

Power-law scaling and fractal nature of medium-range order in metallic glasses

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The atomic structure of metallic glasses has been a long-standing scientific problem. Unlike crystalline metals, where long-range ordering is established by periodic stacking of fundamental building blocks known as unit cells, a metallic glass has no long-range translational or orientational order, although some degrees of short- and medium-range order do exist^{1–3}. Previous studies^{1–4} have identified solute- (minority atom)-centred clusters as the fundamental building blocks or short-range order in metallic glasses. Idealized cluster packing schemes, such as efficient cluster packing on a cubic lattice¹ and icosahedral packing³ as in a quasicrystal, have been proposed and provided first insights on the medium-range order in metallic glasses. However, these packing schemes break down beyond a length scale of a few clusters. Here, on the basis of neutron and X-ray diffraction experiments, we propose a new packing scheme—self-similar packing of atomic clusters. We show that the medium-range order has the characteristics of a fractal network with a dimension of 2.31, and is described by a power-law correlation function over the medium-range length scale. Our finding provides a new perspective of order in disordered materials and has broad implications for understanding their structure–property relationship, particularly those involving a change in length scales.

Fractals are ubiquitous in nature. Unlike what they appear to be at first glance, clouds are not spheres, mountains are not cones, islands are not circles; instead, they are fractals⁵. Characterized by self-similarity, scale invariance and fractal dimension, a fractal geometry is the same ‘from near or from far’, forming the missing complement to Euclidean geometry and crystalline symmetry^{5,6}. Fractals are also found in a variety of condensed-matter systems including polymers, composite materials, membranes, porous media, colloids and aerosols^{6–9}. The self-similar aggregates of gold nanoparticles in suspension are, for example, a well-recognized class of microscopic fractals manifested by a fractal dimension (D_f) of 2.05 (ref. 8). As for glass systems, aspects of fractals have also been suggested over the years^{10–12}. For instance, light-scattering experiments on superionic borate glasses presented evidence of a crossover frequency between phonons and fractons, or fundamental excitation of a fractal lattice^{10–12}. Borjesson *et al.*¹¹ have used reverse Monte Carlo simulation to analyse the neutron diffraction data of similar glasses. Their simulation results suggested a fractal structure with an upper correlation length of about 15–20 Å, although D_f could not be determined owing to the limited number of atoms used in the simulation. While the results from these early studies are encouraging, there has been no direct evidence that links the structure of a glass to a fractal network. Here, we present such evidence for metallic glasses, which are made by rapid cooling

of molten metals and represent an important class of complex disordered materials.

The initial evidence of a fractal structure in metallic glass came from the analysis of the diffraction peak positions. In a crystalline metal or alloy, atoms are arranged periodically on a lattice and the first Bragg peak in the powder diffraction pattern always corresponds to the largest interplanar distance ($d_1 \propto 1/q_1$, where q_1 is the first peak position in momentum transfer), for example, $d_{(111)}$ in face-centred-cubic copper¹³. When scaling this linear length ($1/q_1$) with the atomic volume (v_a , see below), a power of 1/3 is always obtained. This is also valid when scaling a strained lattice constant under tension or compression, which is in fact the basis of strain measurements by X-ray and neutron diffraction¹⁴. This 1/3 power law is therefore a direct consequence of the crystalline long-range order in the three-dimensional Euclidean space. In a molecular gas, where only short-range order (SRO) is present, $1/q_1$ is related to the interatomic distance following the well-known Ehrenfest relationship¹⁵ and is thus expected to also obey the 1/3 power-law scaling with the molecular volume. In amorphous solids such as a metallic glass, atomic correlations extend well beyond SRO into the medium-range-order (MRO) regime, but the lack of long-range periodicity makes the glass structure look ‘disordered’. A signature of this ‘disordered’ structure is the ‘missing’ (or ‘smearing’ of) Bragg peaks from the diffraction pattern and, as a replacement, the emergence of a few diffuse scattering haloes. The first halo in such a pattern has been referred to as the first sharp diffraction peak¹⁶ (FSDP). Indeed, in metallic glasses, the first diffraction peak shows a typical full-width at half-maximum of 0.4–0.5 Å^{−1}, much sharper than those at high q , the widths of which are 1.4–1.8 Å^{−1}. It is therefore anticipated that the FSDP carries significant information about order in metallic glasses. Thus, in what follows, we will concentrate our analysis on the FSDP.

Table 1 summarizes experimental values of q_1 for a variety of metallic glasses, determined from neutron and X-ray diffraction studies in the present work and in the literature^{4,17–24}. In the present study, metallic glasses of Zr_xCu_{100-x} ($x = 35.5, 38.6, 44.0, 50.0, 54.5, 60.0$) and $Zr_{53.7}Cu_{28.5}Ni_{19.4}Al_{8.4}$ were fabricated using melt-spinning and copper-mould casting, respectively. Neutron scattering experiments of these glasses were carried out on the General Purpose Powder Diffractometer at Argonne National Laboratory. The structure factor $S(q)$ ($q = 4\pi \sin \theta / \lambda$, where θ is half of the scattering angle and λ is the neutron wavelength) and the reduced pair distribution function, $G(r) = (2/\pi) \int_0^{q_{\max}} q[S(q) - 1] \sin(qr) dq$, where r is the distance and $q_{\max}$ is the maximum value of q for the Fourier transform, were obtained by analysing the scattering data as described elsewhere⁴. Also listed in Table 1 are atomic volumes (v_a) determined from mass density (ρ_m) measurements, that is, $v_a = \rho_m / (N_a M)$, where N_a is Avogadro’s number and M is the

Table 1 | The FSDP position (q_1 , Å⁻¹) for metallic glasses determined from neutron (labelled with an asterisk) and X-ray (labelled with a dagger) diffraction measurements.

Metallic glass	q_1	ρ	v_a	$q_1 \cdot v_a^{0.433}$	Reference
Zr _{35.5} Cu _{64.5} *	2.826	7.751	15.72	9.32	Present work
Zr _{38.6} Cu _{61.4} *	2.801	7.673	16.07	9.32	Present work
Zr _{44.0} Cu _{56.0} *	2.763	7.542	16.68	9.35	Present work
Zr _{50.0} Cu _{50.0} *	2.719	7.408	17.35	9.35	Present work
Zr _{54.5} Cu _{45.5} *	2.684	7.306	17.87	9.35	Present work
Zr _{60.0} Cu _{40.0} *	2.656	7.227	18.42	9.38	Present work
Zr _{53.7} Cu _{28.5} Ni _{19.4} Al _{8.4} *	2.675	6.824	18.20	9.40	Present work
Zr _{52.5} Ti ₅ Cu _{17.9} Ni _{14.6} Al ₁₀ *	2.658	6.629	18.30	9.36	Ref. 4
Zr _{54.5} Ti _{7.5} Cu ₂₀ Ni ₈ Al ₁₀ †	2.605	6.47	18.85	9.29	Ref. 17
Zr ₅₇ Ti ₅ Cu ₂₀ Ni ₈ Al ₁₀ †	2.602	6.54	18.92	9.29	Ref. 17
Zr ₅₈ Ti ₄ Cu ₂₀ Ni ₈ Al ₁₀ †	2.599	6.57	18.94	9.29	Ref. 17
Zr ₅₉ Ti ₃ Cu ₂₀ Ni ₈ Al ₁₀ †	2.597	6.59	19.00	9.29	Ref. 17
Zr ₆₀ Ti ₂ Cu ₂₀ Ni ₈ Al ₁₀ †	2.595	6.62	19.02	9.29	Ref. 17
Zr _{80.0} Fe _{20.0} †	2.524	6.75	20.71	9.38	Refs 18,19
Zr _{76.0} Fe _{24.0} †	2.535	6.78	20.27	9.33	Refs 18,19
Zr _{75.0} Fe _{25.0} †	2.543	6.80	20.12	9.33	Refs 18,19
Zr _{73.0} Fe _{27.0} †	2.562	6.84	19.83	9.34	Refs 18,19
Zr _{67.0} Cu _{33.0} †	2.588	7.07	19.27	9.32	Ref. 20
Zr _{60.0} Cu _{40.0} †	2.624	7.19	18.52	9.29	Ref. 20
Zr _{54.0} Cu _{46.0} †	2.674	7.31	17.84	9.31	Ref. 20
Zr _{50.0} Cu _{50.0} †	2.699	7.39	17.39	9.30	Ref. 20
Zr _{46.0} Cu _{54.0} †	2.731	7.47	16.96	9.30	Ref. 20
Zr _{40.0} Cu _{60.0} †	2.778	7.64	16.23	9.29	Ref. 20
Zr _{34.0} Cu _{66.0} †	2.822	7.83	15.48	9.24	Ref. 20
Zr ₆₅ Ni ₃₅ †	2.620	6.98	18.99	9.37	Ref. 21
Ti ₆₀ Ni ₄₀ *†	2.910	5.96	14.57	9.28	Ref. 21
La ₆₂ Al ₁₄ (Cu _{5/6} Ag _{1/6}) ₁₄ Ni ₅ Co ₅ †	2.20 [#]	6.190	28.36	9.36	Ref. 22
Mg ₆₅ Cu ₂₅ Tb ₁₀ †	2.52 [#]	3.790	20.85	9.39	Ref. 23
Y ₅₅ Al ₂₅ Co ₂₀ †	2.23 [#]	5.802	27.18	9.32	Ref. 24
La ₅₅ Al ₂₅ Co ₂₀ †	2.32 [#]	6.373	25.03	9.35	Ref. 24
Pr ₅₅ Al ₂₅ Co ₂₀ †	2.35 [#]	6.584	24.68	9.42	Ref. 24
Nd ₅₅ Al ₂₅ Co ₂₀ †	2.33 [#]	7.343	23.76	9.19	Ref. 24
Gd ₅₅ Al ₂₅ Co ₂₀ †	2.36 [#]	7.488	23.50	9.26	Ref. 24
Tb ₅₅ Al ₂₅ Co ₂₀ †	2.35 [#]	7.560	23.71	9.26	Ref. 24
Dy ₅₅ Al ₂₅ Co ₂₀ †	2.42 [#]	7.888	23.00	9.41	Ref. 24
Ho ₅₅ Al ₂₅ Co ₂₀ †	2.39 [#]	8.157	22.51	9.20	Ref. 24
Er ₅₅ Al ₂₅ Co ₂₀ †	2.36 [#]	4.863	23.03	9.18	Ref. 24

Also listed are mass densities (ρ , g cm⁻³), atomic volumes (v_a , Å³ per atom) obtained from mass density measurements, and $q_1 \cdot v_a^{0.433}$, which demonstrates the universal scaling relationship. q_1 values marked with a hash symbol were determined from digitized data.

molecular weight. It is noted that, as v_a decreases from 28.56 to 14.57 (by ~50%), q_1 increases from 2.20 to 2.91 (by ~30%). Plotting q_1 versus v_a on a logarithmic scale revealed a scaling relationship, as shown in Fig. 1. All data points fall on a line, despite the diversity of metallic glasses ranging from binaries to quaternaries. Although the present study was undertaken for metal-metal glasses, a similar scaling relationship seems to hold also for metal-metalloid glasses based on a preliminary analysis of a rather limited data set. Linear fitting of the data in Table 1 yields the following relationship,

$$q_1 \cdot v_a^{0.433 \pm 0.007} = 9.3 \pm 0.2.$$

As discussed above, a power of 1/3 is expected when scaling $1/q_1$ with v_a for crystalline metals with long-range order and for molecular gas with SRO alone. However, in contrast, the best fit to the metallic-glass data yields a power of 0.433 ± 0.007 , significantly different from 1/3. This large discrepancy shows that the metallic-glass structure is distinctly different from its crystalline counterpart. We interpret this discrepancy as evidence

of a fractal network, with the fractal dimension given by $D_f = 1/0.433 = 2.31$. We notice that our observed D_f of 2.31 in metallic glasses is comparable to the fractal dimension of silica particle aggregates (2.27–2.65) determined by small-angle scattering⁷, and to that of 2.56 for aggregating proteins⁹ and 2.05 for colloidal gold particles⁸. It is also noted that the D_f of metallic glasses is close to the fractal dimension of quasicrystals (2.72 (ref. 25)), which exhibit a quasiperiodic long-range order and are characterized by a hierarchy of atomic clusters^{26,27}, demonstrating the structural similarity between metallic glasses and quasicrystals²⁸.

In addition to exhibiting a universal scaling relationship, the FSDP position also correlates closely with q_{21} and q_{22} , the positions of the second peak and its shoulder in $S(q)$, as shown in the inset of Fig. 2. In particular, for the Zr_xCu_{100-x} glasses, our neutron data show that

$$q_{21}/q_1 = 1.74 \pm 0.02,$$

$$q_{22}/q_1 = 1.96 \pm 0.02,$$

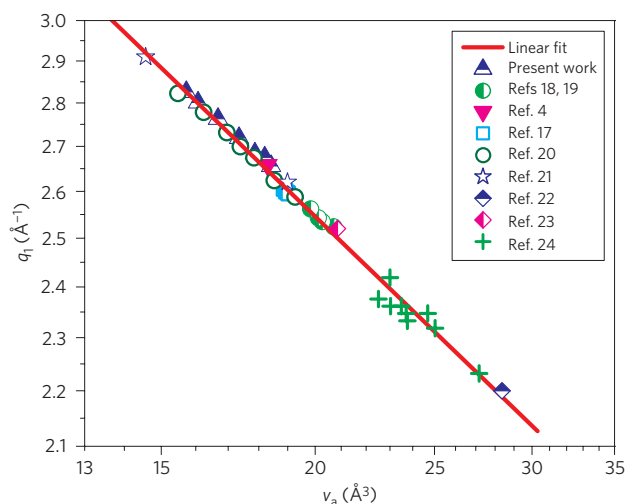


Figure 1 | Power-law scaling of the FSDP (q_1) versus atomic volume (v_a) for a variety of metallic glasses. Both q_1 and v_a are in a logarithmic scale. The solid line represents a linear fit to the data.

where q_{21} and q_{22} were obtained by fitting the second peak and its shoulder in the $S(q)$ using two Gaussian functions²⁹.

Figure 2 shows the $G(r)$ of a $\text{Cu}_{64.5}\text{Zr}_{35.5}$ glass, obtained by Fourier transforming the $S(q)$ (see the inset) terminated at a value of q_{max} . Two cases have been investigated corresponding to q_{max} of 15.0 and $6.9 \text{ \AA}^{-1}$ (indicated by the arrow in the inset), respectively. It can clearly be seen that the $G(r)$ profiles beyond the second coordination shell ($r \geq 6.2 \text{ \AA}$, indicated by the arrow in Fig. 2) are essentially the same. Thus, the medium-range $G(r)$ is determined primarily by the $S(q)$ in the q -range of less than $6.9 \text{ \AA}^{-1}$, which covers q_1 , q_{21} and q_{22} . Because q_1 , q_{21} and q_{22} are related, this result further demonstrates that the MRO is indeed embodied by the FSDP, as has been noted by Cargill³⁰. We therefore conclude that the scaling relationship of q_1 in metallic glasses comes from the MRO.

Next, we demonstrate that analytically, the experimentally determined atomic pair distribution function fits the description of a fractal network. From $G(r)$, the differential pair distribution function, $g(r) - 1 = (G(r)/4\pi r \rho_0)$ (where ρ_0 is the number density) was determined and is plotted in Fig. 3. The following discussions follow closely the framework of a monodispersed colloidal system. Colloids are small particles dispersed in a medium, usually fluid. Colloids are a convenient tool to study particle packing³¹. Recently, densified colloidal systems have been used to study glass transitions, often with confinement as a tuning parameter³², and the structural rearrangement of shear-transformation zones under applied load³³. If, in metallic glasses, the MRO is indeed described by packing of quasi-equivalent clusters on a fractal network, then the cluster number follows a power-law distribution, that is, $N(r) \sim r^{D_f}$ (ref. 7), where $N(r)$ is the number of clusters within a radius r around a given cluster. This leads to a differential cluster correlation function of the form $C(r) = g_{\text{cluster}}(r) - 1 \sim A/r^{D-D_f}$, where A is a constant. Following the work by Freltoft *et al.*⁷, which considers the fractal structure of aggregating particles in a colloidal system, we can express $C(r)$ as

$$C(r) = (A/r^{D-D_f})\exp(-r/\xi)\sin(q_1 r + \phi), \quad (1)$$

where an exponential cutoff function is used to account for the finite cluster-size and cluster-entanglement effects^{6,7} and ξ is the cutoff length. Here, a sinusoidal function $\sin(q_1 r + \phi)$ was introduced to describe the oscillatory correlation of the experimental $[g(r) - 1]$, with q_1 being the position of the FSDP and ϕ being the phase shift. As shown in Fig. 3, a good fit was

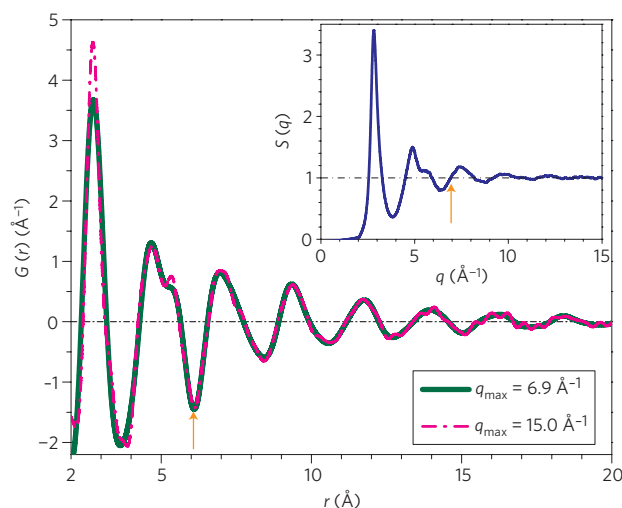


Figure 2 | Correlation between FSDP and MRO. A comparison is made for two reduced pair distribution functions $G(r)$ of glassy $\text{Cu}_{64.5}\text{Zr}_{35.5}$ obtained by Fourier transforming the experimental $S(q)$ (see the inset) with two termination values (q_{max}). The arrows indicate the onset of the third shell in the main figure and $q_{\text{max}} = 6.9 \text{ \AA}^{-1}$ in the inset, respectively.

obtained to the experimental $[g(r) - 1]$ with equation (1) in the medium range of r from 6.5 to $25 \text{ \AA}$ for a typical metallic glass $\text{Zr}_{35.5}\text{Cu}_{64.5}$. In this fitting process, the value of $D - D_f$ was fixed as $0.69 (= 3 - 2.31)$ as determined from Fig. 1. The best fit yielded the following parameters: $A = 3.2 \pm 0.2$, $\xi = 4.00 \pm 0.08 \text{ \AA}$ and $\phi = 0.23 \pm 0.01$. It is remarkable that equation (1), with a single q_1 value ($2.826 \text{ \AA}^{-1}$), can account so well for the experimental $[g(r) - 1]$ for $r > 6.5 \text{ \AA}$. On the other hand, equation (1) failed to describe $[g(r) - 1]$ for $r < 6.5 \text{ \AA}$. This demonstrates again that fractal behaviour is only observed in the medium-range length scale. We also attempted to determine $D - D_f$ directly by fitting $[g(r) - 1]$, but this proved to be difficult. Nevertheless, by fitting to the amplitudes of the peaks and valleys of $[g(r) - 1]$ using equation (1) without the sinusoidal function, as described in the Methods section and shown in the inset of Fig. 3, we obtained a $D - D_f$ value of 0.67 ± 0.06 after averaging the fitting results for six Zr-Cu glasses and two Zr-based bulk metallic glasses (see Table 1). This value is consistent with what was extracted from the power-law scaling of q_1 (0.69 ± 0.04). The excellent fitting results shown in Fig. 3 demonstrate that a power-law distribution function given by equation (1) provides an adequate description of the medium-range amorphous structure, confirming the fractal nature of cluster packing in metallic glasses.

To understand the fractal aspect of metallic glasses, it is helpful to examine the structure of a quasicrystal. The structure detail of a quasicrystal was recently visualized for the first time with a binary $\text{YbCd}_{5.7}$ quasicrystal²⁷. Here, the basic building block, which comprises the bulk of the quasicrystal, is a rhombic triacontahedron (RTH), as illustrated in Fig. 4 of ref. 27. The RTH units themselves cannot fill the space, because of the local five-fold icosahedral symmetry. Two other types of building block are required, the so-called acute and obtuse rhombohedra, to fill in the gaps and connect the RTH units. The incomplete space filling by the RTH units leads to a number density that is dependent on r . In fact, as pointed out earlier, quasicrystals are fractals with a dimension of 2.72 (ref. 25). In $\text{YbCd}_{5.7}$, the RTH units form a hierarchical self-similar structure, with an inflation factor τ^3 , where $\tau = (1 + \sqrt{5})/2$ is the golden ratio.

The cluster packing in metallic glasses can be understood in a similar way. In metallic glasses, the fundamental building blocks are solute-centred clusters, rather than individual atoms, with solute or

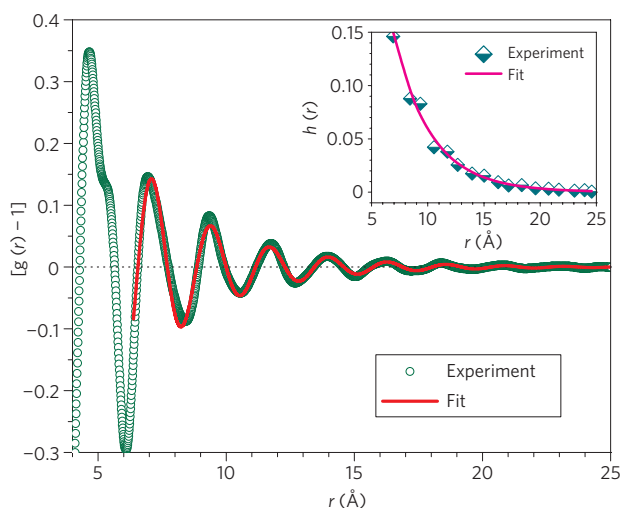


Figure 3 | Demonstration of fractal packing with experimental $[g(r) - 1]$. The experimental data were obtained for glassy alloy $\text{Cu}_{64.5}\text{Zr}_{35.5}$, and the solid line is a fit using equation (1). The inset shows the best fit to the amplitudes of the peaks and valleys of $[g(r) - 1]$ that yields an estimate for $D - D_f$ (see Methods).

minor atoms at the centre surrounded by solvent or majority atoms. Some of these clusters are tightly connected, as they share atoms at vertices, edges or faces. In addition, it is also important to recognize that none of the clusters in metallic glasses is perfect—they are plagued by chemical and topological disorder. At the local level, the clusters follow either cubic or icosahedral packing, as pointed out by Miracle¹ and Sheng *et al.*³. However, such kinds of cluster packing cannot continue beyond the length scale of a few clusters, owing to the five-fold icosahedral symmetry and chemical and topological disorder. Our study shows that over the medium-range length scale, the clusters are in fact connected via a fractal network with reduced dimensionality. Regions between clusters are empty or occupied by lone atoms that do not form clusters. The former is related to the free volumes, whereas the latter could be termed as glue atoms, as in quasicrystals, that connect the clusters. Because of the chemical and topological disorder, space filling in metallic glass is even more difficult than in quasicrystals. Presumably this is why the fractal dimension of metallic glasses (2.31) is lower than that of 2.72 for quasicrystals.

It has been recognized that the apparently distinct properties of metallic glasses exhibit striking correlations with each other³⁴. For example, the elastic moduli are related to the glass-transition temperature³⁵. On the other hand, diffraction patterns for metallic glasses also look similar^{21,28,36}. As the structure determines properties, these experimental observations already provide a strong hint of some kind of structural commonality.

With the picture of cluster packing in mind, the diffraction patterns from metallic glasses can be regarded as scattering from highly correlated clusters, which is a product of the scattering due to individual clusters and the correlation between the clusters, respectively. The high- q portion of the diffraction pattern is dominated by the scattering function of individual clusters (SRO), as the correlation between clusters approaches unity. The low- q portion of the scattering pattern is due to the correlation between the clusters (MRO), which produces the FSDP. The scattering contrast comes from the fluctuation in the cluster number density, as a result of partial space filling by the clusters. The fact that the diffraction patterns for metallic glasses have the same characteristics and the scaling relationship demonstrated in this study show that cluster packing in metallic glasses follows a common rule, that is, self-similar packing on a fractal network.

In summary, the fractal nature of metallic glasses is revealed by the power-law scaling of the FSDP with the atomic volume, and is further verified by fitting the experimentally determined differential pair distribution function with a cluster correlation function over the medium-range length scale. This finding paves the way for understanding the MRO in metallic glasses using well-established mathematical tools developed for describing the structure and dynamics in fractals^{10,37}. The position of the FSDP, q_1 , characterizes the medium-range correlation, which can be quite useful for gaining insights into structural evolutions involving a change in length scales. It would be interesting to examine, for example, how the fractal network of solute-centred clusters responds to applied load. From *in situ* synchrotron experiments, Poulsen *et al.*³⁸ reported that under a uni-axial load, the nearest-neighbour atomic shell exhibits the stiffest response, whereas the responses from higher-order shells are progressively softer eventually approaching that of the strain gauges, suggesting that mechanical deformation is inhomogeneous at SRO and MRO length scales. As we mentioned earlier, a similar scaling relationship seems to hold also for metal-metalloid glasses, despite the difference in atomic bonding and cluster types. In fact, the diffraction patterns for metal-metalloid and metal-metal glasses look very much similar. These experimental observations suggest that fractal packing is a universal behaviour for metallic glasses. Further study is needed to fully establish the scaling relationship for metal-metalloid glasses, and to examine the influence of atomic bonding and cluster types. The framework of the present study will also find a wide range of applications for exploring fractals in a broad field of disordered condensed-matter systems.

Methods

Estimation of $D - D_f$ from correlation functions. A direct determination of $D - D_f$ from fitting with equation (1) is difficult because it correlates strongly with ξ and the parameter ϕ also needs to be determined. To eliminate the influence of ϕ and to test the sensitivity of $D - D_f$, we alternatively fitted only the amplitudes (h) of the peaks and valleys of the correlation function $[g(r) - 1]$ over the r range of 7–25 Å, with the function $h(r) = A/r^{D-D_f} \exp(-r/\xi)$. In the fitting process, we set A , $D - D_f$ and ξ as fitting parameters. The use of a power-law function (r^{D-D_f}) along with the exponential cutoff function leads to a much reduced χ^2 than that with an exponential function alone. By fitting each set of the peaks and valleys data obtained from neutron scattering experiments for six Zr–Cu glasses and two Zr-based bulk metallic glasses, $\text{Zr}_{53.7}\text{Cu}_{28.5}\text{Ni}_{19.4}\text{Al}_{8.4}$ and $\text{Zr}_{52.5}\text{Ti}_{15}\text{Cu}_{17.9}\text{Ni}_{14.6}\text{Al}_{10}$ (see Table 1), we determined an average value of 0.67 ± 0.06 for $D - D_f$, which is consistent with the $D - D_f$ value of 0.69 ± 0.04 obtained from analysis of the scaling relationship for q_1 .

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Additional information

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