



Revealing a hidden dynamic signature of the non-Arrhenius crossover in metallic glass-forming liquids

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ABSTRACT

We report a scaling collapse of the temperature dependence of structural relaxation in 12 model metallic glass-forming liquids by introducing a characteristic temperature and characteristic time scale under constant dynamic heterogeneity condition. Moreover, we find the onset temperature of cooperative motions, T_A , separating Arrhenius and non-Arrhenius behaviors of the relaxation time turns out to be one of the characteristic temperatures, which is evidenced by the constant dynamic heterogeneity at T_A for all systems investigated. Our findings reveal a new dynamic signature hidden in T_A and offer a new perspective, i.e., constant dynamic heterogeneity condition, to study metallic glass-forming liquids.

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The dramatic slowdown of the structural relaxation on approaching the glass transition in metallic glass-forming liquids is a crucial but unsolved problem [1–4]. It's believed that an imperative step to the ultimate understanding of this issue is to generally describe the temperature dependence of structural relaxation time, $\tau_\alpha(T)$, in metallic glass-forming liquids with different dynamic fragilities [5–10]. However, the general description of $\tau_\alpha(T)$ in metallic glass-forming liquids remains a conundrum.

A typical feature accompanying the dynamic slowdown is the increasing dynamic heterogeneity that refers to spatiotemporal fluctuations of local dynamics in glass-forming liquids [9,11–13]. However, how structural relaxation is correlated to dynamic heterogeneity had raised a lot of controversies over a period of time [14–16]. Recently, a general link between dynamic heterogeneity and relaxation time has been revealed in a variety of model glass-forming liquids with pairwise potentials by using the identical dynamic heterogeneity condition, and the long-sought scaling collapse of $\tau_\alpha(T)$ has been achieved [17]. Nevertheless, the investigation of the role played by dynamic heterogeneity in metallic glass-forming systems with many-body potentials is still in its infancy. Moreover, it is unclear whether the simple universality involving relaxation time and dynamic heterogeneity working well in simple glass-forming liquids with two-body interactions still holds in metallic glass-forming systems.

The non-Arrhenius crossover phenomenon of structural relaxation happening at the crossover temperature T_A , marks the deviation of relaxation time τ_α (or viscosity η) from its high-temperature Arrhenius dependence [8,18–21]: $\tau_\alpha = \tau_0 \exp(E/k_B T)$ or $\eta = \eta_0 \exp(E/k_B T)$, where τ_0 (or η_0) is the relaxation time (or viscosity) at extremely high temperature, E is activation energy and k_B is Boltzmann constant. T_A has been proven to be above or near the liquidus temperature in metallic liquids and about twice of the glass transition temperature T_g , attracting much attention recently [7,22–25]. Physically, T_A is believed to indicate the onset temperature of cooperative motion with increasing dynamic heterogeneity [8,23,26,27], but quantification of this cooperativity is still lacking. Moreover, Blodgett et al. [7] found that through introducing T_A and η_0 , a general curve that fits the viscosities of various metallic glass-forming liquids could be obtained in experiments. But there have been no studies trying to reveal the underlying properties at T_A concerning the reason why using T_A to scale temperature can lead to the general description of $\eta(T)$ for metallic liquids to date. Considering the linear relation of τ_α and η , whether introducing T_A can lead to a scaling collapse of $\tau_\alpha(T)$ is worth further study. Meanwhile, revealing dynamic properties hidden at T_A can help to get deep insight into the vitrification process of metallic liquids from the high-temperature aspect.

In this work, a scaling collapse of $\tau_\alpha(T)$ for 12 metallic glass-forming liquids is obtained by introducing a characteristic temperature and characteristic time determined from an identical dynamic heterogeneity condition. Furthermore, we reveal a new

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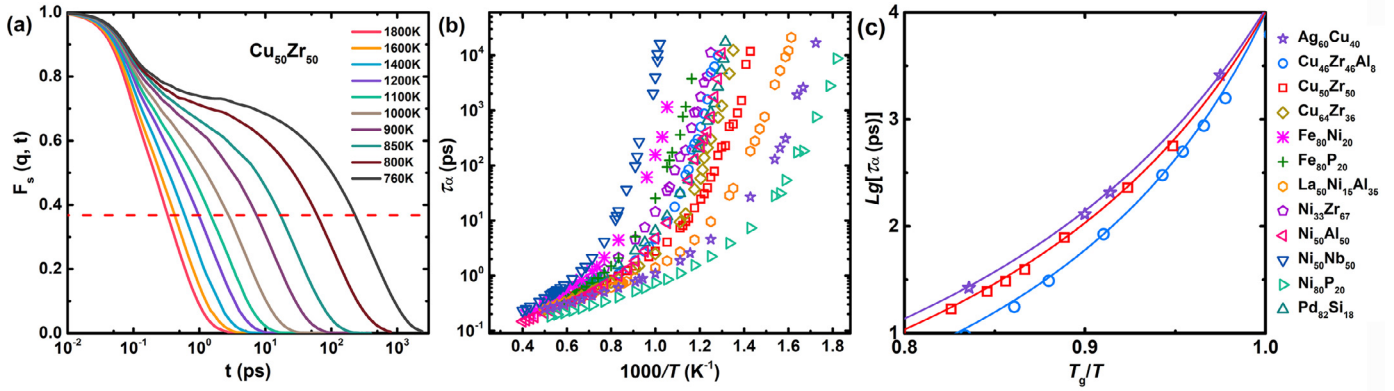


Fig. 1. (a) The self-intermediate scattering function $F_s(q, t)$ for $\text{Cu}_{50}\text{Zr}_{50}$ liquids at different temperatures. The dashed line indicates $F_s(q, t) = 1/e$. (b) The temperature dependence of structural relaxation time τ_α for 12 metallic glass-forming liquids. (c) Angell plots of τ_α versus scaled reciprocal temperature T_g/T for 3 representative systems. In order to have a better visualization of the steepness of the T_g/T dependence of τ_α approaching T_g , only data points at lower temperatures near T_g are shown here. The solid lines are fits to Vogel-Fulcher-Tamman (VFT) equation: $\tau_\alpha = \tau_\infty \exp[DT_0/(T - T_0)]$, where τ_∞ , D and T_0 are fitting parameters.

dynamic signature hidden at T_A , i.e., dynamic heterogeneities at T_A in all systems examined are the same.

We performed molecular dynamics simulations in 12 metallic glass-forming systems using the open-source code LAMMPS [28] in this study. Embedded atom method (EAM) potentials were used to describe the atomic interactions [29–39]. Each system contains 4000 atoms, except for $\text{Fe}_{80}\text{Ni}_{20}$ and $\text{Fe}_{80}\text{P}_{20}$ systems composing of 54,000 atoms. Periodic boundary conditions were applied in three directions. The NPT ensemble (constant number N , constant pressure P and constant temperature T) of each initial configuration was first melted and equilibrated at a sufficiently high temperature (2500 K for $\text{Fe}_{80}\text{Ni}_{20}$ and $\text{Ni}_{50}\text{Nb}_{50}$; 2000 K for the other systems) for at least 1 ns and then it was quenched at a rate of 1 K/ps. The configurations at different temperatures were collected upon cooling and relaxed to equilibrium at corresponding temperatures in NPT, followed by the NVT ensemble (constant N , constant volume V and constant T) for further dynamic analysis. The time step was set to 0.002 ps and the temperature was controlled by the Nosé-Hoover thermostat [40].

To characterize the dynamic behaviors of investigated metallic glass-forming liquids, we firstly measure the self-intermediate scattering function [41], $F_s(q, t) = \frac{1}{N} \langle \sum_{i=1}^N \exp[i\vec{q} \cdot (\vec{r}_i(t) - \vec{r}_i(0))] \rangle$, where $\vec{r}_i(t)$ is the location of atom i at time t and $|\vec{q}|$ is close to the first peak of the static structure factor [42]. Fig. 1(a) shows the evolution of $F_s(q, t)$ with time for $\text{Cu}_{50}\text{Zr}_{50}$ glass-forming liquids as the temperature decreases. The structural relaxation time τ_α is defined as the time when $F_s(q, t) = 1/e$ [41]. Fig. 1(b) shows the temperature dependence of τ_α for 12 metallic glass-forming liquids. The glass transition temperature T_g is usually determined as the temperature when τ_α reaches 100 s in experiments [6]. However, due to the limited time window of our simulations, we determine T_g as the temperature when $\tau_\alpha = 10^4$ ps, and this kind of definition has been used before in previous simulation studies [43,44]. Then we calculate the dynamic fragility m of each system through [45] $m = \frac{d \log \tau_\alpha(T)}{d(T_g/T)}|_{T=T_g}$. In Fig. 1(c) we show visibly different Angell plots for 3 representative systems, suggesting clearly that fragilities in some of the metallic liquids investigated here are different.

According to the hints in simple glass-forming liquids with two-body interactions, it is important to probe the relationship between structural relaxation and dynamic heterogeneity in metallic glass-forming liquids. In order to characterize dynamic heterogeneity, we measure non-Gaussian parameter [46,47], $a_2(t) = \frac{3\langle \Delta r^4(t) \rangle}{5\langle \Delta r^2(t) \rangle^2} - 1$, where $\Delta r(t)$ is the displacement of one

atom during time t . $a_2(t)$ characterizes the degree of deviation of particle displacements from the Gaussian distribution [46] (see the Supplementary Materials for more details). The time dependence of a_2 for $\text{Cu}_{50}\text{Zr}_{50}$ system is shown in Fig. 2(a) at different temperatures. It can be seen that $a_2(t)$ is non-monotonic with time and we in this study utilize the maximum $a_2(t)$, $a_{2, \max}$, to quantify the dynamic heterogeneity. In Fig. 2(b) we show the increasing $a_{2, \max}$ during cooling for all systems studied, which is consistent with the observation in previous works that the dynamics of glass-forming liquids become more heterogeneous with decreasing T [13,44,46]. Moreover, the growing dynamic heterogeneity accompanying dynamic slowdown can also be seen clearly from the monotonic increase of $a_{2, \max}$ with increasing τ_α (see Fig. 2(c)), despite the distinctions of $a_{2, \max}(\tau_\alpha)$ curves in different systems.

Analogous to the scaling procedure proposed in ref [17], we can choose a reference state randomly and then fix the dynamic heterogeneity at that state; in our study we chose a reference state with $a_{2, \max} \approx 0.8$. Then, the characteristic temperature T^* and characteristic time scale τ^* in each system are defined from $a_{2, \max}(T) \approx 0.8$ and $a_{2, \max}(\tau_\alpha) \approx 0.8$, respectively. Interestingly, by scaling T with T^* , we can collapse the $a_{2, \max}(T)$ for all the 12 metallic glass-forming systems onto a single master curve as shown in Fig. 3(a). Furthermore, as shown in Fig. 3(b), a nice scaling collapse of $a_{2, \max}(\tau_\alpha)$ curves can also be achieved when we scale τ_α with τ^* , evidencing there also exists a universal link between dynamic heterogeneity and structural relaxation in metallic glass-forming liquids. Besides, the characteristic time τ^* seems to have an approximate power law relation with fragility m though there are large fluctuations in several systems (see Fig. 3(c)), suggesting dynamic fragility plays an important role analogous to a characteristic time in revealing the link between structural relaxation and dynamic heterogeneity in metallic glass-forming systems with many-body potentials. Finally, we show a nice scaling collapse of $\tau_\alpha(T)$ curves for all systems studied when plotting τ_α/τ^* against T^*/T in Fig. 4(a). To the best of our knowledge, this is the first simulation result achieving a universal description of $\tau_\alpha(T)$ for various metallic glass-forming systems over such a wide range of temperatures, simply through the characteristic time scale and characteristic temperature determined by the identical dynamic heterogeneity state.

Based on the master curve of the scaled $\tau_\alpha(T)$ in Fig. 4(a), we can make one step forward and focus on the dynamic crossover behavior at the onset temperature T_A existing in high-temperature liquids. By introducing the characteristic temperature T^* and characteristic time τ^* defined by iso- $a_{2, \max}$, we can switch the

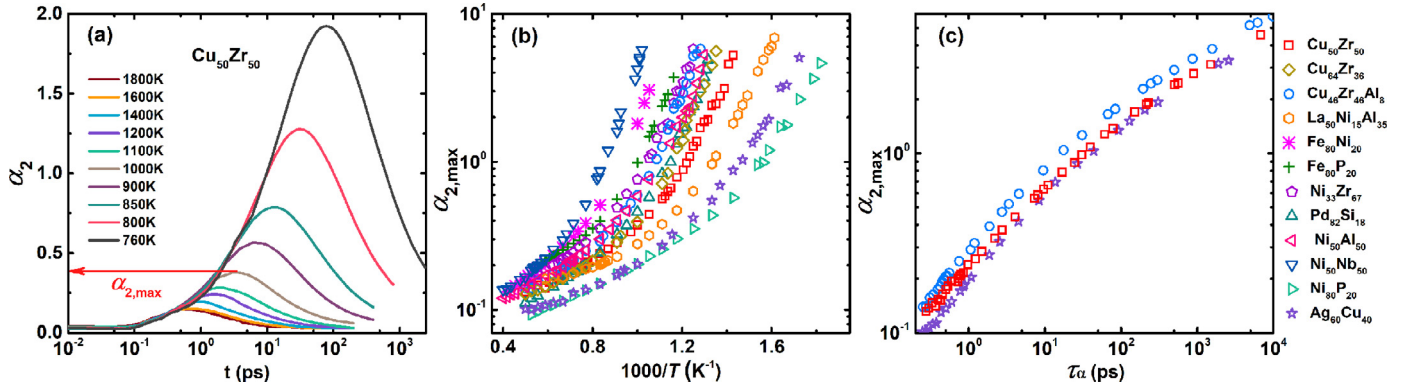


Fig. 2. (a) Non-Gaussian parameter α_2 versus time t for $\text{Cu}_{50}\text{Zr}_{50}$ liquids. The horizontal arrow illustrates how we determine $\alpha_{2,\max}$ (the height of α_2). (b) The temperature dependence of $\alpha_{2,\max}$ for 12 metallic glass-forming liquids. (c) $\alpha_{2,\max}$ versus τ_α for the same 12 representative systems as shown in Fig. 1(c).

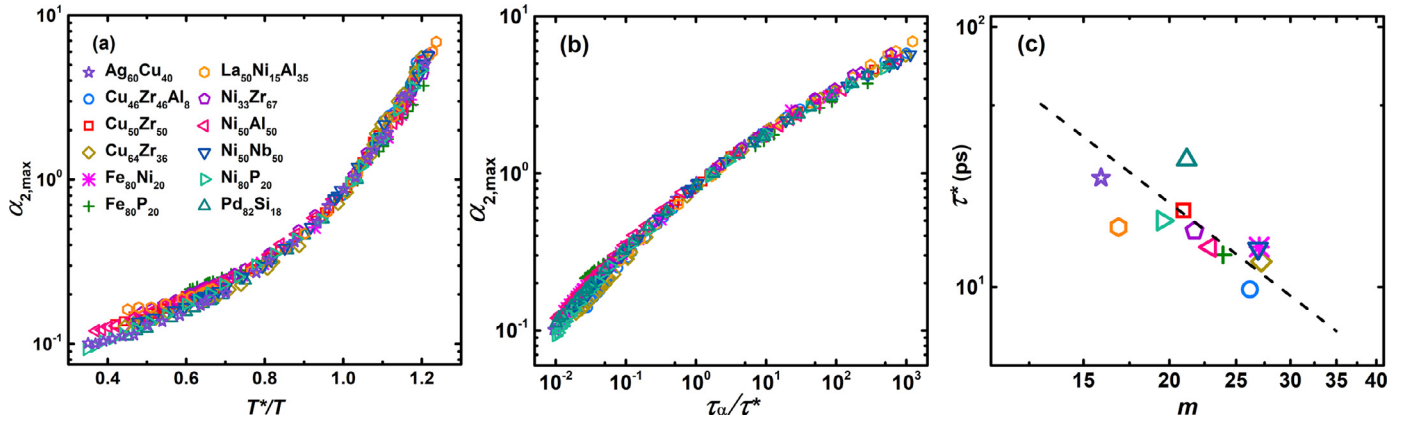


Fig. 3. (a) $\alpha_{2,\max}$ versus scaled reciprocal temperature T^*/T . (b) $\alpha_{2,\max}$ versus reduced structural relaxation time τ_α/τ^* . (c) Correlation between τ^* and dynamic fragility m . The dashed line is a guide for the eyes here.

Arrhenius equation to another form: $\tau_\alpha/\tau^* = \tau_0/\tau^* \exp[\frac{E}{k_B T^*} \cdot \frac{T^*}{T}]$, which means the relation between τ_α/τ^* and (T^*/T) follows this Arrhenius form at high temperatures above T_A . As shown in Fig. 4(a), the master curve of $\tau_\alpha/\tau^*(T^*/T)$ can be fitted directly by the Arrhenius form in the high-temperature range as expected and exhibits a clear deviation point when T^*/T is 0.65 and hence $T^*/T_A = 0.65$. Alternatively, we can also check the relation between T^* and T_A by detecting directly the values of T_A for all the metallic glass-forming systems studied here (see Fig. S1 and Fig. S2 in Supplementary Materials), and the correlation between T_A and T^* is shown in Fig. 4(b). It is interesting to find there is a nicely linear relation between T_A and T^* and the ratio of T^*/T_A is 0.65, which is exactly consistent with the location of non-Arrhenius crossover in Fig. 4(a). It can be expected in Fig. 3(a) that this crossover temperature, i.e., $T^*/T_A = 0.65$, corresponds to a specific but the same value of $\alpha_{2,\max}$ in all systems examined. Fig. 4(c) further shows that the specific value of $\alpha_{2,\max}$ is about 0.2 at T_A for all the systems studied here.

Since T_A corresponds to the constant dynamic heterogeneity, i.e., $\alpha_{2,\max} \approx 0.2$, it is natural to think of obtaining scaling collapses regarding dynamic heterogeneity and structural relaxation by using the information from the onset temperature T_A . In the Supplementary Materials, we show the nice scaling collapses of $\alpha_{2,\max}(T)$ and $\alpha_{2,\max}(\tau_\alpha)$ for all the liquids studied here by scaling T with T_A and scaling τ_α with τ_A (the structural relaxation time at T_A) in Fig. S3. As regards the most concerned relation between relaxation time and temperature, Fig. 4(d) shows that the $\tau_\alpha(T)$ curves for all the 12 metallic glass-forming liquids studied can be collapsed onto one single master curve by introducing T_A and τ_A . Therefore, our simulated results give a comprehension of

the reason why T_A can lead to the scaling collapse of experimental viscosity data for various metallic glass-forming systems [7]; it is the identical dynamic heterogeneity underlying this temperature that plays an essential role. From this point of view, although T_A is a distinctive crossover temperature in the structural relaxation, it is not so special if looking at dynamic heterogeneity and T_A is just one characteristic temperature T^* with a special value of dynamic heterogeneity in metallic glass-forming liquids.

Though T_A is known as the onset of the collective motions of atoms in previous studies [8,23,26,27], how to quantify the cooperative dynamics at T_A is unknown. Our finding that $\alpha_{2,\max}(T_A) \approx 0.2$ thus provides a simple but meaningful way to quantify the emergence of cooperative dynamics in metallic liquids from the perspective of dynamic heterogeneity. Based on the universal curves of $\tau_\alpha(T)$ and $\alpha_{2,\max}(T)$, it is possible to predict the dynamic properties including the evolution of relaxation time and dynamic heterogeneity upon cooling once T_A and the corresponding τ_A for metallic liquids interested are known. Furthermore, we find there is a negative relation between τ_A and m (see Fig. S5 in Supplementary Materials), indicating that some dynamic properties of supercooled liquid are already buried in the high-temperature melts. This finding combined with the quantitative relationship between T_A and T_g (see Fig. S2(b)) conveys a message that signals of glass transition process may inherit from the high-temperature metallic liquids, further strengthening similar viewpoints proposed in previous studies [7,48,49]. Therefore, T_A is a very important temperature which bridges structure relaxation and dynamic heterogeneity.

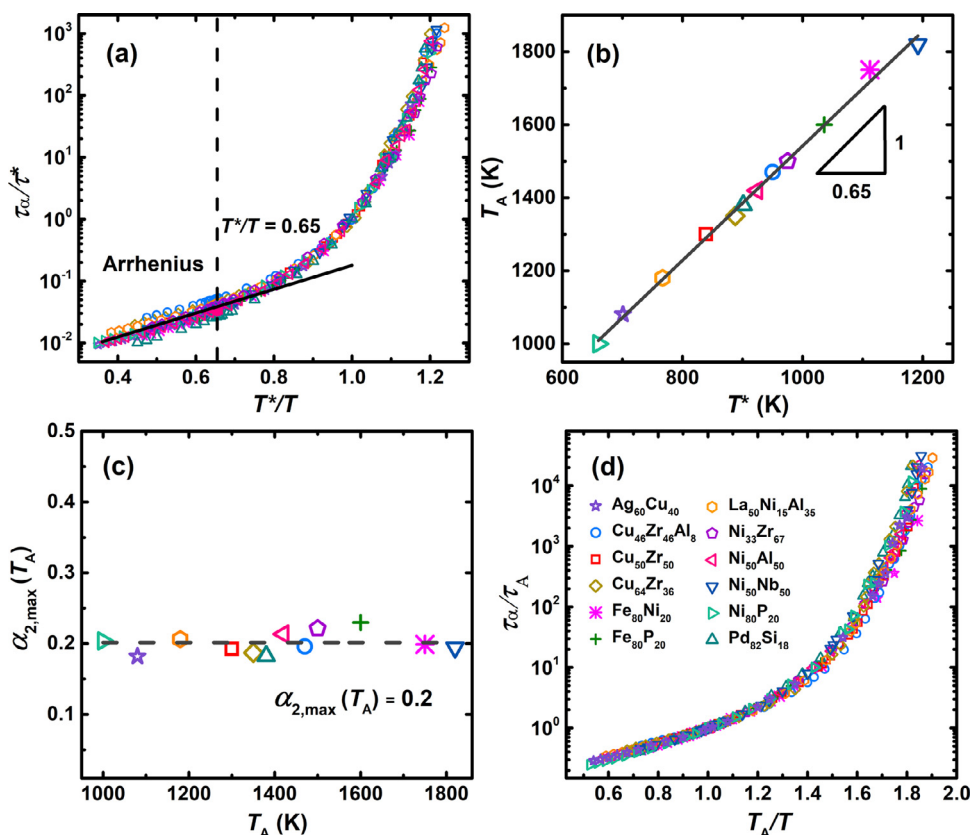


Fig. 4. (a) τ_α/τ^* versus T^*/T with τ^* and T^* corresponding to the iso- $\alpha_{2,\max}$ condition. The solid line is a fit to Arrhenius form. The dashed line marks where the deviation from Arrhenius starts. (b) The correlation between T_A and T^* . The solid line is a linear fit to $T^* = 0.65T_A$. (c) $\alpha_{2,\max}$ at T_A for all the 12 metallic glass-forming systems. (d) τ_α/τ_A versus T_A/T with T_A corresponding to the onset temperature and τ_A corresponding to the relaxation time at T_A .

In summary, the general descriptions of structural relaxation and dynamic heterogeneity upon cooling is obtained for 12 metallic glass-forming liquids, by introducing a characteristic time scale and characteristic temperature under the identical dynamic heterogeneity condition. We reveal that the onset temperature of cooperative motion, T_A , corresponds to the same dynamic heterogeneity ($\alpha_{2,\max} \approx 0.2$) in various metallic glass-forming liquids, which provides a new and quantitative way to detect the onset of collective atomic motion. Our findings further enhance the significance of T_A as well as the dynamic heterogeneity in studying metallic glass-forming liquids.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2020.02.012.

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