

Candidate Atomic Cluster Configurations in Metallic Glass Structures

Daniel B. Miracle¹, Eric A. Lord² and Srinivasa Ranganathan²

¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, OH USA

²Department of Metallurgy, Indian Institute of Science, Bangalore, India

A growing body of evidence supports the importance of solute-centered atomic clusters in the structure and stability of metallic glasses. Beyond a few simple cases, a broad account of these clusters has not been provided elsewhere. Detailed characteristics of a canonical collection of efficiently packed hard sphere clusters are presented here as idealized structural elements in metallic glasses. The nomenclature, topology, geometry and packing efficiency of these clusters are provided and their relevance to the structure of metallic glasses is discussed.
[doi:10.2320/matertrans.47.1737]

(Received February 16, 2006; Accepted May 25, 2006; Published July 15, 2006)

Keywords: atomic clusters, metallic glasses, hard sphere model, sphere packing

1. Introduction

It has long been suggested that atomic clusters may provide representative structural elements in metallic glasses. The dense random packing model described atomic clusters surrounding interstices, or Bernal's canonical 'holes,' in systems of equal-sized spheres.¹⁾ Solute-centered atomic clusters were introduced as a modification of the dense random packing model, where solute atoms in transition metal-metalloid glasses were proposed to occupy the interstices in the center of Bernal's canonical clusters formed by the transition metal solvent atoms.²⁾ It was later shown that the concentrations of 'holes' of the sizes necessary to accommodate the metalloid solutes were too small to account for observed glass compositions³⁾ so that this model has not been developed further.

Rather than fitting passively into interstices formed by a pre-existing array of solvent atoms, solute atoms may control and define their local environment. The stereo-chemically defined model (SCD) implicitly takes this view to rationalize the dominance of a single atomic cluster.⁴⁾ A tri-capped trigonal prism (TTP), one of Bernal's canonical clusters, was considered based on the measured coordination number of solvent atoms around metalloid solutes and on the observation that crystal structures of compositionally similar alloys often show a strained version of such local polyhedra around the metalloid solutes. Experimental evidence for strained TTP clusters has been obtained by high-resolution electron micro-diffraction combined with atomistic simulations.⁵⁾ Icosahedral clusters have often been proposed as an important structural element in metallic glasses based on analysis of experimental data⁶⁻¹²⁾ and computational results.¹³⁻¹⁵⁾ This, along with the observation that many glass-forming alloys are compositionally similar to quasicrystalline and icosahedral alloys, provides adequate support for the expectation that icosahedra may exist in many metallic glasses.

The number N of equal-sized atoms or spheres that can be first nearest neighbors about a different-sized atom or sphere will change in direct relation to the relative sizes of atoms.¹⁶⁾ This idea has been applied to the local structure of metallic glasses by considering efficiently packed solute-centered clusters with solvent atoms only in the first coordination

Table 1 Values of N and corresponding idealized values of $R^*(N)$ for efficiently packed clusters.

N	$R^*(N)$	N	$R^*(N)$
3	0.154701	14	1.04733
4	0.224745	15	1.11632
5	0.361654	16	1.18318
6	0.414214	17	1.24810
7	0.518145	18	1.31123
8	0.616517	19	1.37271
9	0.709914	20	1.43267
10	0.798907	21	1.49119
11	0.884003	22	1.54840
12	0.902113	23	1.60436
13	0.976006	24	1.65915

shell.¹⁷⁾ The radius ratio R (radius of solute divided by radius of solvent atoms) determines the greatest number of solvent atoms that can be coordinated to a solute atom. For a given N , more efficient packing corresponds to smaller values of R . An absolute lower bound R^* for the possible radius ratios for any given N was obtained¹⁷⁾ and is shown in Table 1. Analysis showed that the values of R in a large number of metallic glasses are quite close to the theoretically predicted lower bound, and it was concluded that efficiently packed solute-centered atomic clusters are an important feature in the structure of metallic glasses.¹⁷⁾ This idea provides the basis of the efficient cluster packing (ECP) structural model for metallic glasses.¹⁸⁾ Good quantitative agreement between experimental observations and predictions from the ECP model supports the conclusion that efficiently packed solute-centered clusters provide a meaningful description for the structure of metallic glasses.

A range of distinct atomic clusters is likely to be important in the structure of metallic glasses, and coordination numbers as low as 8 and as high as 20 are suggested by the values of R in known metallic glasses.^{17,18)} Experimentally measured local coordination numbers similarly suggest clusters with a wide range in N . However, only the TTP ($N = 9$) and icosahedron ($N = 12$) have been discussed in any detail in the context of metallic glass structures. On the other hand, a

great deal of work is available in the mathematics community to describe the optimal packing of N equal-sized spheres about a central sphere of different size. Optimal packing can be defined and quantified in different ways, and in the present context we are interested in clusters that provide the minimum radius ratio R for a given coordination number N . This is well-known as the Fejes¹⁹⁾ or Tammes²⁰⁾ problem, and is posed as the placement of N equal spheres on the surface of a different-sized sphere so as to maximize the minimum included angle between the N sphere centers. Rigorous mathematical solutions have been achieved for clusters with $2 \leq N \leq 14$ and for $N = 24^{21-23}$ and putative optimal solutions have been proposed for other clusters with values of N in excess of 100.²⁴⁻²⁷⁾ Readers are referred to other sources for a more complete description of the body of work surrounding this problem.^{19,22,27)}

The clusters discussed in this paper are hard sphere models representing a single central solute atom coordinated to N solvent atoms forming a coordination shell. The purpose is to present and discuss clusters that are likely local representative structural constituents in metallic glasses. Although the clusters in actual metallic glasses are likely to be distorted relative to these idealized clusters, this analysis may nevertheless provide useful insights for visualizing the structure of metallic glasses. Optimally packed clusters and putative optimal clusters are included here, as well as other clusters of special symmetry or marginally sub-optimal packing. For completeness, and for reference to other amorphous solids such as oxide glasses, clusters with $3 \leq N \leq 20$ are described. Specific details regarding cluster nomenclature, topology, symmetry and packing efficiency are presented, and a brief discussion of the proposed influence of soft spheres is provided.

2. Candidate Atomic Clusters

A selection of rigorous optimally packed clusters, putative optimally packed clusters and sub-optimally packed clusters is listed in Table 2 and is shown in Fig. 1. Coordinates for the clusters in Fig. 1 were taken from.²⁷⁾ The list given here is not exhaustive. Each cluster is characterized by unique values of R and N . The value δ is the minimum angular separation between two sphere centers in the first coordination shell, or equivalently is the solid angle subtended by a single sphere in the shell. An optimally packed cluster will have a minimum value of R and a maximum value of δ for a given N . The two parameters are related by $\sin(\delta/2) = 1/(1 + R)$. A number of other descriptors is provided for each cluster and they are described below.

Efficiently packed clusters typically have at least one rotational axis of symmetry. Föppl notation^{24,26,28)} provides an intuitive description of the configuration for such clusters and is used here. This notation consists of a series of integers (n_i) representing the number of solvent spheres at a given latitude for successive parallel planes progressing from the N to the S pole of the cluster, so that $\sum n_i = N$. Thus, a tetrahedron is represented as (1, 3) or (2, 2), and an octahedron is (1, 4, 1) or (3, 3). Where more than one axis of rotational symmetry exists, the highest symmetry axis is preferred. Adjacent rings with equal values of n , such as

(2, 2), (3, 3) or the (... 5, 5 ...) rings in a (1, 5, 5, 1) icosahedron, are assumed to have an antiprism orientation, since this gives the most efficient packing. The n spheres at a given latitude generally form a regular polygon—exceptions for the clusters presented here are mentioned below. A few clusters have selected spheres that do not share an axis of rotational symmetry with the remaining spheres in that cluster, and these spheres are indicated with a tilde overbar in the Föppl notation.

To each Föppl symbol there corresponds a unique cluster with the largest possible δ (equivalently, the smallest possible R) where spheres in the coordination shell come into contact. The *connectivity symbol* $2^i 3^j 4^k 5^l$ lists the numbers of spheres in the coordination shell in contact with 2, 3, 4 or 5 others (6 is not possible since this corresponds to a planar arrangement), where $i + j + k + l = N$. We have, essentially, a network whose nodes are sphere centres and whose edges are lines joining centers of pairs of spheres in contact. The *ring structure* $\{3^u 4^v 5^w\}$ of this network indicates the number of triangles, quadrilaterals and pentagons formed by the edges.

The trigonal cluster (3), tetrahedron (1, 3), octahedron (1, 4, 1), icosahedron (1, 5, 5, 1) and cuboctahedron (4, 4, 4) are well-known in many fields of science. If one sphere is removed from the optimal octahedral cluster (1, 4, 1) the five remaining spheres are free to move relative to each other without losing contact with the central sphere, but only if the central sphere does not decrease in size. Therefore, for $N = 5$ there are an infinite number of optimal configurations with the same radius ratio $\sqrt{2} - 1$. Those with a non-trivial point symmetry are (1, 4), (1, 3, 1) and (1, 2, 2). Spheres in the three-fold ring of (1, 3, 1) are not fully constrained and are free to move independently around the cluster equator. The (3, 3, 3) cluster is distinct from the TTP with three half octahedral¹⁾ often discussed in the literature. The latter cluster is based on the primitive trigonal prism with $R = 0.528$ and $N = 6$ and the spheres that form the three half octahedra do not contact the sphere at the center of the cluster, while all nine spheres in the (3, 3, 3) cluster are in rigorous hard sphere contact with the central sphere. Several clusters with similar packing efficiencies exist for $N = 10$, including (2, 4, 2, 2), (1, 3, 3, 3) and (1, 4, 4, 1). The (1, 5, 5) cluster is an icosahedron with one sphere removed. The (3, 6, 3) cluster has two distinct conformations; one is the (4, 4, 4) cuboctahedron cluster of the *fcc* structure and the other is a sub-unit of the *hcp* structure. A slight distortion of the sub-optimal (3, 3, 3, 3, 3) produces the putative optimal (3, 3, $\tilde{3}$, $\tilde{3}$, 3), and in the same way the (1, 2, 2, 4, 2, 2, 2, 2, 1) cluster is a slight distortion of (1, 4, 4, 4, 4, 1).²⁹⁾ Careful inspection of Figs. 1(s) and 1(t) shows that (1, 3, 3, $\tilde{6}$, $\tilde{5}$, 1) is a distorted version of (1, 3, 3, 6, 3, 3, 1), where a (... 3, 3 ...) ring pair decomposes to the (... $\tilde{5}$...) configuration when one of the spheres is removed. The spheres at a given latitude do not necessarily form a regular polyhedron. Non-regular polygons include the (... 4 ...) configurations in (2, 4, 2, 2), (1, 4, 2, 2, 4, 1) and (1, 4, 2, 2, 4, 2, 2), and the (... 6 ...) configuration in (1, 3, 3, 6, 3, 3, 1).

In Table 2 a *packing fraction* and a *packing efficiency* are given for each of the clusters. For sphere packing with crystalline symmetry a *packing fraction* is readily defined as

Table 2 Efficiently packed cluster characteristics.

N	Föoppl Notation	δ	R	Connectivities	Ring Structure	Point Symmetry	Packing Fraction	Packing Efficiency	Comments	Citation
3	3	120.0000	0.154701	2^3	$\{3^4\}$	$\bar{6}m2$	0.1570	1	Optimum	(21, 22)
4	1, 3 or 2, 2	109.4712	0.224745	3^4	$\{3^4\}$	$\bar{4}3m$	0.7615	1	Optimum (tetrahedron)	(21, 22)
5	1, 3, 1	90.0000	0.414214	2^33^2	$\{4^3\}$	$\bar{6}m2$	0.6746	0.833	Optimum	(21, 22)
	1, 4	90.0000	0.414214	3^4	$\{3^44\}$	$4mm$	0.6746	0.833	Optimum	
	1, 2, 2	90.0000	0.414214	23^4	$\{3^24^2\}$	mm	0.6746	0.833	Optimum	
6	1, 4, 1 or 3, 3	90.0000	0.414214	4^6	$\{3^8\}$	$m\bar{3}m$	0.8045	1	Optimum (octahedron)	(21, 22)
7	1, 3, 3	77.8695	0.591254	3^44^3	$\{3^44^3\}$	$3mm$	0.7152	0.905	Optimum	(21, 22)
8	4, 4	74.8585	0.645329	4^8	$\{4^6\}$	$\bar{8}2m$	0.7537	0.963	Optimum (square antiprism)	(21, 22)
	2, 2, 2, 2	73.6935	0.667566	3^44^4	$\{3^44^4\}$	$\bar{4}m$	0.7328	0.937	Sub-optimal	
9	3, 3, 3	70.5288	0.732051	4^9	$\{3^84^3\}$	$\bar{6}m2$	0.7540	0.974	Optimum	(21, 22)
	1, 4, 4	70.0747	0.741826	3^44^5	$\{4^5\}$	$4m$	0.7454	0.962	Sub-optimal	
10	2, 4, 2, 2	66.1468	0.832465	$3^64^25^2$	$\{3^64^25^2\}$	$mm2$	0.7400	0.963	Optimum	(21, 22)
	1, 3, 3, 3	66.0856	0.833970	3^44^6	$\{3^44^6\}$	$3m$	0.7389	0.961	Sub-optimal	
	1, 4, 4, 1	65.5302	0.847759	3^84^2	$\{4^6\}$	$\bar{8}2m$	0.7283	0.946	Sub-optimal	
11	1, 5, 5	63.4349	0.902113	4^55^6	$\{3^{15}5^1\}$	$5mm$	0.7483	0.981	Optimum	(21, 22)
12	1, 5, 5, 1 or 3, 3, 3, 3	63.4349	0.902113	5^{12}	$\{3^{20}\}$	$5m\bar{3}$	0.8066	1	Optimum (icosahedron)	(21, 22)
	3, 6, 3 or 4, 4, 4	60.0000	1.00000	4^{12}	$\{3^84^6\}$	$m\bar{3}m$	0.7344	0.900	Sub-optimal (cuboctahedron)	
13	1, 4, 4, 4	57.1367	1.09115	3^44^9	$\{3^44^9\}$	$4mm$	0.7254	0.888	Optimum	(23)
14	1, 4, 2, 2, 4, 1	55.6706	1.14164	4^{14}	$\{3^84^8\}$	$\bar{4}2m$	0.7393	0.911	Optimum	(23)
	1, 4, 4, 4, 1	54.7355	1.17533	3^84^6	$\{4^{12}\}$	$m\bar{3}m$	0.7205	0.882	Sub-optimal (rhombic dodecahedron)	
15	3, 3, $\bar{3}$, $\bar{3}$, 3	53.6579	1.21568	$3^34^95^3$	$\{3^{11}4^35^3\}$	1	0.7380	0.909	Putative optimal.	(25, 27)
	5, 5, 5	52.5002	1.26096	4^{15}	$\{3^{10}4^55^2\}$	$5/mm$	0.7147	0.872	Sub-optimal	
	3, 3, 3, 3, 3	52.4757	1.26194	4^95^6	$\{3^{14}4^6\}$	$3mm$	0.7143	0.871	Sub-optimal	
16	4, 4, 4, 4	52.2444	1.27125	4^{16}	$\{3^84^6\}$	$\bar{8}2m$	0.746	0.921	Putative optimal.	(24, 25)
17	1, 4, 2, 2, 4, 2, 2	51.0903	1.31899	$3^44^85^4$	$\{3^84^{11}\}$	mm	0.7554	0.938	Putative optimal	(25, 27, 29)
	1, 5, 5, 5, 1	51.0266	1.32169	$3^{10}4^55^2$	$\{4^{15}\}$	$5/mm$	0.7540	0.936	Sub-optimal	(24, 29)
18	1, 2, 2, 4, 2, 2, 2, 2, 1	49.5567	1.38602	$2^23^44^{10}5^2$	$\{3^24^{14}5^2\}$	mm	0.7544	0.937	Putative optimal.	(25, 27, 29)
	1, 4, 4, 4, 4, 1	49.5517	1.38624	3^84^{10}	$\{4^{16}\}$	$\bar{8}2m$	0.7543	0.936	Sub-optimal	(24)
19	1, 3, 3, $\bar{6}$, $\bar{5}$, 1	47.6919	1.47354	$4^{13}5^6$	$\{3^{14}4^85^1\}$	1	0.7440	0.918	Putative optimal	(25–27)
20	1, 3, 3, 6, 3, 3, 1	47.4310	1.48635	$3^24^65^{12}$	$\{3^{18}4^9\}$	$\bar{6}m2$	0.7661	0.956	Putative optimal	(25, 27)

the fraction of space within a unit cell occupied by the spheres. For a finite cluster there is no corresponding unique definition. A cluster *packing fraction* can be defined as the fraction of space occupied by the spheres of the cluster within a spherical region characteristic of the cluster. Three reasonable choices for the region suggest themselves: (1) the smallest sphere concentric with the cluster centre, that contains all the spheres of the cluster, radius $2 + R$; (2) the sphere through the *centres* of the spheres of the coordination shell, radius $1 + R$; (3) the sphere through the *contact points* of the spheres of the shell, radius $(1 + R)\cos(\delta/2)$. The cluster *packing fraction* we have calculated and listed in Table 2 are the packing fractions within region (2). The two conformations of the (3, 6, 3) cluster provide a useful benchmark, since they are representative units of the face-

centred cubic and hexagonal close-packed structures that form the basis for many crystalline materials. The packing fraction for these crystal structures is $\pi/(3\sqrt{2}) = 0.7405$, which is close to the packing fraction determined here for the isolated clusters. The clusters in Table 2 typically have packing fractions at least as high as the (3, 6, 3) cluster (Fig. 2(a)). This supports earlier suggestions that efficiently packed solute-centered clusters may be important in systems where efficient filling of space is required.^{17,18)}

Packing efficiency is a convenient parameter that serves to distinguish more densely packed from less densely packed configurations. Various definitions of *packing efficiency* are possible. A *packing efficiency* for a cluster can be defined as the actual cluster packing fraction divided by the ideal cluster packing fraction that would be achieved if R could be reduced

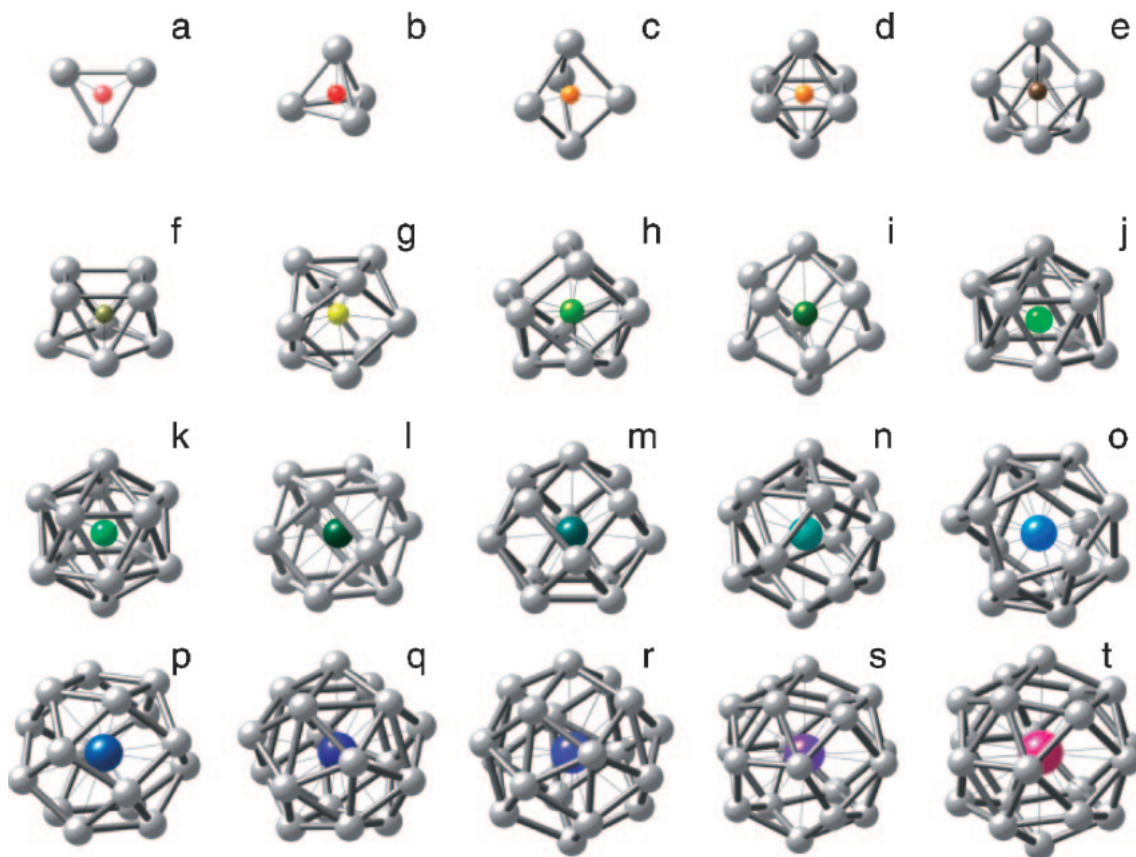


Fig. 1 Efficiently packed clusters with Föpl notations of (a) 3; (b) 1, 3; (c) 1, 3, 1; (d) 1, 4, 1; (e) 1, 3, 3; (f) 4, 4; (g) 3, 3, 3; (h) 2, 4, 2, 2; (i) 1, 4, 4, 1; (j) 1, 5, 5; (k) 1, 5, 5, 1; (l) 4, 4, 4; (m) 1, 4, 4, 4; (n) 1, 4, 2, 2, 4, 1; (o) 3, 3, $\bar{3}$, $\bar{3}$, 3; (p) 4, 4, 4, 4; (q) 1, 4, 2, 2, 4, 2, 2; (r) 1, 4, 4, 4, 4, 1 (s) 1, 3, 3, $\bar{6}$, $\bar{5}$, 1; and (t) 1, 3, 3, 6, 3, 3, 1.

to $R^*(N)$. This definition involves the same arbitrary choice of region involved in the definition of cluster packing fraction. A definition of *packing efficiency* that is free of this arbitrariness, which was used to calculate the efficiencies in Table 2, is $N/N^*(R)$, where $N^*(R)$ is the function inverse to that for $R^*(N)$:¹⁷⁾

$$N^* = \frac{2\pi}{\pi + q(\beta - \pi/2)} \quad (1)$$

where $\cos \beta = \cos(\delta/2) \sin(\pi/q)$, $\sin(\delta/2) = 1/(1 + R)$ and q is the surface connectivity.³⁰⁾ Here, q is the greatest connectivity allowable for the particular value of N ($q = 2$ for $N = 3$, $q = 3$ for $N = 4$; $q = 4$ for $5 \leq N \leq 10$ and $q = 5$ for $N \geq 11$).¹⁷⁾ As for packing fraction, many of the clusters described here display packing efficiencies higher than the (3, 6, 3) cluster. The variation of packing efficiency with N is shown in Fig. 2(a).

The variation of R with N is shown in Fig. 2(b). Less efficiently packed clusters not considered here yield higher values of R for a given N . The theoretical lower bound R^* achievable for a given N is shown by the solid line.¹⁷⁾ Discontinuities occur at R values where q changes from 2 to 3 ($R = 0.224745$), from 3 to 4 ($R = 0.414214$) and from 4 to 5 ($R = 0.902113$). Maximum values of connectivity q are common in efficiently packed clusters with $N \leq 12$, and as a result the most efficiently packed clusters fall close to the predicted curve, with the exception of (1, 3, 3). However, the maximum surface connectivity of $q = 5$ is relatively un-

common for hard sphere clusters with $N \geq 13$ (Table 2), so that they have R values higher than theory by about 0.1. The estimate of¹⁷⁾ assumes that each sphere in the coordination shell has the maximum q allowed for that value of R , but packing constraints for hard spheres restrict the ability to achieve these efficiently packed configurations. However, soft spheres may allow these efficiently packed local surface symmetries to be achieved, producing fundamentally new cluster geometries. A good correlation between the idealized radius ratios R^* and atomic radius ratios in metallic glasses¹⁷⁾ supports the view that efficiently packed clusters of soft spheres may provide a meaningful physical model for metallic glasses.

While subtle inconsistencies are sometimes found in the literature regarding details of the clusters described here, the primary purpose of the present paper is to describe efficiently packed clusters that may be important in the atomic structure of metallic glasses. Internal strains, atomic relaxations and soft spheres in condensed physical systems are likely to overwhelm the mathematical distinction between touching and ‘nearly touching’ hard spheres in idealized clusters. Thus, small mathematical distortions between otherwise similar idealized clusters are not likely to have a major impact on actual structures in condensed physical systems.

3. Atomic Clusters in Condensed Systems

Adequate experimental evidence exists for the occurrence

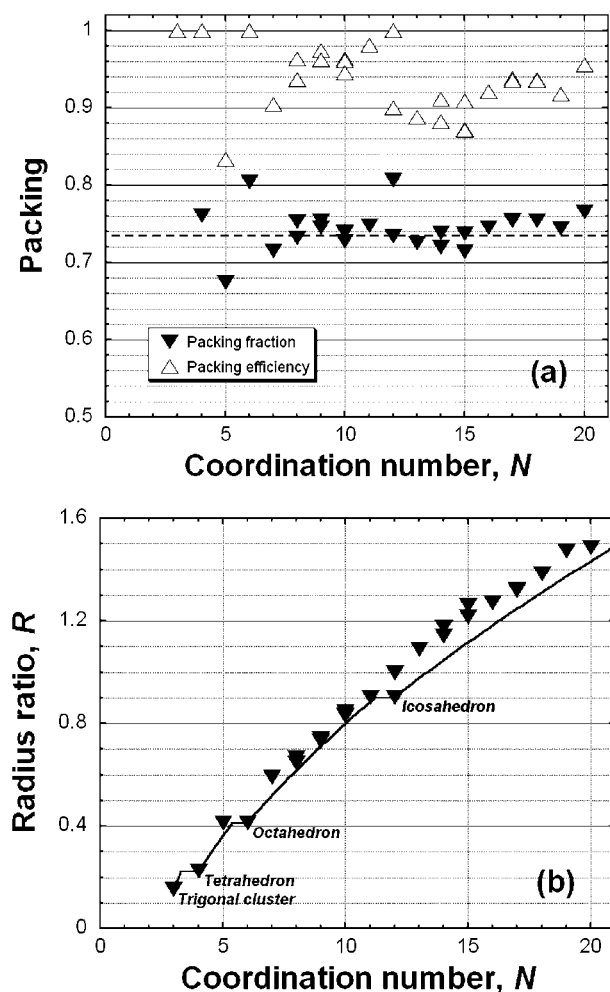


Fig. 2 Influence of cluster coordination number N on (a) packing fraction and packing efficiency and (b) radius ratio R . The dashed line in (a) shows the packing fraction for the (4, 4, 4) cuboctahedron cluster that comprises the face-centred cubic crystal structure. The solid line in (b) is the theoretical minimum radius ratio R^* from¹⁷⁾ shown for comparison.

of the clusters shown here as isolated ‘magic number particles’ which have chemical and electronic properties that suggest large ‘superatoms’.^{31–33)} High performance computers now make possible the prediction of properties of nanomaterials, and the employment of simulation techniques to search for materials with desirable properties.^{34,35)} In this context knowledge of the possible cluster configurations that can be formed from atoms of specific size ratios is important. Direct experimental evidence also exists for the occurrence of some of these clusters in condensed systems. The trigonal cluster, tetrahedron, octahedron, icosahedron and cuboctahedron are well-known in the structures of condensed matter. A number of the remaining clusters in Table 2 also often occur as local coordination polyhedra in inorganic crystalline compounds.^{36,37)} Nevertheless, many clusters in Table 2 have not been discussed widely in the structure of condensed matter.

The three Frank-Kasper polyhedra for $N = 14, 15, 16$ ³⁰⁾ do not represent optimally packed local configurations and so are not represented here. The Frank-Kasper configurations are conceived as subunits of a polytetrahedral structure, so that the coordination polyhedra are deltahedra (all faces are

triangular). For $N = 12$ it is possible for all edges to be equal and in this case we do get a close-packed configuration. Deltahedra necessarily have 6-connected vertices for $N > 12$, which constrains Frank-Kasper clusters to be less efficiently packed. For example, Frank-Kasper clusters with $N = 14$ and $N = 16$ are (1, 6, 6, 1) and (1, 6, 6, 3), respectively. The sphere at the polar position in the (1, 6...) configuration cannot simultaneously provide rigorous hard sphere contact with all of the spheres in the adjoining six-fold ring. For the cluster concept adopted here surface coordination is defined by rigorous hard sphere contact, while in Frank-Kasper clusters surface coordination is defined in a different way that does not require physical contact of hard spheres.

It is difficult to obtain direct experimental evidence for specific atomic cluster configurations in metallic glasses. Nevertheless, there is broad general support for the occurrence of clusters in metallic glasses from experimental,^{4–12,31)} computational^{13–15,31,32,35,38,39)} and modeling^{17,18,30,34,36,37,40–44)} efforts. Rather than simply occurring in metallic glasses, the ECP model provides quantitative agreement with a broad range of experimental observations from the assumption that the structure in metallic glasses is entirely built of solute-centered atomic clusters.^{18,44)} The ECP model further assumes that efficient atomic packing is a major structure-forming principle, and the clusters discussed here are consistent with that requirement. The (3, 3, 3) cluster has been shown to exist in the structure of metal-metalloid glasses,⁵⁾ and (4, 4, 4, 4) and (1, 5, 5, 5, 1) clusters have been discussed as possible representative structural elements in Al-based glasses.⁴²⁾ A recent thorough computational study has validated the major features of the ECP model, and further introduces the concept of quasi-equivalent clusters.³⁹⁾

Internal strains in the ECP model¹⁸⁾ suggest that the actual local structures may be distorted, producing sub-optimal packing configurations such as those provided in Table 2. It is even possible that the actual local atomic configurations in metallic glasses may bear only little resemblance to the idealized geometric hard sphere clusters in Fig. 1 and Table 2. Structural variations may result from packing defects that result in multiple atomic species of different atomic sizes occupying the first coordination shell, from influences of atomic bonding and electronic structure, and from the metastable condition of the glass due to rapid quenching. Nevertheless, the clusters described here provide efficient cluster packings for the range of N relevant for metallic glasses, and it is proposed that these clusters can be considered as idealized representative structural elements in metallic glasses.

4. Summary

The relevance of efficiently packed cluster configurations to isolated atomic clusters is well-known, and it is becoming widely accepted that solute-centered atomic clusters are important structural elements in metallic glasses. A canonical collection of efficiently packed clusters presented here are proposed as idealized representations of the local structure in metallic glasses. The radius ratio between solute and solvent atoms is the major variable that controls the occurrence and characteristics of these clusters. Most clusters described here

display packing fractions and packing efficiencies higher than the (3, 6, 3) cluster that fully comprises the face-centered cubic and hexagonal close-packed crystal structures. Internal strains in actual metallic glass structures and deviation from the assumption of simple hard sphere atoms are expected to produce distortions in these idealized clusters. Nevertheless, the ability to provide quantitative agreement with a range of experimental observations in metallic glasses suggests that these idealized clusters can provide a meaningful description for the local structure of metallic glasses.

Acknowledgements

DM acknowledges helpful discussions with M. Eberhard, P. Harrowell, J. Fernandez, H. Sheng and E. Ma, and is grateful for financial support under Air Force Office of Scientific Research (AFOSR) Task 01ML05-COR (Drs. C. Hartley and J. Tiley, Program Managers). EL and SR acknowledge funding from the AFOSR Asian Office of Advanced Research and Development under Contract Number 044044 (Drs. K. Goretta and J. P. Singh, Program Managers). The sponsorship of the Defense, Research and Development Organisation, Ministry of Defense, Government of India (Project Reference DRDO/MMT/SRG/526) is gratefully acknowledged.

REFERENCES

- 1) J. D. Bernal: *Nature* **185** (1960) 68–70.
- 2) D. E. Polk: *Acta Metall.* **20** (1972) 485–491.
- 3) H. J. Frost: *Acta Metall.* **30** (1982) 889–904.
- 4) P. H. Gaskell: *Glassy Metals II*, ed. by H. Beck and H.-J. Guntherodt, (Springer-Verlag, Berlin, Germany, 1983) pp. 5–49.
- 5) Y. Hirotsu, M. Matsushita, T. Ohkubo, A. Makino and T. Oikawa: *Mat. Sci. Eng.* **A226–228** (1997) 274–279.
- 6) C. L. Briant and J. J. Burton: *Phys. Stat. Sol. (b)* **85** (1978) 393–402.
- 7) E. Matsubara, K. Harada, Y. Waseda, H. S. Chen, A. Inoue and T. Masumoto: *J. Mat. Sci.* **23** (1988) 753–756.
- 8) L. Cervinka: *J. Non-Cryst. Sol.* **156–158** (1993) 94–97.
- 9) L. Zhang, Y. Wu, X. Bian, H. Li, W. Wang, J. Li and N. Lun: *J. Phys.: Condens. Matter* **11** (1999) 7959–7969.
- 10) L. Zhang, Y. Wu, X. Bian, H. Li, W. Wang and S. Wu: *J. Non-Cryst. Sol.* **262** (2000) 169–176.
- 11) D. Holland-Moritz, T. Schenk, V. Simonet, R. Bellissent, P. Convert, T. Hansen and D. M. Herlach: *Mat. Sci. Eng. A* **375–377** (2004) 98–103.
- 12) W. K. Luo, H. W. Sheng, F. M. Alamgir, J. M. Bai, J. H. He and E. Ma: *Phys. Rev. Lett.* **92** (2004) 145502.
- 13) H. Jonsson and H. C. Andersen: *Phys. Rev. Lett.* **60** (1988) 2295–2298.
- 14) D. W. Qi and S. Wang: *Phys. Rev. B* **44** (1991) 884–887.
- 15) X.-D. Wang, M. Qi and C. Dong: *Chin. Phys. Lett.* **20** (2003) 891–893.
- 16) T. Egami: *Mat. Sci. Eng.* **A226–228** (1997) 261–267.
- 17) D. B. Miracle, W. S. Sanders and O. N. Senkov: *Phil. Mag. A* **83** (2003) 2409–2428.
- 18) D. B. Miracle: *Nature Materials* **3** (2004) 697–702.
- 19) L. Fejes-Toth: *Lagerung in der Ebene, auf der Kugel und im Raum*, (Springer, Berlin, Germany, 1952).
- 20) P. M. L. Tammes: *Recueil Travaux Botaniques Neerlandais* **27** (1930) 1–84.
- 21) H. T. Croft, K. J. Falconer and R. K. Guy: *Unsolved problems in Geometry*, (Springer-Verlag, New York, NY USA, 1991).
- 22) T. Aste and D. Weaire: *The Pursuit of Perfect Packing*, (Institute of Physics, Bristol, UK, 2000).
- 23) S.-H. Lee: *Arrangements of 13 and 14 points on the unit sphere with maximum minimum distance*, Ph.D. thesis, (Department of Mathematics, University of California at Berkeley, Berkeley, CA, 1993).
- 24) A. L. Mackay, J. L. Finney and K. Gotoh: *Acta Cryst.* **A33** (1977) 98–100.
- 25) D. A. Kottwitz: *Acta Cryst.* **A47** (1991) 158–165.
- 26) B. W. Clare and D. L. Kepert: *J. Math. Chem.* **6** (1991) 325–349.
- 27) N. J. A. Sloane, R. H. Hardin, W. D. Smith and others: *Tables of Spherical Codes: Nice arrangements of points on a sphere in various dimensions*, (Published electronically at <http://www.research.att.com/~njas/packings/>, 2000) Accessed in 2005.
- 28) L. Foppl: *J. Reine Angew. Math.* **141** (1912) 251–302.
- 29) T. Tarnai and Z. Gaspar: *Math. Proc. Camb. Phil. Soc.* **93** (1983) 191–218.
- 30) F. C. Frank and J. S. Kasper: *Acta Cryst.* **11** (1958) 184–190.
- 31) *Metal Clusters*, ed. by W. Ekardt, (Wiley, Chichester, 1999).
- 32) V. Kumar, K. Esvarjani and Y. Kawazoe: *Clusters and Nanomaterials*, ed. by Y. Kawazoe, T. Kondow and K. Ohno, (Springer, Berlin, Germany, 2001) pp. 109–131.
- 33) O. C. Thomas, W. Zheng and J. K. H. Bowen: *J. Chem. Phys.* **114** (2001) 5514–5519.
- 34) D. E. Bergeron, P. J. Roach, A. W. C. Jr., N. O. Jones and S. N. Khanna: *Science* **307** (2005) 231.
- 35) V. Kumar: *Sadhana* **28** (2005) 815.
- 36) L. Pauling: *The Nature of the Chemical Bond*, 3rd ed., (Cornell University Press, Ithaca, NY, 1960).
- 37) A. F. Wells: *Structural Inorganic Chemistry*, 5th ed., (Clarendon Press, Oxford, UK, 1984).
- 38) J. Fernandez and P. Harrowell: *J. Chem. Phys.* **120** (2001) 9222–9232.
- 39) H. W. Sheng, W. K. Luo, F. M. Alamgir, J. M. Bai and E. Ma: *Nature* **439** (2006) 419–425.
- 40) P. H. Gaskell: *Materials Science and Technology*, Vol. 9 Glasses and Amorphous Materials, ed. by J. Zarzycki, (VCH, Cambridge, UK, 1991) pp. 175–278.
- 41) G. J. Fan and H. J. Fecht: *J. Chem. Phys.* **116** (2002) 5002–5006.
- 42) D. B. Miracle and O. N. Senkov: *J. Non-Cryst. Sol.* **319** (2003) 174–191.
- 43) D. B. Miracle: *J. Non-Cryst. Sol.* **242** (2004) 89–96.
- 44) D. B. Miracle: *Acta Mater.*, Accepted for publication.