

# Percolation structure in metallic glasses and liquids

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**Abstract:** The atomic-level structures of liquids and glasses are similar, obscuring any structural basis for the glass transition. To delineate structural differences between them, we characterized the atomic structures using the integrated radial distribution functions (RDF) from molecular dynamics (MD) simulations for several metallic liquids and glasses:  $\text{Cu}_{46}\text{Zr}_{54}$ ,  $\text{Ni}_{80}\text{Al}_{20}$ ,  $\text{Ni}_{33.3}\text{Zr}_{66.7}$ , and  $\text{Pd}_{82}\text{Si}_{18}$ . We find that the integrated RDF leads to cumulative coordination numbers (CN) that are similar for all four metallic glasses and for all four liquids, but are consistently different between the liquid and glass phases. We find that metallic liquids have a fractal dimension of  $d_f = 2.54 \pm 0.06$  from the center atom to the first coordination shell whereas the metallic glasses have  $d_f = 2.66 \pm 0.04$ , which suggests the development of weak ordering during the glass transition. Beyond the second coordination shell, the CN indicates a dimension of  $d = 3$  as for a crystal. Crossovers in dimension from  $d_f \sim 2.54$ - $2.66$  to  $d = 3$  between the first and second coordination shells imply an underlying percolation structure in metallic liquids and glasses.

**KEYWORDS:** Molecular dynamics, fractal dimension, coordination number, crossover

The viscosities and relaxation times of glasses and liquids across the glass transition temperature ( $T_g$ ) are separated by many orders of magnitude.<sup>1</sup> This large increase in viscosity over a short temperature range is not accompanied by significant changes in the long-range

atomic structure, which remains amorphous. Metallic glasses are locally more ordered in the short- and medium-range than their liquid counterparts,<sup>2,3</sup> but this distinction is merely correlated to the glass transition, the origin of which remains a topic of active research.<sup>4</sup> A structural model that captures both liquids and glasses is needed for understanding the subtle changes that occur across  $T_g$  and their relationship to the glass transition phenomenon.

The fractal dimension  $d_f$  is a measure of how, on average, the mass of atoms within a spherical section of material with radius  $r$  scales,  $M(r) \propto r^{d_f}$ .<sup>5</sup> In relating the positions of the first sharp X-ray diffraction peaks ( $q_1$ ) to volume ( $V$ ), several groups have reported a scaling relationship in metallic glasses, with exponent,  $d_f \sim 2.31-2.5$ , which deviates from the  $d = 3$  expected under the assumption that  $q_1 \propto 1/a$ , where  $a$  is the interatomic spacing.<sup>6,8</sup> Recent experiments on electrostatically levitated metallic liquids also show a non-cubic power law exponent of  $d_f \sim 2.28$ .<sup>9</sup> These power law exponents may be related to the dimension of the atomic structure, and the observations of an exponent/dimension less than 3 have led to suggestions of an underlying fractal structure in metallic glasses.<sup>6,8</sup> The long-range scaling relationship in metallic glass structure is not fractal because no macroscopic pores or voids are present in their microstructure, with such pores serving as a defining characteristic of fractals that maintain their scaling relationships over all length scales (e.g. the Sierpinski triangle).

To help resolve these issues Chen et al. proposed that metallic glasses at the atomic-level can be described using percolation,<sup>8</sup> a model that captures the interconnectivity of sites on a lattice or spheres in a continuum.<sup>5</sup> Three-dimensional percolation models, such as hard sphere and overlapping sphere continuum models, exhibit a fractal dimension of  $d_f \sim 2.52$  at lengths below a correlation length,  $\xi$ , and a crossover to a dimension  $d \sim 3$  above  $\xi$ , where  $\xi$  is roughly the diameter/length of finite, non-percolating clusters.<sup>5</sup> Using molecular dynamics (MD) simulations, Chen et al. found that two dissimilar metallic glasses exhibit a fractal dimension, estimated to be  $d_f \sim 2.5$ , over short lengths below  $\xi \sim 2$  atomic diameters, but with a crossover to an exponent of 3 over longer lengths. This suggested that metallic glasses are structurally similar to a continuum percolation of spherical particles.<sup>8</sup> This crossover at  $\xi$  may explain the anomalous non-cubic scaling exponents in  $q_1$  vs.  $V$  observed experimentally in macroscopically homogeneous and fully dense metallic glasses and liquids.<sup>6,9</sup> Such a connection between percolation structure and glasses has also been suggested by Orbach, who applied percolation

theory to describe high frequency (short length) vibrational states in glassy systems and also suggested that amorphous materials may exhibit fractal properties at short length scales.<sup>10</sup>

The question remains whether liquids exhibit a crossover in dimension from  $d_f$  to  $d$ . Percolation structure has been studied in hard spheres,<sup>11,12</sup> overlapping spheres,<sup>13,14</sup> and recently metallic glasses,<sup>8</sup> suggesting a likely connection to metallic liquids, which share structural similarities with both metallic glasses and hard sphere systems<sup>15</sup>. One previous method to measure fractal dimension utilized hydrostatic pressures to induce peak shifts in radial distribution functions (RDF) that were compared to corresponding volume changes.<sup>8</sup> However, this hydrostatic pressure-induced RDF peak shift method is not well suited for studying liquids, in which atoms rearrange and exchange neighbors under pressure. Moreover, the broadness of the RDF peaks leads to results that are sensitive to the specific method of generating and measuring the RDF.<sup>16</sup> To overcome this issue of sensitivity, we chose here to integrate the RDFs to obtain cumulative coordination numbers (CN). This integral method calculates the local dimension of the structure using system snapshots without the need for applying hydrostatic pressures or measuring small shifts in broad amorphous peak positions, methods that we used previously<sup>8</sup>. With this CN analysis, we observe a crossover in dimension from  $d_f = 2.54 \pm 0.06$  in metallic liquids and  $d_f = 2.66 \pm 0.04$  in metallic glasses, to  $d = 3$  for the second coordination shell and beyond, suggesting that  $\xi \sim 2$ . We also refined our previous estimates of  $d_f$  for metallic glasses, which led to a  $\sim 0.1$  increase in  $d_f$  for metallic glasses compared to metallic liquids, indicating that some degree of order develops across the glass transition.

### *Percolation structure*

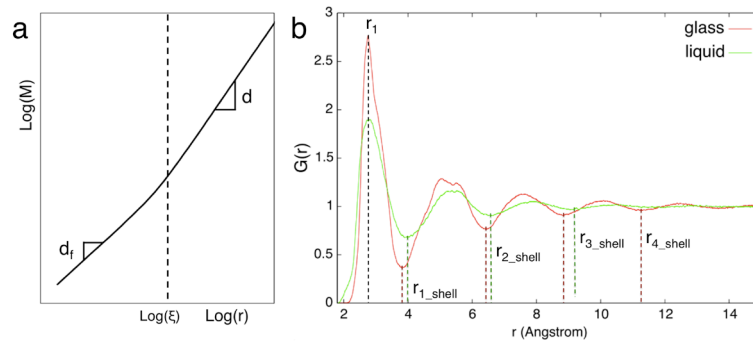
Fractal dimension arises from the scaling of extensive properties with size such as mass, i.e.  $M(r) \propto r^{df}$ , where  $M(r)$  is the mass contained in a sphere of radius  $r$ .  $M(r)$  is calculated as an average over the entire system by choosing different atoms as the center of the sphere.<sup>5</sup> In our analysis, we used the value  $CN+1$  to represent the average number of atoms within a sphere of radius  $r$  (1 added to account for the center atom), an extensive property that is proportional to average mass. The scaling relationship for a percolation structure above the percolation threshold,  $\phi_c$ , exhibits a crossover in dimension from  $d_f \sim 2.52$  to  $d \sim 3$  at  $\xi$ , where  $\xi \propto (\phi - \phi_c)^{-\nu}$ .<sup>5</sup> The parameter definitions are:  $\phi$  is the packing fraction,  $\nu = 0.8764$  is the critical

exponent for the correlation length,<sup>17</sup> and  $\phi_c$  is the percolation threshold in 3-dimensional continuum percolation.<sup>5</sup> The expected crossover point for several of the metallic systems studied here has been estimated to be  $\xi \sim 2$ .<sup>8</sup> This value represents the average size of clusters in units of atomic diameters, and suggests that the crossover point occurs around the first atomic coordination shell. To avoid inaccuracies that may arise from determining precise peak locations from broad amorphous peaks, we obtain the dimension of each atomic structure by measuring the slope of  $\ln(\text{CN}+1)$  versus  $\ln(r)$  for  $\text{Cu}_{46}\text{Zr}_{54}$  (two separate force fields), and  $\text{Ni}_{80}\text{Al}_{20}$  metallic liquids and glasses. We find that a crossover from  $d_f$  to  $d$  occurs in all cases beyond the first to second coordination shell. We compare these results to those for pure Cu and Zr (SI) in liquid and crystalline phases.

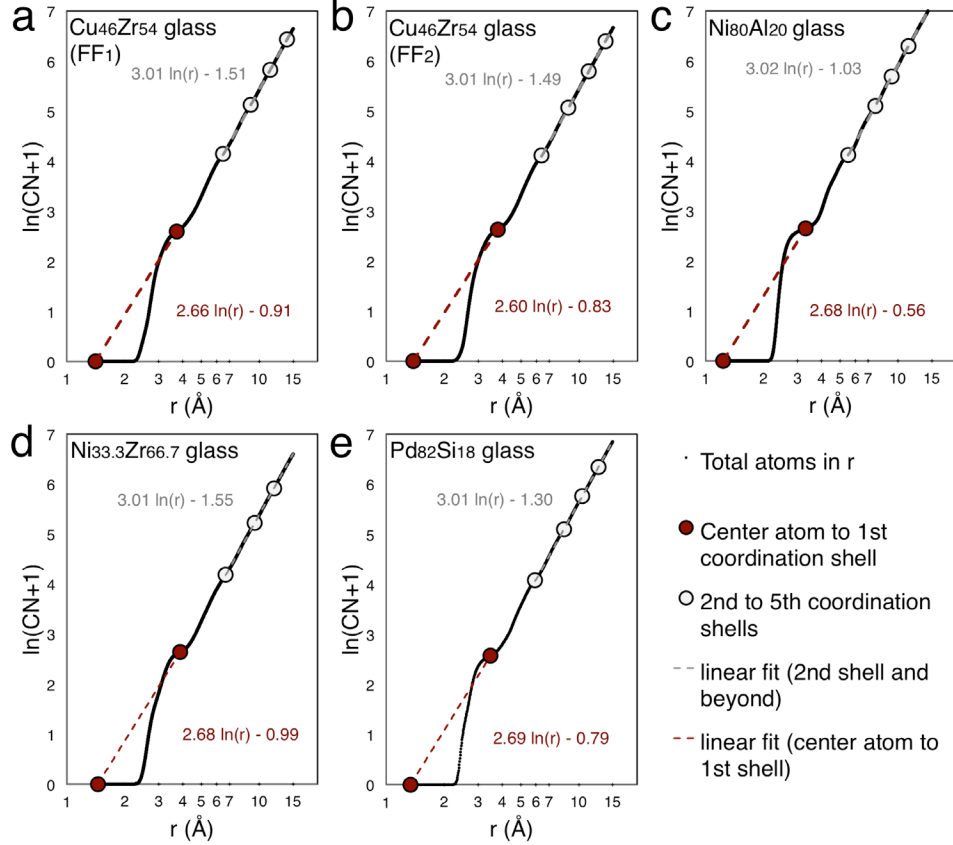
### *Fractal dimension of metallic glasses*

We measure  $d_f$  by performing a linear fit between the radius of the center atom,  $r_{\text{center}}$ , and the outer radius of the first coordination shell,  $r_{1\text{-shell}}$ . The  $r_{\text{center}}$  is calculated by dividing the position of the first RDF peak,  $r_1$  (Figure 1), by two (i.e.  $r_{\text{center}} = r_1/2$ ), which is representative of the average metallic radius of the center atom. There is on average one atom (i.e. the center atom) within this radius, making it an appropriate first point in the analysis of the dimension. Using this approach, we establish the following estimates of dimensions:  $d_f = 2.68$  for  $\text{Ni}_{80}\text{Al}_{20}$ ,  $d_f = 2.68$  for  $\text{Ni}_{33.3}\text{Zr}_{66.7}$ ,  $d_f = 2.69$  for  $\text{Pd}_{82}\text{Si}_{18}$ , and  $d_f = 2.66$  or  $2.60$  for  $\text{Cu}_{46}\text{Zr}_{54}$  using  $\text{FF}_1$ <sup>18</sup> or  $\text{FF}_2$ <sup>19</sup>, respectively (Figure 2), all at 300 K. Our  $\text{Ni}_{80}\text{Al}_{20}$  displays pronounced ordering in the first coordination shell; the coordination number rises more steeply and has a flatter plateau than the other systems studied (Figure 2c). This may be due to the covalent nature of the Al bonding. The average dimension for metallic glasses of  $d_f = 2.66 \pm 0.04$  is  $\sim 0.14$  higher than what would be expected from percolation theory, where  $d_f \sim 2.52$ ,<sup>5</sup> and is higher than previous measurements of  $\sim 2.3$ - $2.5$ <sup>6,7</sup> (diffraction experiments) and  $\sim 2.5$ <sup>8</sup> (molecular dynamics with hydrostatic pressure). In the region between the center atom and first coordination shell,  $r_{\text{center}}-r_{1\text{-shell}}$ , CN rises sharply due to the discrete nature of the atom counting procedure. A continuous measure of the CN that allows for fractions of atoms to be counted would give a smooth, filled-in curve between the center atom and first coordination shell. Between the outer radii of the first and second coordination shells,  $r_{1\text{-shell}}-r_{2\text{-shell}}$ , the dimension crosses over to 3 for all cases, suggesting that

these metallic glasses have percolation structures with a correlation length around  $\xi \sim 2$ , in agreement with previous estimates.<sup>8</sup> Within the first to second coordination shell, free volume arising from packing inefficiencies contributes to a fractal dimensionality in the structure. This fractal dimension cannot proliferate to greater lengths because the free volume necessarily remains smaller than the volume occupied by atoms, whose relative positions are dictated by long-range attraction and low kinetic energy. At longer length scales, where free volume is less significant and the atom clusters appear closely packed, we find that the dimension of the structure is 3.



**Figure 1.** a) Diagram of expected crossover in log-log plot of mass versus radius. Short-range fractal dimension  $d_f$  crosses over to long-range dimension  $d=3$  at the correlation length  $\xi$ . b) Radial distribution functions for  $\text{Cu}_{46}\text{Zr}_{54}$  ( $\text{FF}_2$ ) in the glass and liquid phase. Dashed lines indicate positions for the first peak,  $r_1$ , and coordination shells,  $r_{i\_shell}$ .

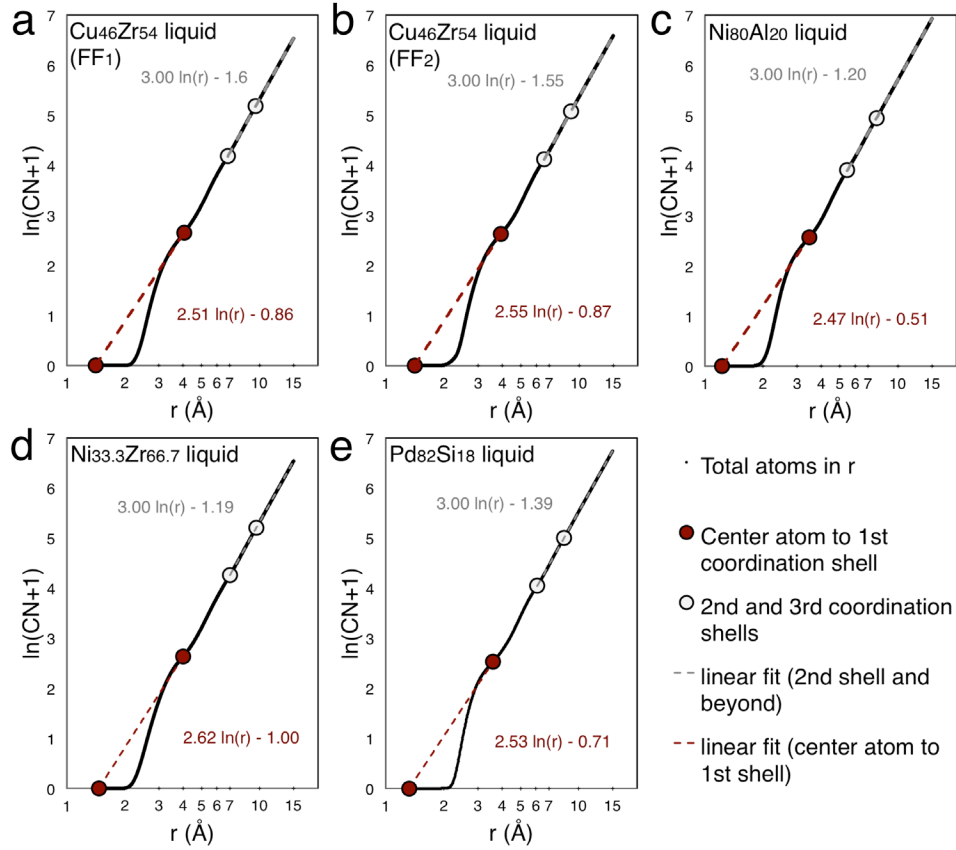


**Figure 2.** Log-log plots of total atom number (CN+1) versus radius,  $r$ , showing dimensions  $d_f$  and  $d$  for metallic glasses of  $\text{Cu}_{46}\text{Zr}_{54}$  a) FF<sub>1</sub>, b) FF<sub>2</sub>, c)  $\text{Ni}_{80}\text{Al}_{20}$ , d)  $\text{Ni}_{33.3}\text{Zr}_{66.7}$ , and e)  $\text{Pd}_{82}\text{Si}_{18}$ . Fractal dimension  $d_f$  is measured through a linear fit between the radius of the center atom and the outer radius of the first coordination shell. Long-range dimension  $d$  is measured from a linear fit of points beyond the outer radius of the second coordination shell.

### Fractal dimension of metallic liquids

Applying the same method to metallic liquids, we measure  $d_f = 2.51$  for  $\text{Cu}_{46}\text{Zr}_{54}$  FF<sub>1</sub> at 2500 K,  $d_f = 2.55$  for FF<sub>2</sub> at 2000 K,  $d_f = 2.47$  for  $\text{Ni}_{80}\text{Al}_{20}$  at 3000 K,  $d_f = 2.62$  for  $\text{Ni}_{33.3}\text{Zr}_{66.7}$  at 2500 K, and  $d_f = 2.53$  for  $\text{Pd}_{82}\text{Si}_{18}$  at 2000 K (Figure 3). The average value of  $d_f = 2.54 \pm 0.06$  is in line with the expected value of  $\sim 2.52$  from percolation theory,<sup>5</sup> and is roughly  $\sim 0.1$  lower than the average value obtained from the quenched metallic glasses, suggesting that some order develops in the glass that contributes to a higher  $d_f$ . This order may be related to the formation of dense clusters, such as icosahedra, which reduce local free volume.<sup>3,20,21</sup> A crossover in dimension from

$d_f$  to  $d$  occurs in the same region as in the metallic glasses, which indicates that the liquids also have percolation structures with a correlation length around  $\xi \sim 2$ , in agreement with previous suggestions.<sup>8</sup> The correlation length is inversely related to the atomic packing fraction, and more loosely packed liquid structures may exhibit longer crossover lengths. Metallic liquids are dense, possessing packing fractions of around  $\phi \sim 0.67$  (FF<sub>2</sub> at 2000 K), a value that is only  $\sim 8\%$  lower than their glassy counterparts ( $\phi \sim 0.73$  for FF<sub>2</sub> glass at 300 K). To observe structures with  $\xi \sim 3$  or longer, we estimate that we would need to study liquids and glasses with packing fractions in the neighborhood of  $\phi \sim 0.5$ , which is not feasible for our metallic systems, as a first-order phase transition to the gaseous phase would likely precede such a low packing fraction in the liquid phase.



**Figure 3.** Log-log plots of total atom number (CN+1) versus radius,  $r$ , showing dimensions  $d_f$  and  $d$  for metallic liquids of Cu<sub>46</sub>Zr<sub>54</sub> a) FF<sub>1</sub> at 2500 K, b) FF<sub>2</sub> at 2000 K, c) Ni<sub>80</sub>Al<sub>20</sub> at 3000 K, d) Ni<sub>33.3</sub>Zr<sub>66.7</sub> at 2500 K, and e) Pd<sub>82</sub>Si<sub>18</sub> at 2000 K. Fractal dimension  $d_f$  is measured through linear fit between the radius of the center atom and the outer radius of the first coordination shell.

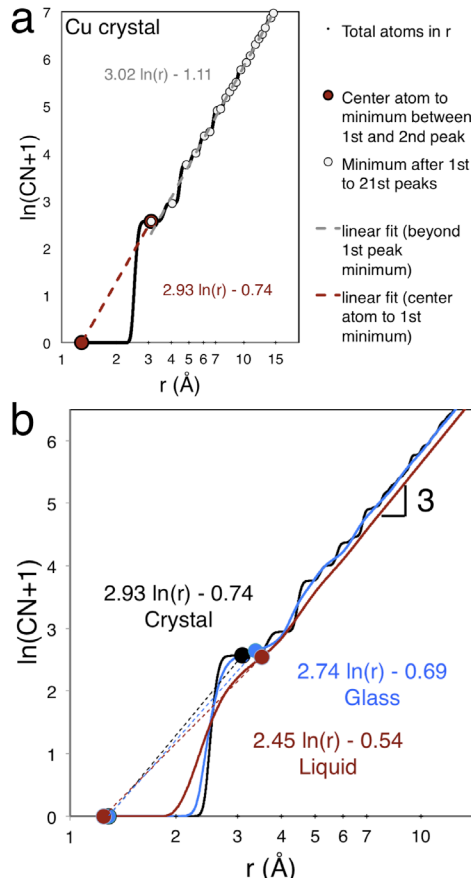
Long-range dimension  $d$  is measured from a linear fit of points beyond the outer radius of the second coordination shell.

### *Comparison to pure Cu*

We compare our results to those for crystalline Cu at 300 K, which has a dimension of 2.93 between the center atom and the minimum after the first peak (measured at the midpoint between the first and second peak (SI)). Beyond the first peak, the dimension is  $\sim 3$  (Figure 4). We expect the crystal dimension to be exactly 3 because it is a close-packed cubic structure; the observed deviation suggests that our short-range measurement is not precise, yielding a value of 2.93. We attribute this to the discrete nature of the atom counting process, which counts atoms by their center of mass position, disregarding the volume occupied by the atoms. In a continuous counting procedure, the curve would be smoothed, enabling more accurate measurement of the dimension.

Comparison of the crystalline, glassy, and liquid phases of Cu shows that the major contribution to fractal dimensionality in the liquid and glassy phases is the short-range structure, which is locally more open. The overall coordination number curve is shifted toward higher radii for the liquid phase, which reduces the short-range fractal dimension,  $d_f$ . The short-range structure in the glass phase is denser and more ordered compared to the liquid – the coordination number rises more steeply in the first shell, increasing  $d_f$  towards a close-packed, crystalline value.





**Figure 4.** Comparison of dimensions in pure Cu systems. a)  $d_f \sim 2.93$ -3 in crystalline Cu. b)  $d_f \sim 2.45$  in liquid Cu and  $d_f \sim 2.74$  in amorphous Cu. The liquid structure is notably more open than the glass and crystal, shifting its coordination number curve (red) toward higher  $r$  and leading to a lower  $d_f$  value.

### Discussion

The glass transition may be related to the densification/ordering that occurs in the local glass structure, but the connection is not clear. Previous analyses comparing amorphous and crystalline structures have emphasized that radii ratios of  $\sim 0.6$ - $0.95$  in binary systems favors formation of amorphous phases,<sup>22</sup> and local icosahedral structure in the first shell plays an important role in driving glass formation for Cu-Zr-Al metallic glasses.<sup>18,23</sup> In our analysis, the increase in  $d_f$  above  $\sim 2.5$  for the glass phase compared to the liquid phase suggests that the atomic structure may be deviating from the percolation structure across the glass transition. In simple percolation models, the constituent units occupy lattice sites or are allowed to overlap one another<sup>5</sup> such that no limit

exists for the site occupancy probability or volume fraction of overlapped spheres. In real systems and hard sphere percolation models, the constituent spherical particles (e.g. metallic atoms) have excluded volume. A fundamental limit exists in the random close packing fraction of hard spheres, which is  $\sim 0.637$  for monodisperse spheres,<sup>24</sup> and  $\sim 0.64-0.83$  for bi-disperse spheres, depending on their radii ratios and compositions.<sup>25</sup> Stable binary metallic glasses have high packing fractions:  $\sim 0.73$  for our  $\text{Cu}_{46}\text{Zr}_{54}$  ( $\text{FF}_2$ ) and above  $\sim 0.7$  for other binary alloys.<sup>26</sup> The increase in  $d_f$  above  $\sim 2.52$  for our glassy systems suggests that the packing fraction of our systems may be approaching geometrical limits allowed by random packing of spheres with excluded volume, which forces a deviation from percolation structure and giving rise to rigidity and large viscosity increases across the glass transition. This concept may be related to jamming or a rigidity percolation.<sup>27,28</sup>

### *Summary*

We find that the cumulative CN analysis allows the short-range order in metallic glasses to be distinguished from that in liquids. We observe that the short-range dimension is fractal,  $d_f \sim 2.47-2.69$  for both liquids and glasses. The long-range dimension,  $d$ , crosses over to 3 beyond the second coordination shell, which suggests that the underlying structure in these metallic liquids and glasses is related to percolation, a model that exhibits similar values of short-range fractal dimension,  $d_f \sim 2.52$ , and also has a crossover. These observations indicate that both the liquid and glassy phases possess underlying percolation structures marked by short-range clusters with free volume that contributes to a fractal dimensionality. Clusters in the glass phase are smaller and more ordered than those in the liquid phase, leading to a higher value for  $d_f$  ( $2.66 \pm 0.04$  in the glass compared to  $2.54 \pm 0.06$  in the liquid) that deviates from the expected dimension in percolation structures, where  $d_f \sim 2.52$ .

### *Molecular dynamics methods*

All molecular dynamics simulations of the metallic liquids and glasses discussed here used embedded atom model (EAM) potentials:

- The  $\text{Cu}_{46}\text{Zr}_{54}$  systems (54,000 atoms) were prepared using two potentials, Cheng et al.<sup>18</sup> (FF<sub>1</sub>) and Mendeleev et al.<sup>19</sup> (FF<sub>2</sub>).
- The  $\text{Ni}_{80}\text{Al}_{20}$  systems (32,000 atoms) were prepared using Pun et al.,<sup>29</sup>
- The  $\text{Ni}_{33.3}\text{Zr}_{66.7}$  systems (32,000 atoms) were prepared using Mendeleev et al.<sup>30</sup>, and
- The  $\text{Pd}_{82}\text{Si}_{18}$  systems (32,000) were prepared using Ding et al.<sup>31</sup>.

In all cases the binary metallic glasses were quenched from the liquid phase (2000-3000 K) at a rate of  $\sim 10^{12}$  K/s to room temperature (300 K). The Cu crystal (13,500 atoms), liquid (2048 atoms) and glass (2048 atoms) are prepared from FF<sub>2</sub>. The Cu metallic glass was quenched at a rate of  $\sim 10^{14}$  K/s.

The RDFs were calculated by binning the atomic structure (100,000 bins for binary systems and Cu crystal, 5000 bins for Cu liquid and glass). Coordination numbers are obtained by integrating the total RDF.

**Supporting Information.** Coordination number dimension analysis for Zr crystal, different RDF binning conditions, and applied hydrostatic pressures (30 GPa).

## AUTHOR INFORMATION

### Notes

The authors declare no competing financial interests.

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DMR-0520565 CSEM computer cluster. Q.A. and W.A.G. received support from NSF (DMR-1436985). This material is based upon work supported by the National Science Foundation (NSF) Graduate Research Fellowship under Grant No. DGE-1144469. Any opinion, findings, and conclusions or recommendations expressed in the material are those of the authors and do not necessarily reflect the views of the NSF.

## REFERENCES

- 1 Angell, C. A. Formation of Glasses from Liquids and Biopolymers. *Science* **267**, 1924-1935, doi:Doi 10.1126/Science.267.5206.1924 (1995).
- 2 Sheng, H. W., Luo, W. K., Alamgir, F. M., Bai, J. M. & Ma, E. Atomic packing and short-to-medium-range order in metallic glasses. *Nature* **439**, 419-425, doi:Doi 10.1038/Nature04421 (2006).
- 3 Cheng, Y. Q. & Ma, E. Atomic-level structure and structure-property relationship in metallic glasses. *Prog Mater Sci* **56**, 379-473, doi:Doi 10.1016/J.Pmatsci.2010.12.002 (2011).
- 4 Debenedetti, P. G. & Stillinger, F. H. Supercooled liquids and the glass transition. *Nature* **410**, 259-267, doi:Doi 10.1038/35065704 (2001).
- 5 Bunde, A. & Havlin, S. *Fractals and disordered systems*. (Springer-Verlag New York, Inc., 1991).
- 6 Ma, D., Stoica, A. D. & Wang, X. L. Power-law scaling and fractal nature of medium-range order in metallic glasses. *Nat Mater* **8**, 30-34, doi:Doi 10.1038/Nmat2340 (2009).
- 7 Zeng, Q. S. *et al.* Universal Fractional Noncubic Power Law for Density of Metallic Glasses. *Phys Rev Lett* **112**, doi:Artn 185502  
Doi 10.1103/Physrevlett.112.185502 (2014).
- 8 Chen, D. Z. *et al.* Fractal atomic-level percolation in metallic glasses. *Science* **349**, 1306-1310, doi:10.1126/science.aab1233 (2015).
- 9 Gangopadhyay, A. K. *et al.* Thermal expansion measurements by x-ray scattering and breakdown of Ehrenfest's relation in alloy liquids. *Appl Phys Lett* **104**, doi:Artn 191907  
10.1063/1.4876125 (2014).
- 10 Orbach, R. Dynamics of Fractal Networks. *Science* **231**, 814-819, doi:Doi 10.1126/Science.231.4740.814 (1986).
- 11 Powell, M. J. Site Percolation in Randomly Packed Spheres. *Phys Rev B* **20**, 4194-4198, doi:Doi 10.1103/Physrevb.20.4194 (1979).
- 12 Frith, W. J. & Buscall, R. Percolation and Critical Exponents on Randomly Close-Packed Mixtures of Hard-Spheres. *J Chem Phys* **95**, 5983-5989, doi:Doi 10.1063/1.461619 (1991).
- 13 Rintoul, M. D. Precise determination of the void percolation threshold for two distributions of overlapping spheres. *Phys Rev E* **62**, 68-72, doi:Doi 10.1103/Physreve.62.68 (2000).

- 14 Lorenz, C. D. & Ziff, R. M. Precise determination of the critical percolation threshold for the three-dimensional "Swiss cheese" model using a growth algorithm. *J Chem Phys* **114**, 3659-3661, doi:Doi 10.1063/1.1338506 (2001).
- 15 Bernal, J. D. Geometry of the Structure of Monatomic Liquids. *Nature* **185**, 68-70, doi:Doi 10.1038/185068a0 (1960).
- 16 Dr. Jun Ding and Prof. Mark Asta pointed out to us that the analysis reported in ref. 7 is sensitive to the method/algorithm for specifying peak positions of the broad RDF peaks of these amorphous systems. Precise measurements of pressure-induced RDF peak shifts on the order of  $\sim 0.01$  Å are necessary to derive an accurate estimate of  $d_f$ . Hydrostatic pressure-induced peak shifts are small ( $\sim 0.01$  Å/GPa), making the overall fit for  $d_f$  particularly sensitive to the position of the initial peak at 0 GPa. In the previous analysis, a change in initial peak position of  $\sim 0.01$  Å can shift the exponent for  $d_f$  by  $\sim 0.2$ . In our current analysis using cumulative CN, A  $\sim 0.01$  Å change in  $r_{center}$  or  $r1_{shell}$  would result in a  $\sim 0.02$  shift in the estimate for  $d_f$ . With our new analysis, the previous estimates of  $d_f \sim 2.5$  for Cu<sub>46</sub>Zr<sub>54</sub> FF1 and FF2 and Ni<sub>4</sub>Al now become  $d_f \sim 2.66$ , 2.60, 2.68, respectively.
- 17 Wang, J. F., Zhou, Z. Z., Zhang, W., Garoni, T. M. & Deng, Y. J. Bond and site percolation in three dimensions. *Phys Rev E* **87**, doi:Artn 052107  
10.1103/Physreve.87.052107 (2013).
- 18 Cheng, Y. Q., Ma, E. & Sheng, H. W. Atomic Level Structure in Multicomponent Bulk Metallic Glass. *Phys Rev Lett* **102**, doi:Artn 245501  
Doi 10.1103/Physrevlett.102.245501 (2009).
- 19 Mendeleev, M. I. *et al.* Development of suitable interatomic potentials for simulation of liquid and amorphous Cu-Zr alloys. *Philos Mag* **89**, 967-987, doi:Pii 910503793  
Doi 10.1080/14786430902832773 (2009).
- 20 Steinhardt, P. J., Nelson, D. R. & Ronchetti, M. Bond-Orientational Order in Liquids and Glasses. *Phys Rev B* **28**, 784-805, doi:Doi 10.1103/Physrevb.28.784 (1983).
- 21 Soklaski, R., Tran, V., Nussinov, Z., Kelton, K. F. & Yang, L. A Locally-Preferred Structure Characterizes All Dynamical Regimes of a Supercooled Liquid. *arXiv:1502.01739* (2015).
- 22 Lee, H. J., Cagin, T., Johnson, W. L. & Goddard, W. A. Criteria for formation of metallic glasses: The role of atomic size ratio. *J Chem Phys* **119**, 9858-9870, doi:10.1063/1.1615494 (2003).
- 23 An, Q. *et al.* Predicted Optimum Composition for the Glass-Forming Ability of Bulk Amorphous Alloys: Application to Cu-Zr-Al. *J Phys Chem Lett* **3**, 3143-3148, doi:10.1021/jz3014425 (2012).
- 24 Scott, G. D. & Kilgour, D. M. Density of Random Close Packing of Spheres. *J Phys D Appl Phys* **2**, 863-&, doi:Doi 10.1088/0022-3727/2/6/311 (1969).
- 25 Farr, R. S. & Groot, R. D. Close packing density of polydisperse hard spheres. *J Chem Phys* **131**, doi:Artn 244104  
10.1063/1.3276799 (2009).
- 26 Miracle, D. B. The density and packing fraction of binary metallic glasses. *Acta Mater* **61**, 3157-3171, doi:Doi 10.1016/J.Actamat.2013.02.005 (2013).

- 27 Torquato, S. & Stillinger, F. H. Multiplicity of generation, selection, and classification procedures for jammed hard-particle packings. *J Phys Chem B* **105**, 11849-11853, doi:Doi 10.1021/Jp011960q (2001).
- 28 Trappe, V., Prasad, V., Cipelletti, L., Segre, P. N. & Weitz, D. A. Jamming phase diagram for attractive particles. *Nature* **411**, 772-775, doi:Doi 10.1038/35081021 (2001).
- 29 Pun, G. P. P. & Mishin, Y. Development of an interatomic potential for the Ni-Al system. *Philos Mag* **89**, 3245-3267, doi:Pii 917305480

Doi 10.1080/14786430903258184 (2009).

- 30 Mendeleev, M. I., Kramer, M. J., Hao, S. G., Ho, K. M. & Wang, C. Z. Development of interatomic potentials appropriate for simulation of liquid and glass properties of NiZr<sub>2</sub> alloy. *Philos Mag* **92**, 4454-4469, doi:10.1080/14786435.2012.712220 (2012).
- 31 Ding, J., Cheng, Y. Q., Sheng, H. W. & Ma, E. Short-range structural signature of excess specific heat and fragility of metallic-glass-forming supercooled liquids. *Phys Rev B* **85**, doi:Artn 060201

10.1103/Physrevb.85.060201 (2012).

## Supplemental Information for “Percolation structure in metallic glasses and liquids”

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Here we provide additional analysis on a Zr crystal, where the dimension from the center atom to the minimum after the first peak is  $d \sim 2.9$ , and in the long-range  $d=3$  (Fig. S1). We show that our measurements in the main manuscript are robust and are not affected by changes in binning number or hydrostatic pressures (Fig. S2). Radii measurements in the main manuscript (e.g.  $r_c$ ,  $r_{1\_shell}$ ) are provided in Tables S1-3.

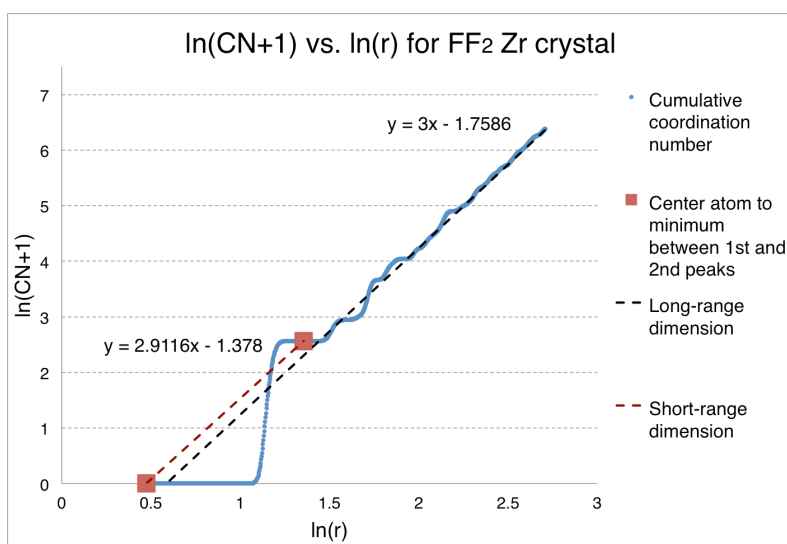


Figure S1: Cumulative coordination number versus radius on log-log plots for **A)** Cu, **B)** Zr crystals from FF<sub>2</sub>. Short-range dimensionality is homogeneous,  $d \sim 2.91$  and the long-range dimensionality  $d=3$ .

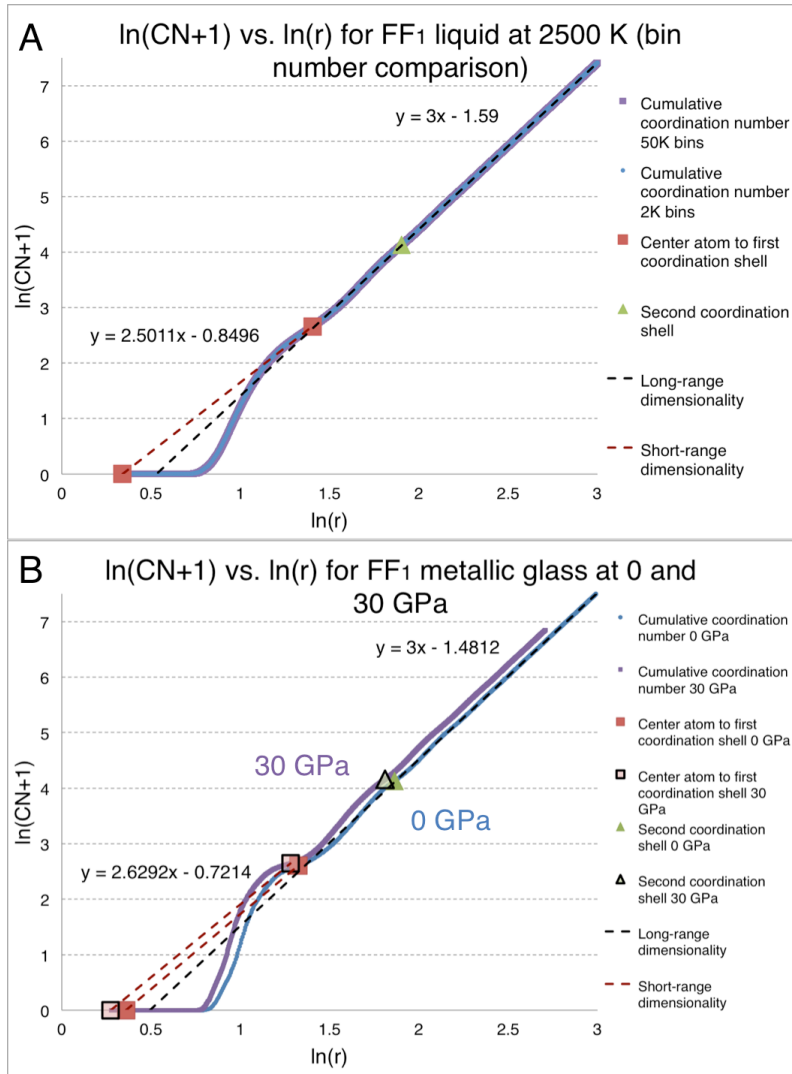


Figure S2: Cumulative coordination number versus radius on log-log plots for **A)**  $\text{Cu}_{46}\text{Zr}_{54}$  liquid at 2500 K and calculated from 2K and 50K bins. Results are unchanged for different binning conditions. **B)**  $\text{Cu}_{46}\text{Zr}_{54}$  metallic glass at 0 GPa and 30 GPa, both from  $\text{FF}_1$ . Hydrostatic pressure shifts the overall curve toward lower  $r$ ;  $d_1 \sim 2.63$  and  $d \sim 3$ .

Table S1: Radii measurements in metallic glass systems

Potential	$r_c$ (Å)	$r_{1 \text{ shell}}$ (Å)	$r_{2 \text{ shell}}$ (Å)
$\text{Cu}_{46}\text{Zr}_{54}$ $\text{FF}_1$	1.435	3.758	6.443
$\text{Cu}_{46}\text{Zr}_{54}$ $\text{FF}_2$	1.374	3.814	6.424
$\text{Ni}_{80}\text{Al}_{20}$	1.231	3.296	5.501
$\text{Ni}_{33.3}\text{Zr}_{66.7}$	1.449*	3.881	6.698
$\text{Pd}_{82}\text{Si}_{18}$	1.339*	3.491	5.933

\*: Split first peak;  $r_1$  value taken from weight averages of  $r_1$  partials. For  $\text{Pd}_{82}\text{Si}_{18}$ , the Si-Si partial does not contribute to the first peak.



Table S2: Radii measurements in liquid systems

Potential	$r_c$ (Å)	$r_{1\_shell}$ (Å)	$r_{2\_shell}$ (Å)
$\text{Cu}_{46}\text{Zr}_{54}$ FF <sub>1</sub>	1.405	4.073	6.697
$\text{Cu}_{46}\text{Zr}_{54}$ FF <sub>2</sub>	1.398	3.964	6.566
$\text{Ni}_{80}\text{Al}_{20}$	1.228	3.446	5.561
$\text{Ni}_{33.3}\text{Zr}_{66.7}$	1.465	4.005	7.014
$\text{Pd}_{82}\text{Si}_{18}$	1.323	3.604	8.392

Table S3: Radii measurements in crystalline systems using FF<sub>2</sub>

FF <sub>2</sub>	$r_c$ (Å)	$r_{1\_min}$ (Å)
Cu	1.288	3.094
Zr	1.605	3.873