



Configuration correlation governs slow dynamics of supercooled metallic liquids

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The origin of dramatic slowing down of dynamics in metallic glass-forming liquids toward their glass transition temperatures is a fundamental but unresolved issue. Through extensive molecular dynamics simulations, here we show that, contrary to the previous beliefs, it is not local geometrical orderings extracted from instantaneous configurations but the intrinsic correlation between configurations that captures the structural origin governing slow dynamics. More significantly, it is demonstrated by scaling analyses that it is the correlation length extracted from configuration correlation rather than dynamic correlation lengths that is the key to determine the drastic slowdown of supercooled metallic liquids. The key role of the configuration correlation established here sheds important light on the structural origin of the mysterious glass transition and provides an essential piece of the puzzle for the development of a universal theoretical understanding of glass transition in glasses.

metallic glass | dynamics | structure | glass transition

The underlying mechanism of how viscosities (or structural relaxation times) of glass-forming liquids surges by many orders of magnitude on approaching glass-transition points remains one of the most controversial issues in fundamental sciences (1). A large variety of theoretical frameworks involving growing spatial correlations, either dynamic or static, were proposed to explain the origin of the spectacular slowdown (ref. 2 and therein). In their pioneering theory, Adam and Gibbs (3) proposed that the rearrangements of atoms are collective in localized domains during cooling. The size and lifetime of the cooperatively rearranging regions increase with reducing temperature, thereby leading to vanishing configurational entropy and drastic slowing down of dynamics. This picture of heterogeneous dynamics was later supported by advanced experiments and large-scale computer simulations (4, 5), which shows a wide distribution of local dynamics in supercooled liquids with some domains moving significantly faster or slower than the average. The dynamic correlation length quantifying the extent of spatially correlated motions increases remarkably toward the glass transition. Recently, experiments and modeling related to the spatial heterogeneities in metallic glasses (MGs) also support this conception and imply the potential correlation between dynamics and structure (6–9). However, the puzzling fact is that the remarkable dynamic slowdown is not accompanied by any obvious structure changes based on two-point correlators in traditional diffraction and scattering experiments. Thus, the structural origin of the glass transition is still mysterious.

Inspired by Frank's proposal (10) in 1952 that densely packed icosahedron showing incompatible symmetry with crystallographic symmetries would stabilize a liquid with constituents of equal size, many research works have been pursuing the role of these locally preferred structures in determining glassy properties (11–16). The dynamics of the centers of icosahedral clusters was found to be slow, because of strong constraints imposed by their neighbors. Thus, geometrical frustration induced by

icosahedral clusters has long been suggested as the structural origin of slow dynamics in metallic glass-forming liquids (ref. 12 and therein). However, the concentration of icosahedral clusters in MGs is known to be quite low and highly composition dependent (12). What exact role of geometrical orderings determined by local atomic packings plays in MG formation remains arguable. It is urgent to unravel whether there is an intrinsic order-agnostic parameter corresponding to configurations which governs the slow dynamics of supercooled metallic liquids. Furthermore, all previous studies on slowdown of metallic liquids include the influences of changes in temperature, which itself will induce denser packings during cooling and thus cannot provide a direct link between possible structural orderings and dynamical slowdown. Therefore, the mechanism of vitrification in MGs has not yet been well understood. Moreover, although the prominent phenomenon of dynamic heterogeneity has aroused intensive interests and become a central topic in glass physics (17), it is still elusive whether dynamic heterogeneity is the consequence or the primary origin of the dynamical slowdown (18) in metallic glass-forming liquids.

In this work, we studied the slowing down of dynamics in realistic model MGs by molecular dynamics simulations based on embedded-atom method (EAM) potentials (*Materials and Methods*). By including confinement effects in equilibrated supercooled metallic liquids, we observed strong decoupling between local

Significance

The search for a structural origin governing the dynamical slowing down of a supercooled liquid toward glass transition is an active area of the community of amorphous materials. In the past decade, the locally preferred geometrical orderings, that is, those local polyhedral packing clusters extracted from instantaneous atomic configurations, such as icosahedron, have been suggested as the structural origin of slow dynamics in metallic glass-forming liquids. Here, we demonstrate that it is the intrinsic correlation between configurations that captures the structural origin governing slow dynamics. A correlation length extracted from these configurations' correlation plays a more important role than various dynamic correlation lengths in determining the drastic dynamical slowdown of supercooled metallic liquids.

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metallic liquids. In what follows, we will provide a detailed analysis to understand whether dynamic heterogeneity is the origin of slow dynamics or not. To quantify the slowdown of dynamics with confinement, we extracted the corresponding $\tau_{\alpha,z}$. Fig. 1D shows $\tau_{\alpha,z}$ as a function of z at various temperatures in comparison with τ_{α} for the bulk. Obviously, the dynamics near the walls is orders of magnitude slower than those far away from them where $\tau_{\alpha,z} \cong \tau_{\alpha}$. The range of such influence propagates at lower temperatures, indicating some growing length scales (23–25). From the viewpoint of dynamics, a liquid-to-glass transition is likely to occur with the decreasing distance to the walls at a fixed T higher than the glass-transition temperature of the bulk. Since this dynamical slowdown at a constant temperature is different from the traditional hyperquenching, we can study the pure structure evolution of supercooled metallic liquids correlated with dynamical slowdown in the absence of changes in temperature.

Decoupling Between Dynamics and Local Structural Orderings. We used Voronoi tessellation to characterize the local structure (*Materials and Methods*). Given that full icosahedron $\langle 0, 0, 12, 0 \rangle$ is the most frequently discussed structural motif in CuZr-based MGs (12, 13), we show the fraction of $\langle 0, 0, 12, 0 \rangle$ (f_{ico}) as function of z as an example in Fig. 2A. The numbers of the Voronoi index $\langle 0, 0, 12, 0 \rangle$ sequentially represent the number of triangle, tetragon, pentagon, and hexagon in the Voronoi polyhedron. Although f_{ico} increases during cooling, it is unambiguous that its fraction is low and it is almost z -independent albeit with some fluctuations. Similar invariant trends are also observed in other atomic clusters

(*SI Appendix, Fig. S4*). Similar results were also obtained in random pinning and in $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ (*SI Appendix*). Locally preferred clusters have commonly been treated as the key factor controlling dynamical slowdown in MGs (12). If that were the truth, any dynamics change in the glass-forming liquid would be in accord with the change in these structural orderings, including in the confined systems. Fig. 2B shows $\tau_{\alpha,z}$ at various temperatures as a 2D function of z and f_{ico} . Obviously, the relaxation times can change hugely without changing f_{ico} . The sharp contrast between $\tau_{\alpha,z}$ and locally preferred clusters in Figs. 1D and 2A (and *SI Appendix, Fig. S4*) clearly demonstrates decoupling of slow dynamics and local geometrical orderings in the absence of temperature changes. This delivers a strong message that local structural orderings, like icosahedra, shall not play a determining role in the slowing down of dynamics, at least in the pinning-induced slow dynamics. Our findings contrast the common belief that local geometrical orderings extracted from instantaneous configurations be a universal structural origin of slow dynamics in metallic glass-forming liquids.

Coupling Between Dynamics and Configuration Correlation. Now we come to the long-debated question of what order parameter originating from configurations could physically determine the slow dynamics of supercooled metallic liquids in confinement. Instead of just considering one instantaneous configuration, we considered the correlation between two configurations. In the sandwich-pinning geometry (23), we defined an overlap function $q_c(t, z)$ by dividing the space into small cubic boxes of linear size $l = 0.68 \text{ \AA}$ so that there would be no more than one atom in a single box. A binary digit $n_i(t) = 1$ is defined if the i th box is occupied by an atom at t , and $=0$ otherwise. The overlap profile quantifying the similarity between two configurations separated by t in the z direction is measured by $q_c(t, z) = \langle \sum_{i(z)} n_i(t)n_i(0) \rangle / \langle \sum_{i(z)} n_i(0) \rangle$, where the sum runs over all boxes at z from the walls. In this calculation, we considered two instantaneous configurations at a temperature without finding their inherent structures. Fig. 3A shows the decaying behavior of $q_c(t, z)$ at 800 K as an example. For large z , the curves collapse with the bulk sample indicating negligible effects of the confinement, consistent with Fig. 1B and D. At long time limit, these profiles decay to a plateau $q_c(t \rightarrow \infty, z) = q_{rand} = \rho l^3$, where ρ is the number density of the bulk. For small z , $q_c(t \rightarrow \infty, z)$ reaches a value larger than q_{rand} , which means the similarity between two configurations separated by t increases due to the confinement. To quantify this effect, we fitted the final decay of $q_c(t, z)$ to a stretched exponential form, $q_c(t, z) - q_{rand} = A \exp[-(t/\tau)^\beta] + q_\infty(z)$, where A , τ , β , and $q_\infty(z)$ are fitting parameters. Obviously, $q_\infty(z)$ captures the intrinsic configuration correlation at z . We can then obtain the change tendency of $q_\infty(z)$ with respect to z and T (*SI Appendix, Fig. S5*). To explore the role of the configuration correlation in dynamics, it is necessary to establish the relation between $q_\infty(z)$ and $\tau_{\alpha,z}$ at various temperatures. If we consider the supercooled liquid in a mosaic of states in which different patches of the mosaic correspond to different metastable states in the free-energy landscape (FEL) (26), the intrinsic structural correlation $q_\infty(z)$ defined by the similarity between two configurations separated by infinite time reflects the available configuration states in the FEL. For each temperature, $q_\infty(z)$ increases with decreasing z (*SI Appendix, Fig. S5*), indicating that the available configuration states are strongly constrained by the pinning walls. Surprisingly, when we plot $\tau_{\alpha,z}/\tau_{\alpha}$ against $q_\infty(z)/q_0$, as shown in Fig. 3B, curves of all temperatures collapse into a master curve:

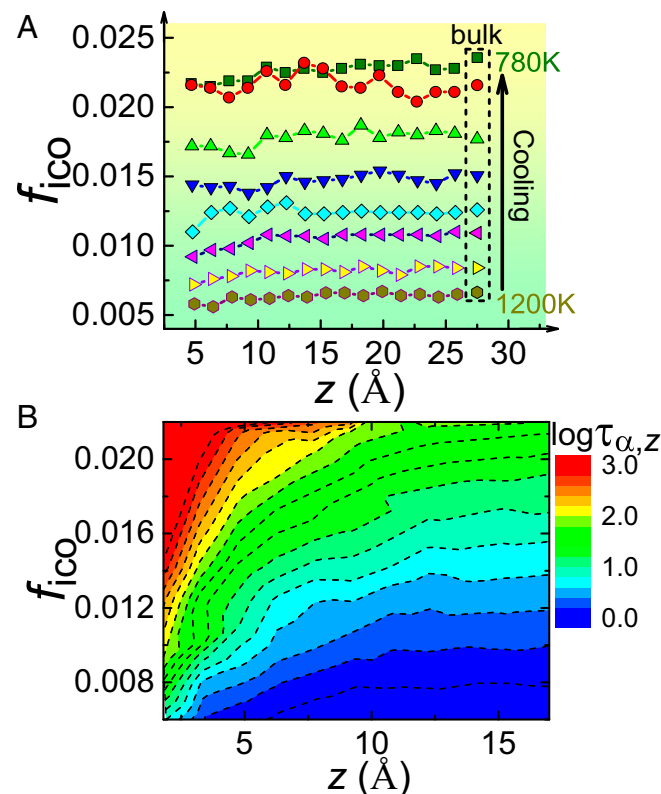


Fig. 2. Local geometrical ordering in confinement. (A) The fraction of full icosahedra $\langle 0, 0, 12, 0 \rangle$ (f_{ico}) as a function of z at different temperatures. The results of the bulk are included in dashed rectangles for comparison. The sharp contrast with Fig. 1D demonstrates the decoupling between slow dynamics and full icosahedra. (B) The contour map of the relaxation times in confinement $\tau_{\alpha,z}$ as a 2D function of f_{ico} and z . It is obvious that $\tau_{\alpha,z}$ can change remarkably when f_{ico} is invariant.

$$\tau_{\alpha,z}/\tau_{\alpha} = \tilde{H}(q_\infty(z)/q_0) \sim \left(\frac{q_\infty(z)}{q_0} \right)^\beta,$$

where $\beta = 1.0$ (see the fit line in Fig. 3B). The q_0 is a temperature-dependent scaling parameter. The scaling collapse of $\tau_{\alpha,z}$ at various temperatures provides direct evidence that the intrinsic

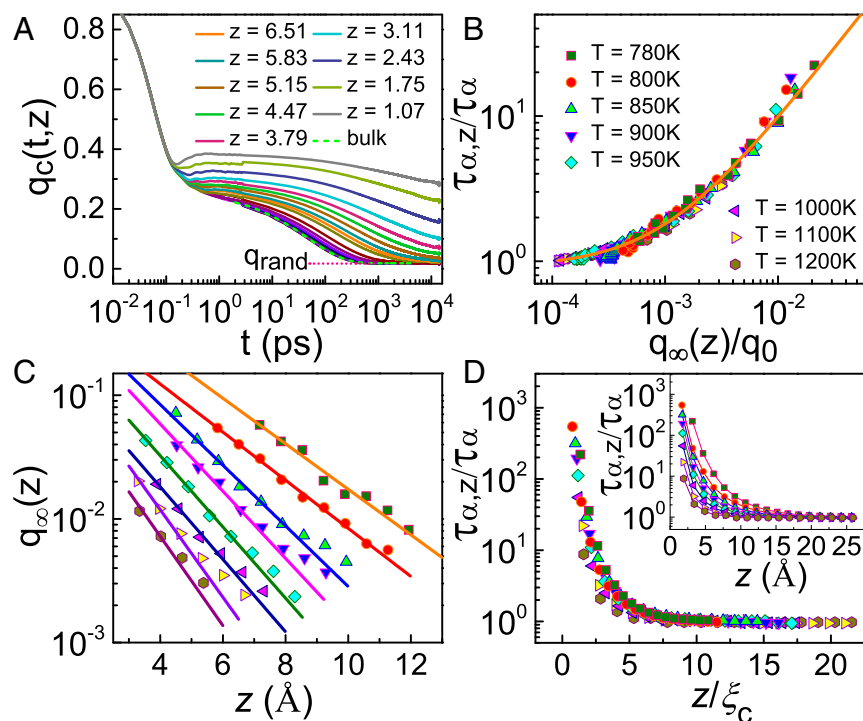


Fig. 3. Correlation length from configuration correlation. (A) The overlap profile $q_c(t, z)$ of $\text{Cu}_{50}\text{Zr}_{50}$ for $T = 800$ K and various values of z . For $z > 6.51$, z increases to 25.55 by an increment of $l = 0.68$ Å. The result from the bulk is also included as the dashed line. $q_{\text{rand}} = \rho^3$. (B) Scaling plot of $\tau_{\alpha,z}/\tau_\alpha$ when $q_\infty(z)$ is scaled by q_0 in $\text{Cu}_{50}\text{Zr}_{50}$. The parameter q_0 is 1.0a, 1.2a, 1.8a, 1.7a, 3.0a, 4.0a, 5.0a, and 7.0a for temperatures from 780 to 1,200 K, respectively, where a is an arbitrary positive constant. The orange line is a linear fit. (C) Temperature dependence of $q_\infty(z)$ at various z . The data have been shifted for clarity. The solid lines are fits to the exponential form $q_\infty(z) = B \exp(-z/\xi_C)$. (D) Scaling plot of $\tau_{\alpha,z}/\tau_\alpha$ when z is scaled by the correlation length ξ_C in $\text{Cu}_{50}\text{Zr}_{50}$. The data are scattering if not considering ξ_C (*Inset*). Thus, the slow structural relaxations are governed by ξ_C in the confined liquid.

structural correlation defined by configuration correlations at infinite time is the key in controlling slow dynamics of supercooled metallic liquids in confinement. It reveals quantitatively the underlying linkage between structural correlation and relaxation dynamics in metallic glass-forming liquids, which will advance further quantitative study on the correlation between atomic configurations and structural relaxations.

Furthermore, as shown in Fig. 3C, the relation between $q_\infty(z)$ and z can be well fitted by an exponential form $q_\infty(z) \sim \exp(-z/\xi_C)$ for all temperatures investigated. Here we only consider the distances where the self-part of $q_c(t, z)$ decays to 0 (*SI Appendix, Fig. S6*). The correlation length ξ_C is the temperature-dependent fitting parameter. Interestingly, the combination of Fig. 3B and C can lead to the universal scaling relation of $\tau_{\alpha,z}$:

$$\tau_{\alpha,z}/\tau_\alpha = \tilde{F}(z/\xi_C) \sim e^{-z/\xi_C}.$$

Therefore, by scaling τ_α and ξ_C , the scaling collapse of $\tau_{\alpha,z}$ for various temperatures is straightforward, as corroborated in Fig. 3D. The collapse is better at lower temperatures in the FEL-dominated region, consistent with previous studies (27), and was also found in $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$ (*SI Appendix*). It indicates that the decoupling relation between $\tau_{\alpha,z}/\tau_\alpha$ and z (Fig. 3D, *Inset*) is controlled by ξ_C as well, which is the robust evidence that ξ_C is the key to connecting structural relaxations and structural correlation, at least in the confined systems. Furthermore, we estimated two dynamic correlation lengths $\xi_{c,\text{dyn}}$ and $\xi_{s,\text{dyn}}$ that stem from the nonlinear response of local dynamics to the walls (23) (*Materials and Methods* and *SI Appendix, Fig. S7*). In contrast, no scaling collapse can be achieved between $\tau_{\alpha,z}/\tau_\alpha$ and $\xi_{c,\text{dyn}}$ or $\xi_{s,\text{dyn}}$ (*SI Appendix, Fig. S8*). These findings deliver a strong message that it is the configuration correlation rather than dynamic heterogeneities measured by the dynamic correlation lengths that controls the slow dynamics in the confined metallic liquids.

Critical Role of the Correlation Length in Governing Slow Dynamics.

Next, we move further to unravel the role of ξ_C in slow dynamics of cooled metallic glass-forming liquids in bulk. Here, we

disentangled these correlation lengths in cooled bulk liquids by the finite-size scaling analysis (18), which is widely accepted by the scientific community to extract the dominant length scale in critical phenomena (see more details about finite-size scaling in glass transition in *SI Appendix*). We calculated τ_α of $\text{Cu}_{50}\text{Zr}_{50}$ at a series of system sizes N (*Materials and Methods*). As shown in Fig. 4A (*Inset*), there is a clear N dependence of τ_α , particularly at low temperatures (18, 28). More importantly, a reasonable scaling collapse is obtained by plotting $\tau_\alpha(N, T)/\tau_\alpha(N \rightarrow \infty, T)$ versus $N/(\xi_C)^3$. This provides strong evidence that ξ_C is also the dominant length scale in supercooled metallic liquid in bulk and confirms the coupling between the slow dynamics and the structural correlation. Meanwhile, the spatial correlation length of $\langle 0, 0, 12, 0 \rangle$ by considering the structure factor of icosahedral centers (29) (*Materials and Methods*) is quite small compared with ξ_C (*SI Appendix, Fig. S9*). This further indicates that not only is its fraction low as shown before, the correlation between $\langle 0, 0, 12, 0 \rangle$ in space during cooling is rather weak by considering high-order correlation functions. Conceptually, ξ_C extracted from intrinsic configurations correlation is more theoretically appealing and universal than certain geometrical clusters in that its definition does not rely on any assumption of specific structural order a priori.

Since dynamic heterogeneity has long been thought to play an important role in explaining slow dynamics, we also calculated four-point dynamic correlation length ξ_4 from spatial correlations of atomic mobility (30) (*Materials and Methods*) in addition to $\xi_{c,\text{dyn}}$ and $\xi_{s,\text{dyn}}$. Although ξ_4 is a standard measurement of the length scale of dynamic heterogeneity in model glass-forming liquids, it has been rarely discussed in MGs (31). The growth of these structural and dynamic correlation lengths is shown in Fig. 4B. Evidently, dynamic length scales grow faster than ξ_C , in accord with the previous studies (23, 32, 33). Because ξ_C could collapse $\tau_\alpha(N, T)$ in finite-size scaling analysis, the relaxation times cannot be superimposed by the dynamic length scales with a larger growth rate. Indeed, remarkable data scattering is observed when $\tau_\alpha(N, T)/\tau_\alpha(N \rightarrow \infty, T)$ is plotted against the scaled dynamic susceptibility $\chi_4(N, T)/\chi_4(N \rightarrow \infty, T)$ (*SI Appendix, Fig.*

around atoms by constructing bisecting planes along the lines joining the central atom and all its neighbors. The Voronoi index $\langle n_3, n_4, n_5, n_6 \rangle$ is used to characterize the geometry feature of atomic clusters, where n_i ($i = 3, 4, 5, 6$) denotes the number of i -edged faces of a Voronoi polyhedron. Voronoi tessellation was performed using the voro++ package (math.lbl.gov/voro++/) (40). For the sandwich-pinning and random-pinning geometries, the configurations for Voronoi tessellation were collected after simulations at least 10 times of the corresponding structural relaxation times. In random pinning, both pinned and unpinned atoms were taken into consideration when conducting Voronoi analysis, to avoid artificial holes created by pinned atoms. However, when calculating the fractions, only unpinned atoms were considered.

Dynamic Correlation Lengths of Nonlinear Reponses. According to the profiles of $q_c(t, z)$ and its self-part $q_{c,s}(t, z)$, the cage effect is much stronger with decreasing z , showing the strong effects of the walls on atomic rearrangements. Such influence is more remarkable at lower temperatures, indicating growing dynamic correlations. To extract the dynamic correlation lengths $\xi_{c,dyn}$ and $\xi_{s,dyn}$, we calculated the areas below the overlaps $q_c(t, z)$ and $q_{c,s}(t, z)$ by considering only when the plateau is shown. The resulting timescales are $\tau_{c,z}$ and $\tau_{s,z}$, respectively (SI Appendix, Fig. S7). By fitting the scaled timescales at large z to the exponential forms, $\log(\tau_{c,z}) = \log(\tau_{c,bulk}) + B_c \exp(-z/\xi_{c,dyn})$ and $\log(\tau_{s,z}) = \log(\tau_{s,bulk}) + B_s \exp(-z/\xi_{s,dyn})$, the dynamic length scales were estimated. Since the dynamics of the center recovers to the bulk behaviors, we used the data from the center represent the bulk dynamics in the fittings.

Four-Point Correlation Lengths. To accurately measure the four-point dynamic correlation length ξ_4 , either quite large sample- or ensemble-independent dynamic susceptibilities is necessary. In this work, we used a large system with $n = 462,150$ to calculate ξ_4 . The box length is around 200 Å, which is large to access small wavevectors. The preparation of equilibrated samples is referred to in *Molecular Dynamics Simulations*. To save computer time, the timestep was chosen as 0.005 ps. To characterize dynamic heterogeneity, we first defined an overlap function $Q(t) = \sum_{j=1}^N \omega(|\vec{r}_j(0) - \vec{r}_j(t)|)$, where the weight function $\omega(r) = 1$ if $r \leq 1.0$ Å ($\sim 0.3d_{Zr}$; d_{Zr} is the atomic diameter of Zr), and = 0 otherwise. The fluctuation of $Q(t)$ defines the dynamic susceptibility

$\chi_4(t) = 1/N[\langle Q(t)^2 \rangle - \langle Q(t) \rangle^2]$. Typically, $\chi_4(t)$ shows a peak at an intermediate timescale τ_p proportional to τ_α . As usual, we calculated the four-point dynamic structure factor $S_4(q; t)$ of immobile atoms at the peak timescale of $\chi_4(t)$ through $S_4(q; t) = 1/N[\langle W(\vec{q}, t)W(-\vec{q}, t) \rangle - \langle W(\vec{q}, t) \rangle \langle W(-\vec{q}, t) \rangle]$, in which $W(\vec{q}; t) = \sum_{j=1}^N \exp[i\vec{q} \cdot \vec{r}_j(0)] \omega(|\vec{r}_j(0) - \vec{r}_j(t)|)$. By fitting the low-wavenumber part of $S_4(q; t)$ to the Ornstein-Zernike function $S_4(q; \tau_p) = S_4(q=0; \tau_p) / [1 + (q\xi_4)^2]$, ξ_4 was obtained. A good data collapse was obtained when q and $S_4(q; \tau_p)$ were scaled by ξ_4 and $S_4(q=0; \tau_p)$, respectively (SI Appendix, Fig. S11). This demonstrates the accuracy of the estimation of ξ_4 by using the large sample. Similarly, we computed the structure factor of full icosahedra $\langle 0, 0, 12, 0 \rangle$ by calculating $S_{4,\langle 0,0,12,0 \rangle}(q) = 1/N[\langle W(\vec{q})W(-\vec{q}) \rangle - \langle W(\vec{q}) \rangle \langle W(-\vec{q}) \rangle]$, in which $W(\vec{q}) = \sum_{j=1}^{N_{\langle 0,0,12,0 \rangle}} \exp[i\vec{q} \cdot \vec{r}_j(0)]$, where $N_{\langle 0,0,12,0 \rangle}$ is the number of icosahedral centers. Then the spatial correlation length of $\langle 0, 0, 12, 0 \rangle$ is evaluated by fitting $S_{4,\langle 0,0,12,0 \rangle}(q)$ to the Ornstein-Zernike function at low-wavenumber region (SI Appendix, Fig. S9).

Finite-Size Scaling. We used the model system $\text{Cu}_{50}\text{Zr}_{50}$ for finite-size scaling analysis. The system size changes from $n = 100$ to $n = 1,600$. The simulation method is similar to the description in *Molecular Dynamics Simulations*. We also included the large system with $n = 462,150$ for analysis. Ten independent simulations were carried out for ensemble average. To obtain $\tau_\alpha(N \rightarrow \infty, T)$, the relaxation time in size limit, we fitted the N dependence of $\tau_\alpha(N, T)$ to a functional form $\tau_\alpha(N, T) = a(T) + b(T)/N$. We also used the dynamic susceptibility at $n = 462,150$ as $\chi_4(N \rightarrow \infty, T)$.

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