Local connectivity modulates multi-scale relaxation dynamics in a metallic glass-forming system

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The structural description for the intriguing link between the fast vibrational dynamics and slow diffusive dynamics in glass-forming systems is one of the most challenging issues in physical science. Here, in a model of metallic supercooled liquid, we find that local connectivity as an atomic-level structural order parameter tunes the short-time vibrational excitations of the icosahedrally coordinated particles and meanwhile modulates their long-time relaxation dynamics changing from stretched to compressed exponentials, denoting a dynamic transition from subdiffusive to hyperdiffusive motions of such particles. Our result indicates that long-time dynamics has an atomic-level structural origin which is related to the short-time dynamics, thus suggests a structural bridge to link the fast vibrational dynamics and the slow structural relaxation in glassy materials.

Supercooled liquid transforms to non-equilibrium glass accompanying by drastically slowing down of dynamics but no obvious change in structures, which makes the description of structure-dynamics relationships in supercooled liquids and glasses one of the most challenging problems in condensed matter physics [1]. A variety of liquids under supercooling are known to exhibit unusual slow dynamics, which is often manifested as a stretched exponential decay in the time correlation functions [2–4]. This reflects a wide distribution of relaxation times typically attributed to the existence of dynamic heterogeneities. However, in out-of-equilibrium materials (e.g., structural glasses [5–6], colloidal suspensions and gels [7–8], and for nanoparticle within glass former matrix [9–10]), compressed correlation functions decaying faster than exponential have instead been reported. This is in sharp contrast to the diffusive or subdiffusive dynamics which relaxes slower-than-exponential typically observed in a supercooled liquid. It was proposed that the faster-than-exponential relaxation was due to the release of internal stresses [7–8] or a cooperative motion induced by the near-vitreous solvent [9–10]. However, a detailed description of the microscopic origin of the dynamics is still lacking. A particle-level structural origin for the subdiffusive to hyperdiffusive dynamics crossover is highly desirable.

Another striking feature of the time correlation functions is the presence of a small valley between the short time (‘microscopic’) process and the caging plateau that precedes the long time α-relaxation. It is suggested [11–15] that the damping oscillation (or valley) in the time correlation function is a time-domain manifestation of the much-discussed boson peaks, which appears as the inelastic process in frequency domain detected by light, x-ray, and neutron scattering [16,17]. Recent studies demonstrated the existence of a direct link between the slow structural relaxation and fast boson peak dynamics [18,19], which correlates the diffusive inter-basin dynamics to the vibrational intra-basin dynamics in glass-forming systems [20]. This raises an interesting question of whether there exists a connection between the long-time compressed exponential decay and the short-time valley in the time correlation functions, which is important for the fundamental understanding of the dynamics of glassy materials. Therefore, a comprehensive study of the structural dependence of this valley and its relationship to the faster-than-exponential relaxations is of crucial importance to reveal the structural link between slow structural relaxation and fast vibrational dynamics in glass-forming systems.

In this letter, by using a model of fragile Cu50Zr50 metallic liquid, we systematically investigated the dynamics of icosahedrally coordinated particles by measuring the incoherent intermediate scattering functions. At short-time scale, a valley is observed in the correlation function between the ballistic regime and the caging plateau, meaning that these particles exhibit the dynamical feature usually belonging to strong glass formers. Further analysis unveils that the valley position and its damping amplitude depend on the local connectivity of the studied particles. Meanwhile, as the local connectivity increases, the long-time behavior of the intermediate scattering function changes from stretched exponential decay to compressed one, indicative of a dynamic crossover from subdiffusive to hyperdiffusive motions. Our result indicates that the local connectivity bridges multi-time scales dynamic processes in supercooled liquids and glasses, suggesting a possible structural origin to reveal the well-recognized correlation between the fast vibrational dynamics and the slow structural relaxation in glass-forming systems.

The studied Cu50Zr50 system consists of \( N = 10000 \) atoms with 5000 Cu and 5000 Zr atoms initially randomly distributed in a cubic box with periodic boundary conditions. The embedded-atom method (EAM) potential is used to characterize the interactions between atoms [21].
In our study, molecular dynamics (MD) simulations are performed using the LAMMPS package [22] with integration time of 1 ns. Each sample is firstly equilibrated for long time (2 ns) at temperature $T = 2000$ K and then cooled down to 1000 K at rate of 1 K/ps along constant pressure $P = 0$ bar. The Nose-Hoover thermostat and barostat is employed for the constant pressure ensemble (NPT-ensemble). All data are collected after another long-time equilibration of 1 ns at 1000 K.

We employed the Voronoi tessellation method to characterize the local atomic structures in supercooled liquid [23]. The particle with icosahedral coordination is identified by its corresponding Voronoi index $(0,0,12,0)$ [24]. The connectivity $k$ of an icosahedrally coordinated particle is defined as the number of other icosahedrally coordinated particles directly ‘connected’ to it (being nearest-neighbors of each other, as shown on the inset of Fig. 1) [25, 26]. For each $k$, we measured the corresponding incoherent intermediate scattering functions (ISF), $F_0(q,t) = (1/N_k)\langle \sum_j \exp(i\vec{q}\cdot(\vec{r}_j(t) - \vec{r}_j(0))) \rangle$, where the summation runs over all particles with the same $k$, and $\vec{r}_j(t)$ is the location of particle $j$ at time $t$. The value of $\vec{q}$ is chosen as $2.8$ Å$^{-1}$, approximately equal to the value of the first peak position in the structure factor, and $\langle \cdot \rangle$ denotes the ensemble average.

![FIG. 1. The incoherent intermediate scattering function (ISF) of icosahedrally coordinated particles with different local connectivity $k$. The inset is an illustration of the local connectivity of a particle, which is defined as the number of its nearest-neighbors having the same local symmetry (represented by the same color in this figure) with it.](image1)

As connectivity $k$ increases. Therefore, the local connectivity is an atomic-level structural order parameter that can modulate both the short-time vibrational dynamics and the long-time relaxation dynamics of the studied particles.

At short times, $0.01$ ps $\leq t \leq 0.4$ ps, the ISF for different $k$ can be well fitted by a linear combination of harmonic oscillators model (LCHO),

$$F_i(q,t) \propto \sum_{i=L,H} C_i \exp\{i\vec{q}[\omega_i t + \delta_i] - A\cos(\delta_i)\}, \quad (1)$$

where $C_{i=L,H}$ is the weight of the harmonic oscillator with vibrational frequency $\omega_{L/H}$ and initial phase $\delta_{L/H}$ with $L$ and $H$ denoting the low and high frequency modes respectively, and $A$ is a fitting parameter to balance...
the dimension of the wave vector $q$. The LCHO model describes the short-time dynamics of particles rattling around their initial positions, which correspond to vibrational excitations within a sub-basin in the perspective of the potential energy landscape shown in the inset of Fig. 2. In general, the sub-basin is rough [27] and aggregated by hierarchy of local minima with different barriers (inset in Fig. 2). The two-level-like (red filled curve in the inset of Fig. 2) LCHO model is a reasonable first-step approximation for excitations within sub-basin.

The vibrational frequency $\omega$ as a function of $k$ is presented in Fig. 3(a). Clearly, frequency $\omega$ is positively correlated with $k$ at short time scale, that is, the larger the local connectivity, the higher the frequency the type of the particle motion. According to previous study by Wakeda et al. [28], the icosahedrally coordinated particle with larger connectivity has a much higher average elastic rigidity, thus giving a reasonable account for the positive trend showing in Fig. 3(a) based on the well-known relationship between vibrational frequency and elastic modulus.

The $k$-dependence of weighted parameters $C_{L/H}$, presented in Fig. 3(b), show different behaviors as $k$ increases. The fraction of the $\omega_H$ mode increase, while the fraction of the $\omega_L$ mode decreases. To identify whether the damped oscillation showing in the ISF curve is a fully localized mode or acoustic-like mode with collective behavior, we measure the incoherent ISF of overall icosahedrally coordinated particles for values of $q$ in the range of $0.1 \text{ Å}^{-1} \leq q \leq 0.6 \text{ Å}^{-1}$ and fit the ISF by the LCHO model. The obtained $\omega_H(q)$ and $\omega_L(q)$ are shown in Fig. 3(c) and 3(d), respectively. It can be seen that $\omega_H(q)$ is approximately $q$-independent in the entire investigated $q$ range, suggesting that the high frequency mode is localized. In contrast, $\omega_L(q)$ is markedly $q$-dependent and increases with increasing $q$, indicating that the collective dynamics persist up to these frequencies. As shown in Fig. 3(d), $\omega_L(q)$ displays linear behavior up to $q=0.35 \text{ Å}^{-1}$. This implies that such excitations are acoustic phonon-like, and the corresponding sound velocity is about 4082 m/s estimated based on $v(q) = \omega_L(q)/q$, comparable with the experimental data reported for the CuZr-based metallic alloys [29]. Therefore, the short-time scale behavior of ISF is a superposition of localized and extended mode with different frequencies. That is, the damped oscillations showing at the short-time scale of the ISF curves in our modeling system can be attributed to the dephasing of localized and extended mode.

We point out that the well-defined acoustic mode exists up to 3 THz (Fig. 3(d)). According to previous studies [30, 31], the value of Boson peak frequency, $\omega_{BP}$, in CuZr alloys is in a frequency range of 2.5 to 3.5 THz. Therefore, our results clearly show that the low frequency extended modes contribute to the boson peak. Moreover, these results also show that the short-time valley in the correlation functions and the vibrational boson peak dynamics are closely correlated.

![Fig. 3](image-url)

**FIG. 3.** The dependence of dynamic properties on connectivity $k$ and dispersion relations. Both the high and low frequency modes, $\omega_H$ and $\omega_L$, increases with increasing $k$ (a), however, the fraction of motion $C_{H/L}$ increases for $\omega_L$ and decreases for $\omega_H$ (b). The high frequency mode $\omega_H(q)$ is approximately $q$-independent, characteristic of localization of the vibrational modes (c), while the low frequency mode $\omega_L(q)$ increases monotonically with increasing $q$, characteristic of collective dynamics (d). The dashed line shown in panel (d) corresponds to the linear fit of the dispersions at low-$q$ values.

![Fig. 4](image-url)

**FIG. 4.** Long-time behavior of the intermediate scattering function. (a) The long-time decay of the correlation functions for particles with different $k$ values. The black solid lines are the Kohlrausch-Williams-Watt (KWW) fits. (b) The $k$ dependence of the exponent $\beta$. $\beta$ is large than 1 for connectivity $k \geq 4$ and less than 1 for $k < 4$, revealing a dynamic crossover from stretched exponential relaxation to compressed one.

We next focus on the behavior of the long-time structural relaxation for particles with different values of $k$ by evaluating the corresponding ISFs. The results are presented in Fig. 4(a). The long-time decay of the correlation function follows the Kohlrausch-Williams-Watt (KWW) expression, $F_q (t) \propto A_q \exp[-(t/\tau)^\beta]$, where $A_q$ is the non-ergodicity factor, $\tau$ is the relaxation time,
and $\beta$ is the shape exponent. Usually, the correlation function at long time scale can be well described by a stretched exponential with exponent $\beta < 1$ in supercooled liquids, a signature of subdiffusive motion of the particles. However, as can be seen in Fig. 4(b), the shape of the ISF changes from stretched-exponential ($\beta < 1$) to compressed exponential ($\beta > 1$) at $k = 4$, which correspond to a dynamic transition from subdiffusive motion to hyperdiffusive motion. Since $k = 4$ enhance the construction of a 3-dimensional network, this dynamic transition has a geometric origin. Interestingly, the transition at $k = 4$ here is similar to the isostatic jamming transition with an average contact number of 4 in 3-dimensions for frictional spheres [32–34].

Compressed-exponential behavior in the correlation functions has been widely reported as a common feature for out-of-equilibrium materials, where the dynamics is controlled by hyperdiffusive motion. In glasses, such hyperdiffusive motion is attributed to the release of internal stress stored in the system during quenching [7], while for nanoparticles suspended in a supercooled solvent, cooperative behavior governed by the near-vitreous solvent is thought to be the origin of the faster-than-exponential relaxations [9, 10]. In our study, cooperative motion and release of internal stress coexist in our system, both of which may contribute to the hyperdiffusive dynamics. Firstly, the developing of more cooperative motions of particles is reflected by the positive correlation between the local connectivity and the contribution from the extended mode shown in Fig. 3(b), consistent with the picture of the hyperdiffusive behavior for suspensions of nanoparticles [9, 10]. Secondly, according to previous study [28], isosahedrally coordinated particles have larger average elastic modulus but smaller average atomic volume with increasing local connectivity, thus particles with large connectivity ($k \geq 4$) assume more local stress (concentration of stress). Therefore, the hyperdiffusive motion of the particles with large connectivity ($k \geq 4$) in our study also has contributions from the release of the local stress. This is similar to the microscopic origin of the internal stress proposed for colloidal gels, where the source of local stress was ascribed to the local deformation of the elastic network due to the syneresis of the gel [7].

Previous studies demonstrated [35] that annealing at temperatures slightly below the glass transition temperature effectively increases the fraction of short-range icosaedral order in metallic glasses. Due to the self-aggregation effect [36], higher fraction of icosaedra is an indication of more particles with local connectivity $k \geq 4$, whose structural relaxation is a compressed exponential decay. It is highly reminiscent of the very recent experimental observation [37] that pre-annealed metallic glasses at 0.9 $T_g$ show fast dynamic modes ($\beta > 1$) exhibiting ballistic-like feature. Researchers [10, 37] have attributed this faster-than-exponential relaxation in metallic glasses to the presence of internal stresses induced by quenching. Our results provide a possible hint of the structural origin for the unexpected dynamics in glassy states.

To summarize, we provide a simulation evidence that metallic liquid under supercooling exhibits quite rich dynamics. The particles ‘protected’ by particular spatial symmetries in fragile liquids possess dynamic features that usually belong to strong glass formers. In addition, the long-time relaxation of such particles decays as stretched or compressed exponential which corresponds to either subdiffusive or hyperdiffusive motion structurally depending on their local connectivity. Therefore, the local connectivity is a good structural order parameter to bridge multi-time scales dynamic processes in supercooled liquids and glasses, which shows that the correlation between the fast vibrational dynamics and the slow structural relaxation in glass-forming system has an atomic-level structural origin. The coexistence of distinct dynamics in one system sheds new light on understanding of the structure-dynamics relationships in supercooled liquids and glasses.

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