Model of Icosahedral Order

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1. Abstract

Metallic glasses, quasicrystals, and crystals may share identical local
icosahedral order. This type of ordering extends to fill a three-
dimensional curved space, producing an icosahedral "polytope" with perfect
short and long-range icosahedral order. In this paper I demonstrate how
to flatten the polytope and fill space with structures possessing the short-
range order of the polytope but various types of long-range order. Both
the rhombohedral packing units required to construct a three-dimensional
Penrose pattern and long-range orientational order arise from rolling the
polytope along special paths in three-dimensional flat space.

2. Introduction

The discovery of sharp diffraction patterns with icosahedral symmetry[1]
emphasizes the importance of icosahedral order in solid metals. In 1952
F. C. Frank suggested local icosahedral order as an explanation for super-
cooling of liquid metals.[2] Others have extended his ideas in recent years
to form a theory of metallic glass.[3] Although this theory succeeds
qualitatively,[4] direct experimental confirmation has not been possible.
Perhaps understanding the structure of quasicrystals will lead to a deeper
understanding of metallic glass. This paper reviews one approach to this
problem by presenting a unified model of icosahedral order in glassy,
quasicrystalline, and crystalline materials.

   This model utilizes a perfect icosahedral crystal, known as a "polytope",
which exists in the three-dimensional curved surface of a sphere embedded
in four-dimensional space.[5] Because curved and flat space are locally
indistinguishable, structures in the curved space map into flat space with
little distortion. Over larger distances defects arise in flat space be-
cause of the curvature mismatch. I demonstrate how to incorporate defects
to model: glass with only short order; quasicrystals with long-range
orientational order and either no long-range translational order or quasi-
periodicity; and Frank-Kasper crystalline phases.

   To map from curved to flat space, roll the four-dimensional polytope
along three-dimensional flat space.[6] Everywhere an atom of the polytope
touches three-dimensional space, place a three-dimensional atom. I show
that long-ranged orientational and translational order arise from rolling
the polytope in a straight line. Rolling around a closed loop places
defects within the loop.[7] For certain types of loops, these defects
maintain orientational order. These special loops bound the faces of the
oblate and prolate rhombohedra of the three-dimensional Penrose pattern.[8]

3. Local Icosahedral Order

Frank proposed that icosahedra would be present in supercooled liquid
metals as a result of the tendency to form tetrahedral clusters of four

atoms. The tetrahedron provides an extremely dense, rigid, energetically favorable configuration. If it could, a metal would consist entirely of tetrahedra. Tetrahedra, however, do not fill space. An interplay of energetic preferences and geometrical constraints determines the real structure of a metal.

Try to fill a small region of space with tetrahedra. Note that any two faces of a tetrahedron meet at an angle of $\cos^{-1}(1/3) = 70.53°$. Thus a total of $360/70.53 = 5.104$ tetrahedra may share a common edge. Of course, tetrahedra only exist in integral units, so only five will fit without distortion. The small gap left over prevents tetrahedra from filling space.
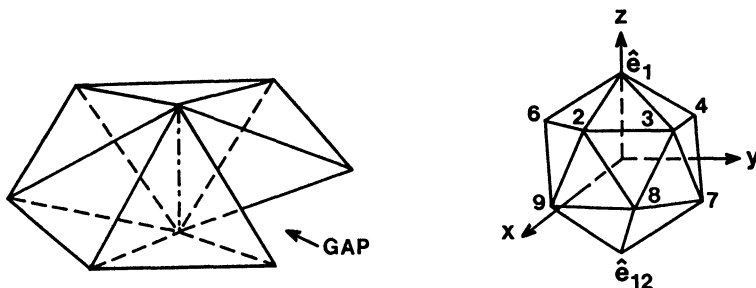

Figure 1a shows five tetrahedra sharing a bond, Fig. 1b shows an icosahedron in the standard orientation

If we distort the five tetrahedra slightly to fill in the gap, the resulting structure forms a fragment of an icosahedron. The distortion of the tetrahedra results in the edge length of the icosahedron being 5% greater than the center to vertex length. Despite the distortion, the icosahedron inherits the traits of high density and low energy. Thus icosahedral clusters should be prevalent in liquid metals near or below their freezing points.

Ideally no distinction exists between the atom at the center of a cluster and the atoms on the surface. Each atom has an equal right to form the center of a cluster. Larger clusters form in such a way that atoms previously at the surface find themselves at the centers of new icosahedra.

Icosahedra themselves cannot pack to fill space. The gap in the cluster of tetrahedra reappears as gaps between atoms on the surfaces of icosahedral clusters. As we enlarge the clusters, the gaps grow in size causing icosahedral frustration.[3] Curving space eliminates the frustration, as I show in the next section.

4. Icosahedral Polytope

Gaps between atoms may be filled by choosing slightly larger atoms to place on the surface of the icosahedral clusters. As more and more atoms are added to the cluster, the atoms on the outer coordination shells must become increasingly large to fill the gaps. Equivalently, one could keep the atoms at a given size but shrink the metric so that the distance between the centers of atoms is always equal to their diameter. The metric found on the curved three-dimensional curved surface of S^3, a sphere in four dimensions, accomplishes this.
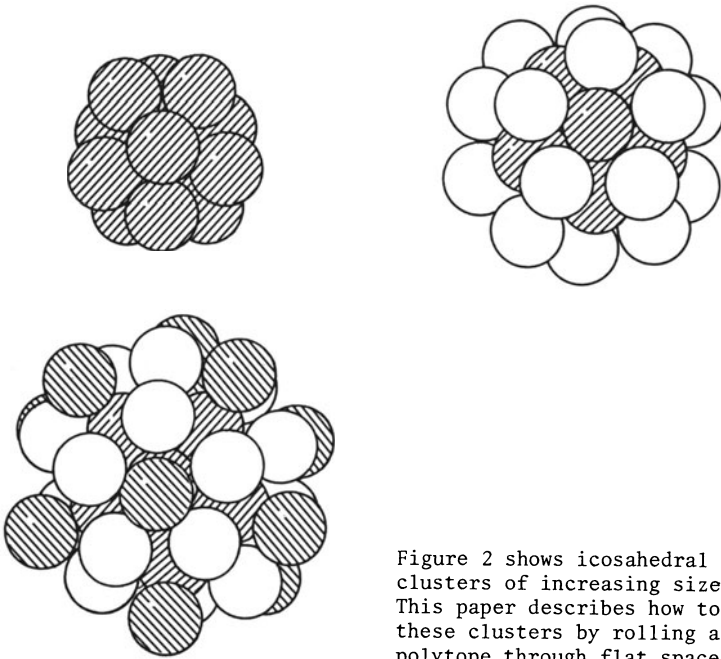
Figure 2 shows icosahedral
clusters of increasing size.
This paper describes how to create
these clusters by rolling a
polytope through flat space

Polytope {3,3,5} places 120 atoms in S^3 so that each atom sits at the center of an icosahedron formed by its twelve neighbors. All 600 cells form perfect tetrahedra. All frustration disappears because there are no gaps between atoms. The polytope forms a non-Euclidean crystal with rotational and translational symmetries.
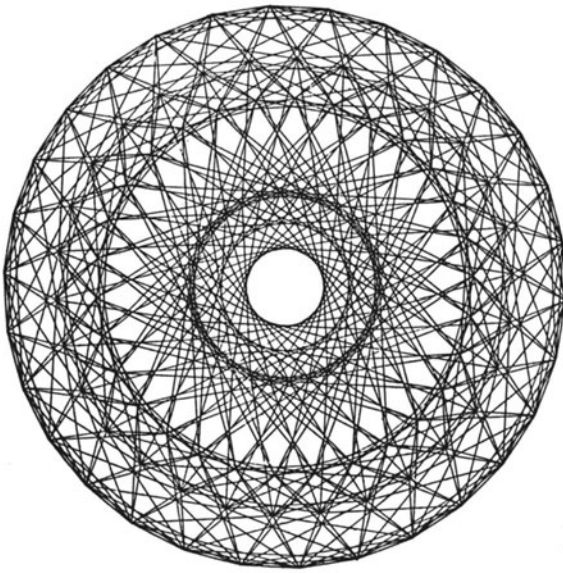

Figure 3. Poyltope {3,3,5}
projected from S^3 onto R^2.
Taken from reference 5

The structure and symmetries of the polytope have been described thoroughly elsewhere.[5,7,9] I will mention just two facts necessary for the remainder of this paper. Denote the separation between neighboring atoms by d and the radius of S^3 by R. A remarkable relationship between the structure of the polytope and the symmetry group of an icosahedron[10] guarantees that the ratio d/R is one half the smallest nonzero angle of rotation which leaves an icosahedron invariant. Thus

$$d = \frac{\pi}{5}R. \tag{1}$$

There is a special, intrinsic coordinate system for S^3 in which the structure of the polytope is especially simple. In this special coordinate system the polytope looks like a crystal with a dodecahedral unit cell translated rigidly along geodesics connecting neighboring atoms. Curiously, when viewed from a parallel transported coordinate system the intrinsic coordinates twist and turn.[11] The dodecahedral unit cell thus rotates around the geodesic by an angle equal to the geodesic distance travelled divided by the radius of S^3.

We fill flat space with atoms by rolling the polytope on R^3. As the polytope rolls in a straight line the point of contact between the sphere S^3 and flat space R^3 traces out a geodesic curve. Thus, if we construct an icosahedron at some point $\vec{R} \in R^3$, roll the polytope to $\vec{R} + \vec{V}$ and construct a new icosahedron, the new icosahedron will be identical to the old icosahedron rotated by

$$\theta = |\vec{V}|/R \tag{2}$$

around the axis $\vec{V}$. Equations (1) and (2) provide the key to creating long-range order.

5. Filling Space With Atoms

How can we use this non-Euclidean crystal to describe noncrystallographic structures in ordinary space? We must flatten the polytope. Strains introduced by flattening create the icosahedral frustration and open up gaps between atoms. Introducing defects into the polytope structure relieves this frustration. Recalling that 5.104 tetrahedra fit around a single bond, we note that placing a sixth tetrahedron on a bond will be a common type of defect. Such a sixfold bond may be viewed as a -72° disclination line in the polytope.

Rolling the polytope on R^3 provides a convenient scheme for placing atoms in flat space. This method automatically incorporates disclination line defects, because rolling the polytope in a straight line is equivalent to a screw transformation in which an icosahedron is simultaneously translated and rotated.[7] Equation 2) makes this notion precise. Because the rotation group So(3) is nonabelian, rolling around a closed loop generally results in a net rotation of the icosahedron. Thus the loop encloses a disclination line.

Imagine the sphere S^3 placed in four dimensions so that the atom at its northpole touches three-dimensional space at the origin, and the twelve neighbors of the northpole sit in the standard orientation shown in Fig. 1. We will place an atom in flat space wherever an atom of the polytope touches R^3. Thus we begin by placing an atom at the origin.

Now roll the polytope a distance d in the direction $\hat{e}_k$ where d is the geodesic separation between atoms in the polytope and $\hat{e}_k$ labels one of the

vertices of the icosahedron in Fig. 1. Now one of the atoms neighboring the northpole of the polytope touches R^3 at the point $d\hat{e}_k$. Repeat this procedure for all twelve directions $\hat{e}_k$. The result is a thirteen atom icosahedral cluster such as is shown in Fig. 2a.

Let's try to extend this construction along the z axis. Figure 4 shows five intersecting icosahedra generated by rolling along the z axis and constructing the local icosahedron at each point.[12] Note how the orientation of the icosahedron centered at (o,o,d) has been rotated by $\pi/5$ around the z axis from the standard orientation at the origin. This is a direct consequence of (1) and (2). The original orientation is restored at (o,o,2d) because rotations by $2\pi/5$ belong to the icosahedral symmetry group.
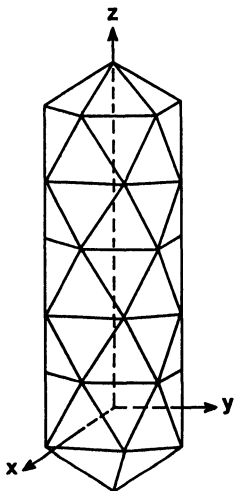

Figure 4 rolls the polytope along the z axis. Constructing the local icosahedron around each point (o,o,nd) where n is an integer. Note how the orientations of the icosahedra at odd values of n differ by $\pi/5$ from the standard orientation at even values of n.

Things get more complicated when the path we roll along turns a corner. Consider a path formed inductively by constructing the icosahedron surrounding the point of contact between the polytope and R^3, rolling the polytope to one of the vertices of this polytopes, then repeating these two steps over and over. Figure 4 shows the special case in which the chosen vertex is always $\hat{e}_1$. In general the path will zig-zag through R^3.

Every time we roll a distance d we rotate the icosahedron through an angle of $\pi/5$. This rotation is not in the symmetry group of an icosahedron. Therefore the new orientation is always distinct from the previous one. Rolling off in some other direction will result in another rotation not in the icosahedral symmetry group. Rolling twice multiplies the individual rotations producing a net rotation which is not, in general, in the icosahedral symmetry group. In fact, we can create any rotation in So(3) with arbitrary precision by rolling a finite distance.

Angular correlations along the path will decay exponentially. The result of filling space with atoms in this manner is a compelling model of metallic glass. One can formulate a Landau theory for rapidly quenched metals based on this picture.[7] The calculated structure function agrees well with experiments.[4] In the final section of this paper I describe how to construct quasicrystalline and crystalline long-range order.

6. Long-Ranged Order

To maintain orientational order over large distances simply roll the poly-
tope an even number of steps in each direction. Because the icosahedron
gets rotated by $\pi/5$ in each step, rolling two steps rotates the icosahedron
by $2\pi/5$. This larger rotation belongs to the icosahedral symmetry group,
so the orientation after rolling two steps is equivalent to the starting
orientation.

The simplest closed loop we can roll around in this manner forms a
rhombus with edge length 2d. Roll up the z axis along $\hat{e}_1$ to (o,o,2d).
Then turn and roll in the direction $\hat{e}_2$ (which is the direction the old $\hat{e}_6$
vertex has been rotated into) to (1.79d,o,2.89d). Then head back down
along $\hat{e}_{12} = -\hat{e}_1$ to (1.79d,o,0.89d). Finally roll back to the origin along
$\hat{e}_{11} = -\hat{e}_2$. This loop forms a rhombus with angles 63.43° and 116.57°. The
net result of rolling around this loop is to rotate the icosahedron by
$-2\pi/5$ around $\hat{e}_8$. Thus a -72° disclination line threads the loop.

Such loops may be joined along their edges to form the faces of solid
bodies. Six loops combine in two ways to form rhombahedra. If three
116.57° angles meet at a point (as $\hat{e}_2$, $\hat{e}_4$, and $\hat{e}_{12}$ meet at the origin), the
three associated rhombuses bound three of the six faces of the oblate
rhombus shown in Fig. 5a. If three 63.43° angles meet at a point (as $\hat{e}_1$,
$\hat{e}_2$, and $\hat{e}_3$ meet at the origin), the three associated rhombuses bound three
of the six faces of the prolate rhombus shown in Fig. 5b.

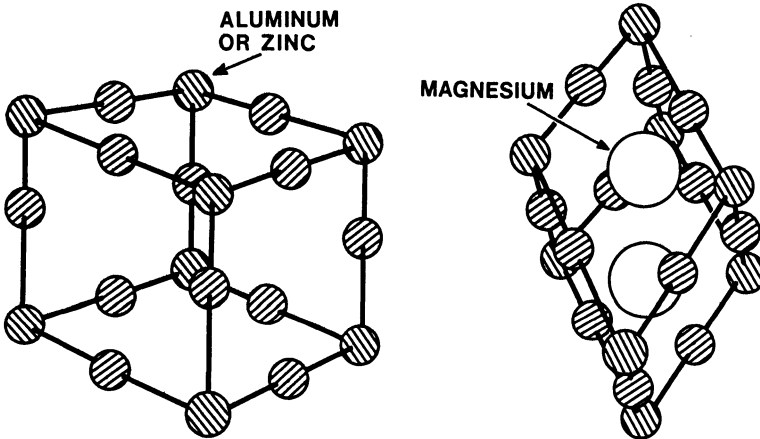**ALUMINUM
OR ZINC**

MAGNESIUM

Figure 5a) and b) show oblate and prolate rhombahedra with decoration by
atoms resulting from rolling polytope along edges of rhombic faces.

The clusters of Fig. 2 are both[9] polytope fragments rolled into flat
space and components of the unit cell of the Frank-Kasper phase[13] of
$Mg_{32}(Al,Zn)_{49}$. We identify the 20 atoms forming a dodecahedral shell in
Fig. 2b as Magnesium atoms. The remainder are aluminum or zinc. Thos mo-
tivates Henley and Elser's[8] identification of the atoms decorating the
rhombahedra in Fig. 5. Each face of a rhombahedron surrounds a -72° dis-
clination line defect. Henley and Elser[8] note that +72° disclinations
occur within the oblate rhombahedron.

This pair of rhombahedra is sufficient to create a three-dimensional
Penrose pattern. Just join up the rhombahedra along their faces while

imposing Penrose pattern-matching rules and the resulting structure's dif-[14]
fraction pattern will have delta function peaks and icosahedral symmetry.
In addition the structure will possess inflation and deflation symmetries
whose physical significance is questionable. Note that the decorated
rhombahedra in Fig. 5 possess no matching rules. Elser has shown that
packing the rhombahedra without regard to matching rules can eliminate the
inflation and deflation symmetries without significantly altering the
diffraction pattern.[15]

   The oblate rhombahedron in Fig. 5a) is unlikely to occur with great
frequency because the +72° disclinations correspond to an unfavorable
arrangement of four tetrahedra around a single bond. It is more likely
that pairs of oblate rhombahedra will combine with pairs of prolate rhom-[8]
bahedra to form a rhombic dodecahadron as described by Henley and Elser.
This combination is common in the Penrose pattern and also in the
$Mg_{32}(Al,Zn)_{49}$ Frank-Kasper phase. We can produce it also by rolling the
polytope along its edges, which are parallel to the $\hat{e}_k$ of an icosahedra.
The resulting decoration of the rhombic dodecahedron with atoms differs
from the decorations of the component rhombahedra because all +72° dis-
clinations have been removed.

   The rhombic dodecahedron may pack together with the prolate rhombahedron
to create the structure of the Frank-Kasper crystalline phase of
$Mg_{32}(Al,Zn)_{49}$. This structure possesses long-ranged icosahedral orienta-
tional order, translational periodicity, and cubic symmetry in its dis-
clination-like network. Alternatively, the rhombic dodecahedron may pack
together with prolate and oblate rhombahedra to create a three-dimensional
Penrose pattern with matching rules observed or not as we choose. These
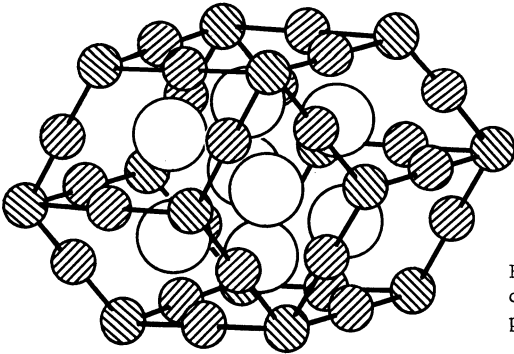structures may model the quasicrystalline phase[16] of $Mg_{32}(Al,Zn)_{49}$.

Figure 6. Rhombic dodecahedron
decorated with atoms by rolling
polytope along each edge

   In conclusion, rolling out the polytope fills space with atoms in
structures which model metallic glass when the path we roll on turns as
often as one atomic diameter. If the paths always continue an even number
of atomic diametrics in a given direction, long-range orientational order
emerges. Rolling around rhombic paths of edge length 2d leads to the
prolate rhombus, the oblate rhombus, and the rhombic dodecahedron, each
decorated with atoms and enclosing disclination line defects. The prolate
rhombus and rhombic dodecahedron pack to form the Frank-Kasper phase of
$Mg_{32}(Al,Zn)_{49}$. One must include the oblate rhombus as well to obtain a
three-dimensional Penrose pattern which may model this material's icosahedral
phase.

7. References

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