $t_0$ by the isothermally annealing data of the supercooled liquids at $T = 0.4$ for the $r_2 = 0.8$ binary systems with varying $x_2$ from 0.1 to 0.9. The results are shown in Fig. 6, where we can find a strong tendency that the icosahedral order is higher and the relaxation time is longer in the supercooled liquids with a higher packing density.
3.3 Atomic mobility in supercooled liquids

In supercooled liquids with a considerably high packing density, the atomic mobility would be highly suppressed, which might lead to an enhancement of stability of the supercooled liquid phase against crystallization. From this point of view, we shall investigate the relation between the packing density and the atomic mobility in the supercooled liquids. The atomic diffusion coefficients can be easily calculated from the mean square displacement of atoms, because the positions of any atom is exactly known at any moment in the MD simulations.

For another series of the \( r_2 = 0.8 \) binary systems with varying \( x_2 \) from 0.1 to 0.9, the atomic diffusivity in the supercooled liquids at \( T = 0.4 \) is calculated. The results are plotted in Fig. 7 as a function of the packing density \( \rho \) of the supercooled liquids. As expected, a strong correlation between the packing density and the atomic mobility is observed, which indicates that a slight change in the packing density would cause a drastic decrease in the atomic mobility.

4. Discussion

We have shown that the structural relaxation in the supercooled liquids of a model alloy system proceeds with the increase of the icosahedral order. Moreover, the increase of the icosahedral order is always accompanied with the increase of the atomic packing density, which causes the decrease of the atomic mobility as well as the elongation of the relaxation time. This change in the transport properties
due to the change of atomic configurations should enhance the stability of the supercooled liquid phases, although the stability of the supercooled liquid phases against crystalline phases is not determined only by such dynamical aspects, but also by the thermodynamical aspects such as the driving force for crystallization and by other aspects such as the structural similarity between the atomic configurations in the liquid phases and the crystalline phases.\footnote{14} For this simple alloy model, it is confirmed that the packing density should be a good indicator to estimate the stability of the supercooled liquid phases in the preceding MD study.\footnote{14} Since the phase stability of the supercooled liquids is directly connected with the glass-forming ability (GFA) of the system, we shall discuss the effect of the atomic size ratio and the heat of mixing between alloying elements on the GFA and its relation to the local atomic configurations in the supercooled liquids.

4.1 Geometrical and chemical effect on GFA

Firstly, we estimate the effect of the atomic size ratio and that of the heat of mixing between alloying elements on the GFA by direct simulations of rapid solidification processes for the model binary alloy systems. Figure 8(a) shows the effect of the atomic size ratio on the GFA, where the glass-forming ranges under cooling rates varying from $1 \times 10^{-3}$ to $1 \times 10^{-5}$ for the binary systems with fixing as $\Delta H = 0$ and varying $(r_2, x_2)$ are denoted by the shaded regions. The darker shaded region corresponds to the slower cooling rate. A drastic enhancement of the GFA is found in the systems with negative heats of mixing as shown Fig. 8(b), which agrees with one of the well-known empirical rules\footnote{3} well. On the other hand, for the binary systems with fixing as $r_2 = 0.95$ and varying $(\Delta H, x_2)$, no noticeable changes are observed in the glass-forming ranges compared to the monatomic system. However, for considerably size-mismatched systems with fixing as $r_2 = 0.95$ and varying $(\Delta H, x_2)$, some enhancement of the GFA is found in the systems with negative heats of mixing as shown Fig. 8(b), which agrees with another one of the empirical rules. However, the enhancement of the GFA in this case is so small that no glass-forming ranges are observed for cooling rates less than $2 \times 10^{-4}$.

4.2 Geometrical and chemical effect on the icosahedral order

Next we try to understand the origin of the above enhancements of the GFA due to the atomic size ratio and the negative heat of mixing by investigating the local structure changes in the supercooled liquids at the cluster level. Figure 9 shows the change of the number $N_{ico}$ of the icosahedral clusters in the supercooled liquid phases at $T = 0.40$ for the $x_2 = 0.5$ binary systems under a variation of the atomic size ratio $r_2$ from 1.0 to 0.80. The considerable increase of $N_{ico}$ with the increase of the atomic size mismatch indicates the enhancement of the stability of the supercooled liquid phases due to a growth of the icosahedral order.

Before we try to estimate the effect of the heat of mixing on the local atomic configurations in the supercooled liquids, we should take into account the change of energy scale due to the variation of $e_{ij}$‘s. For example, if we compare a monatomic system with $e_{ii} = 1$ with another monatomic system with $e_{jj} = 2$, then the properties of the supercooled liquid at $T = 0.4$ of the former system should be compared with those of the supercooled liquid at $T = 0.8$ of the latter system to adjust the conditions of the order of supercooling equivalently, because the melting temperature becomes twice in the latter system. Therefore, as an index of the typical energy scale of the system, we introduce the effective melting temperature $T_m^{eff}$ of the randomly mixed state for multi-component systems as

$$ T_m^{eff} = T_m^0 \sum_{i,j} x_i x_j e_{ij}, $$

where $i$ and $j$ denote the atom species, and $T_m^0$ is the melting temperature for a monatomic system with $e_{ii} = 1$. Here we consider that the supercooled liquids at $T = 0.4T_m^{eff}/T_m^0$ of the corresponding system would have the same order of supercooling as that of the supercooled liquids at $T = 0.4$ of the systems with $e_{ij} = 1$. In other words, supposed that the
effective temperature $T^{\text{eff}}$ is defined as $(T_m^0 / T_m^{\text{eff}})T_e$, the same order of supercooling would be realized at the same $T^{\text{eff}}$. Thus we try to estimate the effect of the heat of mixing by comparing the properties of the supercooled liquids at $T^{\text{eff}} = 0.4$ for systems with different values of $\epsilon_{ij}$.

For the three sets of the $x_2 = 0.5$ binary systems of different atomic ratios with $r_2 = 1.0, 0.95,$ and $0.90$, we can vary the heat of mixing $\Delta H$ from 0 to $-0.3$ by changing $\epsilon_{12}$. In each system, we calculate the number $N_{\text{ico}}$ of the icosahedral clusters in the supercooled liquid phases at $T^{\text{eff}} = 0.40$. The results are shown in Fig. 10. For the system of the same atomic radius, the change of the local structure due to the negative heat of mixing is small, while the icosahedral order grows with the amount of the negative heat of mixing in the systems with a considerable atomic size difference.

These results can be understood in a simple energetic point of view. It is shown$^{11}$ that the energy of icosahedral clusters would be minimized when the atomic size ratio of the centered atom of the cluster to its neighboring atoms is around 0.9 or less. Therefore, alloying the size-mismatched elements makes the energy of icosahedral clusters lower, while alloying the elements with negative heats of mixing causes an enhancement of the driving force to create such low energy clusters, in which the size-mismatched elements are neighboring. That is why the effect of the heat of mixing appears only if it is combined with the effect of the atomic size ratio.

One note should be added here. The above estimation is only based on the energy of a single icosahedral cluster, and if we consider those of bunches of the icosahedral clusters such as shown Fig. 2, the estimation would become highly complicated and the results might be changed. However, we think that the essential roles of the geometrical factor and the chemical factor derived from the above speculation should not be changed.

### 4.3 Packing density of supercooled liquids and GFA

As shown in the section 3, there is a strong correlation between the icosahedral order and the packing density of the supercooled liquids. Moreover, it has been already demonstrated$^{14}$ that the packing density would be a good indicator of the stability of the supercooled liquid phases and the GFA of the system. From this viewpoint, we calculate the packing density of the supercooled liquids at $T^{\text{eff}} = 0.50$ for the binary systems shown in Figs. 8(a) and 8(b). The results are shown in Figs. 11(a) and 11(b). The darker shading corresponds to the higher packing density, and the colors of shading are common in both figures. Figures 11(a) and 11(b) show a considerable agreement to the directly estimated GFA shown in Figs. 8(a) and 8(b). Moreover, Fig. 11(a) predicts the locus of the alloy combination of the best glass-former, which can never be derived from the direct simulations of rapid cooling processes due to the lack of computational power.

In the same manner, we also calculate the glass-forming ranges for a ternary system with atomic size ratio $(r_{11}, r_{22}, r_{33}) = (0.89, 1.0, 1.12)$ and with keeping no heats of mixing as $\epsilon_{ij} = 1$ by direct simulations of rapid solidification, and compare the results with the distribution of the packing density of supercooled liquid phases calculated at $T^{\text{eff}} = 0.50$ in the system. The results are shown in Figs. 12(a) and 12(b), where we can find a considerable agreement between the distribution of the GFA and that of the packing density of the supercooled liquids.

It is interesting if we compare the prediction of the GFA shown in Fig. 12(b) to experimental observations$^{15,16}$ of the ternary systems with similar combination of atomic size ratios, for example, the Cu–Al–Zr system and the Ni–Al–Zr
system, in both of which a sign of the icosahedral order in the supercooled liquid phase and the glassy phase is experimentally observed. \( ^{8,17} \) Although our prediction is based on a quite simple model, in which only the atomic size effect is taken into account and the interaction is described by the two-body LJ potential, the main tendency of the GFA considerably agrees with the experimental results. It indicates that the atomic size effect should be the primary factor to acquire a high GFA in metallic systems.

5. Summary and Conclusion

By performing the MD simulations for a model alloy system, we have clarified that the icosahedral order grows during the structural relaxation in the supercooled liquids and that the growth of the icosahedral order is always accompanied with the increase of the packing density, the elongation of the relaxation time, and the decrease of atomic mobility in the supercooled liquids. These results indicate that the stability of the supercooled liquid phases would be enhanced by the increase of the packing density, which is confirmed by the comparison between the packing density of the supercooled liquids and the GFA of the model system.

Of course, in real alloy systems, the local atomic configurations and the shapes of basic clusters of glassy states might be different from those of this model, and be changed variously depending on the combination of alloying components. For example, a trigonal prism shaped cluster is another candidate of the structural unit in glassy phases for metal-metalloid systems. \( ^{3} \) However, in any glassy alloy system, there should exists some basic units of clusters, and the essential feature in the structural relaxation in the supercooled liquid phases, that is, a low atomic mobility and a long relaxation time due to growing of the density of the basic clusters and the packing density, should be the same as that found in this simple model system studied here.

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