The role of local-geometrical-orders on the growth of dynamic-length-scales in glass-forming liquids

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The precise nature of complex structural relaxation as well as an explanation for the precipitous growth of relaxation time in cooling glass-forming liquids are essential to the understanding of vitrification of liquids. The dramatic increase of relaxation time is believed to be caused by the growth of one or more correlation lengths, which has received much attention recently. Here, we report a direct link between the growth of a specific local-geometrical-order and an increase of dynamic-length-scale as the atomic dynamics in metallic glass-forming liquids slow down. Although several types of local geometrical-orders are present in these metallic liquids, the growth of icosahedral ordering is found to be directly related to the increase of the dynamic-length-scale. This finding suggests an intriguing scenario that the transient icosahedral connectivity could be the origin of the dynamic-length-scale in metallic glass-forming liquids.

After many decades of extensive studies, there is still no generally accepted and fundamentally understood reason for the dramatic growth of structural relaxation time when glass-forming liquids cool towards the glass-transition temperature⁴⁻⁶. Numerous experiments and molecular dynamics simulation results suggest that the occurrence of cooperative process in glass-forming liquids; this in turn implies the presence of cooperative rearranging regions (CRR) over a length scale. The CRR was first invoked by Adam and Gibbs in their description of the dynamics of glass-forming liquids³. The Adam-Gibbs theory connects relaxation time with growing length scales and thermodynamics via configurational entropy. The configurational entropy implies the atomic ordering over certain length scales in glass-forming liquids can be of static and dynamic nature. Recent experimental and theoretical research has been focused on growing static and dynamic length scales when glass-forming liquids cooled towards the glass-transition temperature⁴⁻⁶.

A variety of experiments and numerical studies have shown that the local dynamics in glass-forming liquids is spatially heterogeneous⁷⁻¹². Dynamic heterogeneity (DH) is the term used to describe this aspect, and the presence of DH in liquids has been numerically characterised by studying the non-Gaussian distribution of the displacement of individual particles during a fixed time interval¹³. Experiments and numerical results have shown that particles with similar mobilities tend to form clusters, which resulted in the existence of spatial correlations of local mobility¹⁴,¹⁵. A well-defined clusters of cooperatively moving localised fast particles have been seen in colloids near the glass-transition¹⁴. By simulation, clusters of cooperatively moving particles with string-like structures have been identified¹⁵. These observations clearly indicate that the one or more length-scales, which characterizes the spatial correlation of local mobility, can be obtained by analysis of the size distribution of these clusters. In practice, a qualitative information on dynamic length scale can be derived by identifying slow moving particles by using a cut-off displacements and which are spatially correlated¹⁶. Consequently, the quantitative information about the dynamic length scale of DH has been obtained from multi-point correlation functions¹⁷.

On the other hand, the static structure factor measured at different temperatures of a glass-forming liquid does not indicate any obvious structural change, although the dynamics can be several orders of magnitude different¹⁸,¹⁹. To the contrary, the static length scales in glass-forming liquids computed by different methods, such as point-to-set correlation²⁰, configurational entropy⁴, and bond-orientational order²¹ demonstrate
that it is of the order of interparticle distance and grows by a factor of 2 to 9 as the glass-forming liquids cool towards a mode-coupling critical temperature, $T_c$. Studies on polydispersed glass-forming liquids and a two-dimensional metallic liquids have demonstrated that the static and dynamic are coupled. However, some other studies have shown that the static length scale increases at a slower pace than the dynamic-length-scale in decreasing the temperature of glass-forming liquids. The growth of local geometrical-orders (LGOs) is also argued to be the cause of the rapid rise in the relaxation time of cooling glass-forming liquids. In three-dimensional systems of monodispersed hard-spheres, the icosahedron is the most locally-preferred structure and increasing its number while cooling is believed to be linked directly to vitrification. In multicomponent, polydispersed metallic systems, an increasing number of five-fold symmetry clusters is reported to be the reason for their better glass-forming ability (GFA). However, the role of specific LGO on the growth of dynamic-length-scales is not yet understood, although numerous studies have shown rapid growth of dynamic-length-scales and LGOs on cooling glass-forming liquids towards the glass-transition temperature $T_g$. In this article, we studied a ternary metallic glass-forming system to understand whether the growth of any specific LGO correlates with the increase of dynamic-length-scales by using quasielastic neutron scattering (QENS) and molecular dynamics (MD) simulation techniques.

**Results**

The Cu-Zr-Al is a well-known glass-forming metallic system with a distinct GFA. For this study, we have chosen the following composition: ($\text{Cu}_{x} \text{Zr}_{1-x} \text{Al}_{x}$) ($x = 2, 4, 8, \text{and} 10$). The GFA of the system is found to increase with the addition of Al in $\text{Cu}_{x} \text{Zr}_{1-x} \text{Al}_{x}$. The QENS experiments were conducted on a time-of-flight neutron scattering instrument, Pelican, at Bragg Institute in Sydney, Australia. The self-intermediate scattering functions, $\Phi(Q, t)$, were obtained for the ($\text{Cu}_{x} \text{Zr}_{1-x} \text{Al}_{x}$) liquid at different temperatures. The stretching factor was found to be $\beta < 1$ and temperature dependent, but composition- and Q-independent. At the lowest measured temperature, we obtained a value of $\beta = 0.6 \pm 0.01$, and at the highest temperature $\beta = 0.8 \pm 0.1$. The stretching of the order of interparticle distance and grows by a factor of 2 to 9 as the glass-forming liquids cool towards a mode-coupling critical temperature, $T_c$. Studies on polydispersed glass-forming liquids and a two-dimensional metallic liquids have demonstrated that the static and dynamic are coupled. However, some other studies have shown that the static length scale increases at a slower pace than the dynamic-length-scale in decreasing the temperature of glass-forming liquids. The growth of local geometrical-orders (LGOs) is also argued to be the cause of the rapid rise in the relaxation time of cooling glass-forming liquids. In three-dimensional systems of monodispersed hard-spheres, the icosahedron is the most locally-preferred structure and increasing its number while cooling is believed to be linked directly to vitrification. In multicomponent, polydispersed metallic systems, an increasing number of five-fold symmetry clusters is reported to be the reason for their better glass-forming ability (GFA). However, the role of specific LGO on the growth of dynamic-length-scales is not yet understood, although numerous studies have shown rapid growth of dynamic-length-scales and LGOs on cooling glass-forming liquids towards the glass-transition temperature $T_g$. In this article, we studied a ternary metallic glass-forming system to understand whether the growth of any specific LGO correlates with the increase of dynamic-length-scales by using quasielastic neutron scattering (QENS) and molecular dynamics (MD) simulation techniques.
Φ(q, t) indicates the multiple relaxation processes and the presence of heterogeneous dynamics in CuZrAl liquids. As we mentioned earlier, the DH can be estimated by calculating the four-point correlation function Φ(q, t), but this quantity cannot be evaluated from a QENS experiment. However, recent theoretical advances have shown that the Φ(q, t) is related to the dynamic susceptibility, χT(Q, t), by the fluctuation-dissipation theorem. The χT(Q, t) can be evaluated from the Φ(Q, t) which is readily obtained from QENS experiments. The dynamic susceptibilities were obtained by χT(Q, t) = \frac{∂Φ(Q, t)}{∂Q}. Figure 1b shows the χT(Q, t) of the (Cu50Zr50)94Al4 liquid in a semi-logarithmic representation, which shows that the strength of DH increases with cooling. The strength of DH in (Cu50Zr50)100−xAlx liquids is quite similar, but slightly increases with increasing concentration of Al. It has been proved that the onset of cooperative dynamics in metallic glass-forming melts begin at a temperature ~2T_g, where T_g is the calorimetric glass-transition temperature. Therefore, in these high density liquids our experimental results confirm the presence of dynamic heterogeneities in (Cu50Zr50)100−xAlx well above the T_g to the measured maximum temperature and the increase in the length-scale of correlated atomic motion in cooling the liquids.

The MD simulations were performed with a system of 100,000 atoms using the LAMMPS software and employing the potential developed by Sheng et al. To estimate the strength of DH and its temperature dependence, we first evaluated the self-part of the four-point correlation function:

$$\chi_s(t) = \frac{V}{k_BT_aN_e^2} \sum_{i,j} W(|r_i(t) - r_j(0)|) - \langle Q_i(t) \rangle^2$$

where Q_i(t) = \sum_{j} W(|r_i(t) - r_j(0)|) and W(|r_i - r_j|) are overlap functions that are unity for |r_i - r_j| < a and 0 otherwise (Fig. 1c). We chose the distance parameter a = 1, which is the plateau value of the square of mean square displacement. Although the absolute values of the strength of χT(Q, t) and χ_s(t) obtained from the QENS and MD simulation cannot be compared, the growth rates with respect to the temperature are very similar (see Fig. 1b,c). Our results indicate that the relation between χT(Q, t) and χ_s(t) proposed by Berthier and co-workers holds good in these liquids. A snapshot of the simulation box is shown in the Fig. 1d. To visible the mobilities of interior atoms, a sliced simulation box is shown.

To evaluate types of LGOs in these alloy liquids at different temperatures, we carry out Voronoi tessellation analysis of the atomic configurations generated by the MD simulations. The population of the five most abundant Voronoi clusters in the undercooled state (923 K) of the alloy liquids are shown in Fig. 2a. There are several types...
of polyhedrons in these metallic liquids at all temperature ranges\(^{35}\). However, the most abundant polyhedron in all four systems, above the melting temperature, was found to be \(<0,3,6,4>\) polyhedron, while the next abundant polyhedron was \(<0,2,8,2>\). The population of these two polyhedrons increases with the Al concentration, while the growth of a specific polyhedron in cooling the liquids is dependent on the type of polyhedrons. The growth of the \(<0,3,6,4>\) polyhedron, which is most abundant in these liquids, is saturated in the supercooled liquid (see Fig. 2b). The next most abundant \(<0,2,8,2>\) polyhedron has grown almost linearly while cooling the liquids (see Fig. 2c). Interestingly, the icosahedra, \(<0,12,0,0>\), has grown much faster in the undercooled liquids (see Fig. 2d).

In cooling these four alloy liquids, the growth of specific polyhedrons is similar, but the percentage of icosahedrons increased with the concentration of Al at any given temperature (Fig. 2d).

The dynamic-length-scale in these alloy liquids at various temperatures was obtained by the following procedures. First, we calculated the four-point, time-dependent structure factor for self-overlapping particles, \(S_4(q, t)\), which is defined as,

\[
S_4(q, t) = \frac{L^2}{N^2} \rho(q, t) \rho(-q, t)
\]

where \(\rho(q, t) = \sum_j n_j \exp[i(q \cdot r_j(t) - q \cdot r_j(0))]\), and \(t\) is the time at which the maximum of dynamical four-point susceptibility \(\chi_4(t)\)\(^4,42,43\). The DH is transient in time, reaching a maximum value at around the structural relaxation time, which measures the degree of cooperativity of structural relaxation. Second, the \(S_4\) obtained at low-\(q\) values at a given temperature were fitted with Ornstein-Zernike form (see Fig. 3b),

\[
S_4(q, t) = \frac{S_4(q \rightarrow 0, \tau)}{[1 + (q\xi_4)^2]}
\]

where \(\xi_4\) is the dynamic correlation length or dynamic-length-scale. In decreasing the temperature, the \(\xi_4\) increases exponentially (see Fig. 3b). However, the growth rate of \(\xi_4\) depends on alloy composition, with a higher amount of the Al content in the liquids a faster growth rate of \(\xi_4\) was observed. In the \((Cu_{50}Zr_{50})_{100}Al_{10}\) system, which has the highest Al content, the \(\xi_4\) increases from 2 to 7.5, while in alloys with 2% Al, \(\xi_4\) increases marginally (see Fig. 3b).

As we compare the growth of \(\xi_4\) with different polyhedrons, the growth rate shows two regimes for all types of polyhedron other than the icosahedron. The \(\xi_4\) grew a little with respect to number of \(<0,3,6,4>\) or \(<0,2,8,2>\) polyhedrons in the melts but grew substantially in the undercooled states. Surprisingly, the growth of \(\xi_4\) shows a direct correlation with the population of icosahedrons in these liquids. This relation holds good in these highly dense alloy liquids in a temperature range as low as 300 K below \(T_m\), and as high as 300 K above \(T_m\).

**Discussion**

Our study experimentally confirmed the existence of the dynamic heterogeneity in the glass-forming \((Cu_{50}Zr_{50})_{100}Al_{10}\) liquids and the corresponding length scale of correlated motion over a temperature range of 600 K. This is visible from the stretching of intermediate scattering function and the strength of dynamic susceptibility, respectively. Both the dynamic heterogeneity and the dynamic length scale were found to increase with Al content and cooling of alloy liquids. At the same time, the atomic mobility was found to decrease, which indicates strong coupling between structural relaxation and the dynamic-length-scale. Using the MD simulation, we quantitatively determined the population of different polyhedrons as a function of temperature in these liquids. Although the population of the icosahedron is very little in high temperature liquids, it increases substantially in an undercooled state. The population of icosahedrons grew exponentially in the range of temperature studied. Similarly, the dynamic length scale evaluated from the four-point dynamic structure factor increases exponentially with a decreasing in temperature. However, the growth of other polyhedrons did not follow specific temperature dependence. In fact, the growth of most abundant \(<0,3,6,4>\) polyhedron saturated in undercooled liquids, and the \(<0,2,8,2>\) polyhedron grows almost linearly with temperature. This suggests a strong correlation between the increase of the dynamic-length-scale and growth of icosahedrons in liquids and the possible percolation of a string-like icosahedral medium-range order\(^40\). Additionally, as a function of Al content, the number of icosahedra increases and atomic dynamics slows down. This result suggests that the slowdown of the atomic dynamics in these liquids must have a strong coupling to the growth of icosahedron with a characteristic lengthscale changes as seen also in nonlinear dielectric studies\(^44\).

Entire existing studies in which both static and dynamic-length-scale have been computed for the same glass-forming liquids show that these length scales do not correlate each other\(^44,45\). The value of static-length-scales calculated in various studies generally found to be smaller than the dynamic one and the difference increases with decrease in temperature\(^45,46\). Therefore, we did not attempt to calculate the static-length-scale in the \((Cu_{50}Zr_{50})_{100}Al_{10}\) liquids. However, dynamic-length-scales obtained in our study exhibit a power law behaviour with relaxation time \(\tau = a\xi_4^z\), where \(a\) is constant \(z\) is the dynamic critical exponent. The value of \(z\) varied from 4.37 to 10.06 (see Fig. 3f). Such a power law behaviour has been reported in many glass-forming liquids\(^23,47\). It has also been shown that the icosahedral clusters have a strong tendency for connectivity and form a string-like network\(^48-50\). Therefore, we explored the possibility of a correlation between the increase of dynamic-length-scale and growth of icosahedra in these alloy liquids. We scaled the population of the icosahedron with dynamic-length-scale in the four alloy liquids investigated. Surprisingly, a linear relationship was observed in the alloy liquids (Fig. 3e) investigated. Our result provides evidence that the transient icosahedral connectivity could be the origin of the dynamic length scale in glass-forming liquids.
Materials and Methods

Sample preparation. The alloy samples for the quasielastic neutron scattering (QENS) were prepared by arc melting of the pure elements; Cu (99.99%), Zr (99.2%) and Al (99.999%). The arc melting were done in Ti-gettered argone atmosphere and samples were remelted several time to ensure homogeneous composition. The sample ingots were then powdered and filled in Al₂O₃ hollow cylindrical crucibles. The Al₂O₃ crucibles with powder samples were then remelted two-three times in a very high vacuum furnace. The crucible provides a hollow cylindrical geometry to the samples with a 22 mm diameter, 30 mm height and 1.2 mm thickness. The small thickness is to avoid multiple scattering and with the sample thickness of 1.5 mm only about 8% incoming neutron will be scattered.

Quasielastic neutron scattering experiments. The quasi-elastic neutron scattering (QENS) experiment was performed on the time-of-flight neutron spectrometer, Pelican, at the OPAL reactor, Australian Nuclear Science and Technology Organisation, Australia. The wavelength of the incident neutron was 6 Å which provides

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Figure 3. (a) The four-point dynamic structure factor of (Cu₉₀Zr₅₀)Al₁₀ at various temperatures, while the solid lines fit the Ornstein-Zernicke form (Eq. 3). (b) The dynamic correlation length or the dynamic-length-scale (ξ₄) at various temperatures for the alloy liquids studied. The growth of ξ₄ as a function of (c) <0,3,6,4>, (d) <0,2,8,2>, and (e) <0,0,12,0> polyhedrons. The inverse of diffusion (relaxation time) shows a power law behaviour with the dynamic correlation length. The straight lines represent how the power law fits (D⁻¹ = aξ₄²).
a Q range of 0.2 Å⁻¹–1.9 Å⁻¹ and an energy resolution of 70 µeV for the experimental setup. Since the maximum of static structure factors of the alloy melts are around 2.8 Å⁻¹, the scattered signals from our experiments are mainly due to the incoherent scattering from the Cu atoms of the samples. Therefore, the dynamics that we observed from the QENS data are of the self-dynamics of Cu atoms in the respective alloy liquids. For the high temperature measurements, we used an ILL-designed vacuum furnace. The QENS data were collected from high temperature down to the melting temperature of each alloy (1573 K, 1473 K, 1373 K, 1273 K, and 1223 K). The QENS data were collected over a duration of 4 hours at each temperature. An empty Al₂O₃ sample holder was also measured at each temperature for background subtraction and self-absorption correction. For correcting the detector efficiency, a vanadium crucible with a similar sample geometry was also measured at room temperature for 4 hours.

**QENS data analysis.** The raw data was normalized to the vanadium data, and converted to the dynamic structure factor using LAMP (Large Array Manipulation Program). The self-absorption of the sample S in a container C was corrected using

\[ S_q(2\theta, \omega) = \frac{1}{A_{SS,CC}(2\theta, \omega)} S_{SS,CC}(2\theta, \omega) - \frac{A_{C,SS}(2\theta, \omega)}{A_{SS,CC}(2\theta, \omega) A_{SC,C}(2\theta, \omega)} S_C(2\theta, \omega), \]

where \( S_q \) and \( S_{SS,CC} \) is the scattering from the container, and from both sample and container respectively. \( A_{SC,C}(2\theta, \omega) \) is the correction factor for scattering and self-absorption of the container. \( A_{C,SS}(2\theta, \omega) \) is the correction factor for scattering due to the container and absorption in both sample and container and \( A_{SS,CC}(2\theta, \omega) \) is the correction factor for scattering due to the sample and absorption in both sample and container. At last, the intermediate scattering functions \( \Phi(Q, t) \) were obtained by Fourier transforming the dynamic structure factor.

**Molecular Dynamics Simulation.** The molecular dynamics (MD) simulations were done for the same compositions measured in QENS experiments using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS); a free software obtained from the Sandia National Laboratories, USA. The embedded-atom method (EAM) potential was used to describe the interatomic interactions. The time step used in the simulation was 2 fs and periodic boundary conditions were applied. The Nose-Hoover thermostat was used to control the temperature. For each system, the initial configuration containing 100,000 atoms was equilibrated at 2000 K for 5 ns followed by rapid quenching to the desired temperatures with the rate of \( 2 \times 10^{13} \) Ks⁻¹ in NPT ensemble. The volume of the system was adjusted to give zero pressure during cooling. Before taking the structural configurations, the systems were relaxed for extra 1 ns by the NVT ensemble. Voronoi tessellation calculates the polyhedral cells which have planar faces and completely fill the space by constructing bisecting planes along the lines connecting the target atom and its neighbors. The polyhedrons surrounding the central atom are described by the Voronoi index \( <n_1,n_2,n_3,\ldots> \), where \( n_i \) is the number of i-edged faces of the polyhedron. A cutoff distance of 5 Å was used in this study.

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Author Contributions

S.M.C. conceived, and supervised the project and wrote the manuscript, K.W. carried out QENS experiments and D.Y. supported the QENS experiments, R.P.K and C.J. supported QENS data analysis, Z.L. and D.Q. provided the samples for QENS experiments and D.Y. provided the QENS experiments, K.S. provided a critical assessment of the research.

Additional Information

Competing Interests: The authors declare that they have no competing interests.

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