Tetrahedral motifs in amorphous systems

Matt Chambers
What is the short-range order of a liquid?

Random?
Radial Distribution Function

- The nearest-neighbor distance disproves a complete lack of short-range order.

Zallen, Physics of Amorphous Solids, Wiley&Sons (1983)
What is the short-range order of a liquid?

- Random?
- Micro-crystalline?
What is the short-range order of a liquid?

- Random?
- Micro-crystalline?
  - Disproved by Turnbull’s mercury supercooling
- Quasicrystalline

- Icosahedral coordination shells are energetically more stable

Reichert, Nature 408 (2000) 839
The Problem of Tiling Space

- A plane can be tiled with equilateral triangles
- Hard disc packing is ~90% efficient
- A single tetrahedron is ~78% packing efficiency
- However, perfect tetrahedra do not tile space
Assembling Tetrahedra

- Tetrahedra can *almost* assemble into pentagonal bipyramids or icosahedra.
- A small distortion is needed to complete the regular polyhedron.
- ~5% for icosahedra.

Stranger arrangements are possible

### Icosahedral Packing versus FCC, HCP, RCP

<table>
<thead>
<tr>
<th>Packing Method</th>
<th>Packing Efficiency</th>
<th>Fills Space</th>
<th>Coordination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Icosahedral Packing</td>
<td>0.726 to 0.681 depending on cluster size</td>
<td>No</td>
<td>Icosahedron</td>
</tr>
<tr>
<td>FCC Packing</td>
<td>0.740</td>
<td>Yes</td>
<td>Cube octahedron</td>
</tr>
<tr>
<td>HCP Packing</td>
<td>0.740, less if c/a&gt;1</td>
<td>Yes</td>
<td>Twinned cube octahedron</td>
</tr>
<tr>
<td>Random Close Packing</td>
<td>0.637</td>
<td>Yes</td>
<td>Various</td>
</tr>
</tbody>
</table>
Transformations between cluster types

- Icosahedral clusters of 55 atoms or larger contain atoms with a mixture of arrangements.
- As clusters increase in size, the percentage of atoms with cube-octahedral coordination increases.
- The energy cost to change to fcc or hcp decreases with increasing cluster size.

Mackay, Acta Cryst. 15(1962) 916
Problems scale with size

- Packing density of icosahedra decreases with size (to a minimum of 0.681)
- Icosahedra cannot tile space
- Large icosahedra contain many atoms with a cube-octahedron coordination shell

Mackay, Acta Cryst. 15(1962) 916
Bent Space

- Tetrahedra can tile a space with appropriate curvature

Modified Icosahedra: Frank-Kasper Polyhedra

- The statistical honeycomb model predicts a coordination of 13.4\(^1\)
- Additional atoms can be added to icosahedra as defects
- Added atoms must be added such that\(^2\):
  - The polyhedra remains triangulated
  - They are either \(S_5\) or \(S_6\)

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\(^1\) Nelkon and Spaepen, Solid State Phys. 42 (1989)

\(^2\) Frank, Kasper, Acta Cryst. 11 (1958), 184
Modified Icosahedra: Frank-Kasper Polyhedra

- The regular icosahedra is referred to as Z12.
- Z14, Z15, and Z16 polyhedra are also possible.
- Z13 cannot be made triangulated.
Modified Icosahedra: Frank-Kasper Polyhedra

- Each polyhedra is unique
- The arrangement of $S_6$ atoms in each is precise.
Tiling Space

- Frank-Kasper polyhedra can tile space$^3$
- A mixture of Z12 polyhedra with any of Z14, Z15 and Z16 is sufficient

Disclinations

- Each $S_6$ atom must be shared by at least two polyhedra
- Connecting $S_6$ atoms shared by polyhedra leads to a network
- The network extends throughout the structure
- For $Z14$, $Z15$, and $Z16$, these are negative

4 Doye and Wales, Phys. Rev. Let. 86 (2000) 5719
Disclination Networks

- Z8, Z9, and Z10 polyhedra are also possible, which produce positive disclinations.
- Geometry of positive disclinations is similar to negative disclinations (albeit with $S_4$ atoms).
- Disclinations interact with each other, including entanglement and annihilation interactions.

More about disclinations

- Positive disclinations dominate (recall that the statistical coordination was 13.4)
- Ordered close-packed alloys can be described in terms of ordered disclinations
- Amorphous alloys contain disordered disclinations