



# Correlation between local structure and dynamic heterogeneity in a metallic glass-forming liquid



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## ABSTRACT

Dynamic heterogeneity as one of the most important properties in supercooled liquids has been found for several decades. However, its structural origin remains open for many systems. Here, we propose a new structural parameter to characterize local atomic packing in metallic liquids. It is found that the new parameter in a simulated metallic glass-forming liquid is closely correlated with potential energy and atomic mobility. It also exhibits significant spatial heterogeneities and these structural fluctuations show close correlation with the spatial distribution of the long-time dynamic propensities. Therefore, our results provide a direct evidence of the correlation between atomic structure and dynamical heterogeneity. The new structural parameter might be used to reflect the structural “defect” in metallic liquids and glasses and further play an important role to uncover the structure–property relationship in these disordered systems.

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## 1. Introduction

A liquid is usually thought to be homogenous. However, as a liquid is cooled far below its melting point, dynamics in some regions of the liquid can be orders of magnitude faster than dynamics in other regions only a few nanometers away, which is known as dynamic heterogeneity [1–4]. Dynamic heterogeneity is considered as one of the three key physical features which dominate much of the behavior of liquids as they are supercooled (The other two are the massive increase in the shear viscosity and the temperature dependence of the entropy) [5–7]. Although the existence of dynamic heterogeneity has been established for several decades [6–9], an obvious question, what cause it, still has no universal answer. While there has been some significant progress [10–16], the structural origin of dynamic heterogeneity remains open for many systems. The atoms in icosahedral clusters have been proved to move slower than other atoms in some metallic glass-forming liquids [10,11]. However, in some other systems icosahedral clusters are absent [17]. Even in the systems with a large number of icosahedral clusters in the glassy state, the number of icosahedral

clusters is rather small at high temperatures in the liquid state [18]. Therefore, the icosahedrons cannot be adopted as a universal structural indicator for dynamic heterogeneity. Thus some other indicators are used to predict dynamic heterogeneity. The Debye–Waller factor has been quite successful for predicting the relative long-time dynamical heterogeneity and irreversible arrangement in glass-forming liquids [19]. The localized soft modes are appreciated to play the central role in the dynamic heterogeneity [20–22]. However, both of the two indicators cannot provide a clear picture of local atomic structure. A more general structural parameter is needed to characterize structural heterogeneity and predict dynamic heterogeneity and even other properties in metallic liquids and glasses.

It is natural to relate dynamic heterogeneity with local free volume [23–26]. However, it is found that local free volume does not show strong correlation with local mobility [27,28]. Instead, Ediger and Harrowell suggested that the dynamic heterogeneity in liquids might be caused by some “defects” which are similar to those in the solid state [5]. However, the structural origin of the “defects” is still unknown. It is well known that the atomic packing is usually much looser around the defects in the crystal. Therefore, the “defects” in liquids might be also located at the regions with loose atomic packing. However, the present structure parameters

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cannot describe the atomic packing well.

We propose a new local structure parameter, quasi-nearest atom (QNA), to describe the atomic packing in metallic liquids and study the correlation between structural heterogeneity and dynamic heterogeneity in a simulated metallic glass-forming liquid ( $\text{Cu}_{64}\text{Zr}_{36}$ ). We find that atoms with more QNAs have higher potential energy and higher mobility. The atoms with different number of QNAs show clear spatial heterogeneities and the more QNA regions overlap the regions with higher dynamic propensities, and visa inverse. Therefore, our results provide a direct evidence of the correlation between structural heterogeneity and dynamic heterogeneity in the metallic glass-forming liquid.

## 2. Methods

Classical molecular dynamics simulations are carried out on  $\text{Cu}_{64}\text{Zr}_{36}$  metallic liquid. Our system consists of 128000 Cu atoms and 72000 Zr atoms. The atoms interact via embedded-atom method (EAM) potential [29]. The system is simulated with periodic boundary conditions. Isothermal-isobaric (NPT)-ensemble simulations using the Nose-Hoover thermostat and barostat are employed in our studies. The equations of motion are integrated using the Verlet algorithm with a time step of 1 fs. Eight independent runs are performed for the measurements of structural and dynamical properties at  $T = 1000$  K and zero external pressure.

The local structure is characterized by QNA, which is defined as follows. All the nearest neighbors around each atom in the system are determined by Voronoi tessellation method [30] including all facets. According to this method, each nearest neighbor of the center atom corresponds to one face of the Voronoi polyhedron. If two Voronoi faces share an edge, the two corresponding atoms are defined as an adjacent pair of atoms. Next, if an adjacent pair of atoms are not the nearest neighbors of each other, we identify these two atoms as a pair of QNAs. For instance, as shown in Fig. 1(a), atoms C and D are a pair of QNAs because they satisfy the following conditions: (i) both of them are the nearest neighbors of atom A; (ii) they are adjacent among all the nearest neighbors of atom A; (iii) they are not the nearest neighbors of each other. In Fig. 1, atom A has less QNA than atom J while the atomic packing around A is much denser than that around J. Therefore, QNA can reflect local constraints. The ability to move for an atom is associated with the degree to which the atom is constrained by its surroundings [19]. Thus there might be some correlation between QNA and atomic mobility.

## 3. Results and discussion

We present the distribution of the number of QNAs,  $N_Q$ , at 1000 K in Fig. 1(b). It follows similar behavior for both Cu and Zr atoms. However, the fraction of Cu atoms with small  $N_Q$  is slightly larger than that of Zr, and the situation is opposite for the atoms with large  $N_Q$ . This indicates that the local packing of Cu is denser than that of Zr. We note that the fraction shows a peak at  $N_Q \sim 2$ , suggesting that most of the atoms are not closely packed at 1000 K. The distribution of atomic potential energy with different  $N_Q$  for Cu and Zr is shown in Fig. 1(c) and (d), respectively. It can be seen that the distributions have large overlaps, indicating the correlation between  $N_Q$  and atomic potential energy is not a one-to-one correspondence. Considered that the cutoff distance of potential energy is 6.5 Å, much larger than the scale of  $N_Q$ , it is reasonable for the large overlaps. However, as shown in the insets of Fig. 1(c) and (d), atoms with larger  $N_Q$  have less negative per-atom potential energy shown. In this respect,  $N_Q$  plays an key role in the correlation between local structure and potential energy. This fact suggests that atoms with larger  $N_Q$  tend to have lower thermodynamic stability

and thus might move faster.

We next study the structural relaxation with different local structures. We label all the atoms with different  $N_Q$  at initial time. We obtain the structural relaxation time for atoms with the same  $N_Q$  by calculating the self-intermediate scattering function (SISF) [31],

$$F_s^{ab}(q, t) = \frac{1}{N_{ab}} \sum_{j=1}^{N_{ab}} \langle \exp\{i \vec{q} \cdot [\vec{r}_j(t) - \vec{r}_j(0)]\} \rangle, \quad (1)$$

where  $N_{ab}$  is the number of type  $a$  (either Cu or Zr) atoms with  $N_Q = b$  at  $t = 0$ ,  $\vec{r}$  is the position of each atom,  $\vec{q}$  is the wave vector which corresponds to the first peak of the partial structure factor ( $2.8 \text{ \AA}^{-1}$  for Cu and  $2.7 \text{ \AA}^{-1}$  for Zr) and the average is taken over 8 independent runs. Fig. 2(a) and (b) display the SISFs of Cu and Zr atoms with different  $N_Q$ . In the long-time relaxation (often called  $\alpha$ -relaxation) regime, the SISF with small  $N_Q$  decays more slowly compared to that with larger  $N_Q$ . This indicates that atoms with smaller  $N_Q$  tend to move slower than those with larger  $N_Q$ . The  $\alpha$ -relaxation time is defined as the time at which the SISF decays to  $1/e$  of its initial value. As shown in the insets of Fig. 2(a) and (b), for either component, the relaxation time for atoms decreases with increasing  $N_Q$ .

The above results clearly show a correlation between local structure and dynamics, yet the dynamic behavior of an individual atom is missing. We further quantify the dynamic heterogeneity using an alternative method, to calculate the dynamic propensity of an atom,  $\Delta r_{ic}^2$ , which is defined as  $\langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle$ , where the average is taken over the ensemble of  $N$ -particle trajectories, all starting from the same configuration but with momenta assigned randomly from the appropriate Maxwell–Boltzmann distribution [32]. The time interval needs to be chosen to maximize the observed dynamic heterogeneities. Here we have chosen the interval to be the “maximum non-Gaussian time”, at which the non-Gaussian parameter,  $\alpha_2(t) = 3 \langle r^4(t) \rangle / 5 \langle r^2(t) \rangle^2 - 1$ , reaches the maximum. In this work, the “maximum non-Gaussian time” is about 3.5 ps at 1000 K, which is longer than two times of the relaxation time of the system. In Fig. 2(c) and (d), we plot the distribution of dynamic propensities for Cu and Zr in 8 independent configurations at 1000 K, averaging over 100 runs. For either component, the distribution of propensities for atoms with  $N_Q = 0$  has the highest peak at the end of low propensities, which indicates most of the atoms with  $N_Q = 0$  tend to move slowly. As  $N_Q$  increases, the peak becomes a little lower, and move to the higher propensities. In the insets we show that the average propensity increases with  $N_Q$ . All these show a close correlation between  $N_Q$  and atomic mobility although this correlation is not a one-to-one correspondence.

To quantify the correlation between  $N_Q$  and  $\langle \Delta r_{ic}^2 \rangle$ , the atoms are sorted by their  $\langle \Delta r_{ic}^2 \rangle$  from low to high for each element. Then they are divided into  $n_g$  groups, each containing  $n_A$  atoms. For each group, the average  $N_Q$  ( $\langle N_Q \rangle$ ) and  $\langle \Delta r_{ic}^2 \rangle$  ( $\langle \langle \Delta r_{ic}^2 \rangle \rangle$ ) are calculated. Fig. 3(a) shows  $\langle N_Q \rangle$  exhibits a linear relation with  $\langle \langle \Delta r_{ic}^2 \rangle \rangle$  in log-semi plot with  $n_g = 200$  for Cu and Zr, indicating an exponential dependence of  $\langle \langle \Delta r_{ic}^2 \rangle \rangle$  on  $\langle N_Q \rangle$ , that is,  $\langle \langle \Delta r_{ic}^2 \rangle \rangle (\langle N_Q \rangle) \sim \exp(\langle N_Q \rangle)$ . To measure correlation, we use Pearson correlation coefficient  $K$ , which calculates a linear correlation coefficient of values.

$$K = \frac{E\{[X - E(X)][Y - E(Y)]\}}{D(X)D(Y)} \quad (2)$$

where  $X$  and  $Y$  are two variables,  $E(X)$  and  $E(Y)$  are their average values, and  $D(X)$  and  $D(Y)$  are their standard deviations. Maximum

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