Diffraction from amorphous solids

- No long-range order
  - Only significant order is nearest neighbour spacing
  - Diffraction pattern forms diffuse halo
  - Typical of colloidal suspensions and globular clusters
- Diffraction is large or small angle depending on the size of the “particle”

Polymer order

- Oriented nematic
  - Short-range inter-chain order
  - Local layering

- Oriented smectic-A
  - Short-range inter-chain order
  - Layering extended normal to chains
  - Diffraction spots
**Polymer crystallinity**

- **2-D crystallinity**
  - Hexagonal packing of chains
  - Local layer order

- **3-D crystallinity**
  - Hexagonal packing of chains
  - Long-range layer order

**Small angle scattering**

Large-scale correlations between polymer elements result in low-angle diffraction

Length scales >10 nm
Angles < 5°

Generally assemblies of crystallites
Can distinguish qualitatively between different types of disorder

Random / amorphous
Layer aligned
Doubly aligned
Theorem:
For any family of lattice planes separated by distance \( d \), there are reciprocal lattice vectors perpendicular to the planes, the shortest being \( 2\pi/d \).

Orientation of plane is determined by a normal vector.
The miller indices of a lattice plane are the coordination at the reciprocal lattice vector normal to the plane.

Small Angle X-ray Diffraction

Direct Visualization of Individual Cylindrical and Spherical Supramolecular Dendrimers
*Science* 17 October 1997; 278: 449-452
Small Angle X-ray Diffraction


Close packing structures: Cubic vs. Hexagonal
Unit cell symmetries - cubic

\[ \% = \frac{4 \pi (\frac{a}{2})^3}{3 a^3} = \frac{\pi}{6} \]

52.36%
\( \alpha\)-Iron is body-centered cubic

\[
\% = 2 \times \frac{\frac{4}{3} \pi (\frac{\sqrt{3}a}{4})^3}{a^3} = \frac{3\sqrt{3} \pi}{24}
\]

68%

**Close Packing of Spheres**

*The most efficient way to fill space with spheres*

Is there another way of packing spheres that is more space-efficient? In 1611 Kepler asserted that there was no way of packing equivalent spheres at a greater density than that of a face-centred cubic arrangement. This is now known as the **Kepler Conjecture**.

This assertion has long remained without rigorous proof. In 1998 Hales announced a computer-based solution. This proof is contained in over 250 manuscript pages and relies on over 3 gigabytes of computer files.

http://www.math.pitt.edu/
The square pile is formed, as in the annexed figure.

The number of balls in the top layer is 1\(^2\), in the next layer 2\(^2\), in the next, 3\(^2\), and so on. To find the number of balls in a pile of \( n \) layers, we have the series,

\[
1 4 9 16 25 36, \ldots \text{, &c.}
\]

1st order of diff., 3 5 7 9 11 &c.
2d “ “ 2 2 2 &c.
3d “ “ 0 0 0 &c.

Hence,

\[ a = 1, \ d_1 = 3, \ d_2 = 2, \ d_3 = 0, \ d_4 = 0, \ &c. \]

For BCC; 68.02%
HCP \hspace{1cm} \text{Hexagonal Close-Packing}

CN=12

(0,0,0)
(1/3,2/3,1/2)

Close Packing of Spheres

Alternatives

\begin{align*}
a &= b = c, \alpha = \beta = \gamma = 90^\circ \\
2 \text{ atoms in the unit cell:} \\
(0, 0, 0) \ (1/2, 1/2, 1/2)
\end{align*}

Packing efficiency \( R_{\text{fill}} = \frac{V_{\text{atoms}}}{V_{\text{cell}}} \)

With \( Z = 2, V_{\text{cell}} = a^3, \ 3a^2 = (4r)^2 \)

\( R_{\text{fill}} = 0.68 \)

4r = \sqrt{3}a
**Close Packing of Spheres**

Comparison of Packing Efficiencies

- **Primitive Cubic (α-Po)**
  - Coordination Number 6
  - 52% Packing Efficiency
  - $V_{\text{atom}}/V_{\text{cell}} = 0.52$, since $V_{\text{cell}} = a^3$ and $V_{\text{atom}} = Z \frac{4}{3} \pi r^3$ with $a = 2r$ and $Z = 1$

- **Body-Centered Cubic (W)**
  - Coordination Number 8
  - 88% Packing Efficiency

- **Close-Packed (ccp or hcp)**
  - Coordination Number 12
  - 74% Packing Efficiency

(increased pressure favors higher packing efficiency)
Rare Gas: Ne, He, Ar, Kr, Xe (ccp; fcc)

Metal: Cu, Ag, Au, Ni, Pd, Pt (ccp)

Mg, Zn, Cd, Ti (hcp)

Fe, Cr, Mo (bcc)

Packing of Truncated octahedron

Optical Dark Field Micrograph

Truncated octahedron

Yaghi, Science 2008
Densest lattice packing of an octahedron

The density of a densest lattice packing of an octahedron was already calculated by Minkowski in 1904. In 1948 Whitworth generalized Minkowski’s result to a family of truncated cubes. The density of a densest lattice packing is equal to $\frac{18}{19} = 0.9473...$.


Octahedra

Ionic structures

Can be considered as close packing of large anions with Cation filling in the interstitial sites.

For every anion, there are
1 Octahedral site
2 tetrahedral sites.
Close packing structures: Cubic vs. Hexagonal
Close Packing of Spheres

Different cavity sizes: the octahedral hole
Close Packing of Spheres

Different cavity sizes: the tetrahedral hole

$\frac{1}{2}a\sqrt{2}$

$\frac{1}{2}r_x\sqrt{6}$

$r_M + r_X = r_X \cdot \frac{1}{2}\sqrt{6}$

$r_M/r_X = \frac{1}{2}\sqrt{6} - 1$

$= 0.225$

NaCl; ccp, O sites: 100%
• CCP Ca\(^{2+}\) with F\(^-\) in all Tetrahedral holes
• Lattice: fcc
• Motif: Ca\(^{2+}\) at (0,0,0); 2F\(^-\) at \((1/4,1/4,1/4)\) & \((3/4,3/4,3/4)\)
• 4 CaF\(_2\) in unit cell
• Coordination: Ca\(^{2+}\) 8 (cubic) : F\(^-\) 4 (tetrahedral)
• In the related Anti-Fluorite structure Cation and Anion positions are reversed
**Close Packing of Spheres**

ccp → Li\textsubscript{3}Bi type

filling of all O\textsubscript{i} and T\textsubscript{d} voids

C\textsubscript{60} → K\textsubscript{3}C\textsubscript{60}
**Zinc Blende: ZnS**

- CCP $S^2-$ with $Zn^{2+}$ in half Tetrahedral holes (only $T^+$ {or $T^-$} filled)
- **Lattice:** fcc
- **4 ZnS in unit cell**
- **Motif:** $S$ at (0,0,0); $Zn$ at ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$)
- **Coordination:** 4:4 (tetrahedral)
- Cation and anion sites are topologically identical
**NaCl**
- Very common (inc. 'ionics', 'covalents' & 'intermetallics')
- Most alkali halides (CsCl, CsBr, CsI excepted)
- Most oxides / chalcogenides of alkaline earths
- Many nitrides, carbides, hydrides (e.g. ZrN, TiC, NaH)

**CaF₂ (Fluorite)**
- Fluorides of large divalent cations, chlorides of Sr, Ba
- Oxides of large quadrivalent cations (Zr, Hf, Ce, Th, U)

**Na₂O (Anti-Fluorite)**
- Oxides / chalcogenides of alkali metals

**ZnS (Zinc Blende/Sphalerite)**
- Formed from Polarizing Cations (Cu⁺, Ag⁺, Cd²⁺, Ga³⁺...)
  and Polarizable Anions (I⁻, S²⁻, P³⁻, ...);
- *e.g.* Cu(F,Cl,Br,I), AgI, Zn(S,Se,Te), Ga(P,As), Hg(S,Se,Te)
• HCP As with Ni in all Octahedral holes
• Lattice: Hexagonal - P
• $a = b, c$
• Motif: 2Ni at (0,0,0) (0,0,1/2) 2As at ($2/3,1/3,1/4$) & ($1/3,2/3,3/4$)
• 2NiAs in unit cell
• Coordination: Ni 6 (octahedral) : As 6 (trigonal prismatic)
Wurtzite: ZnS

- HCP S\(^2-\) with Zn\(^{2+}\) in half Tetrahedral holes (only T+ {or T-} filled)
- Lattice: Hexagonal - P
  - \(a = b, c\)
- Motif: 2S at \((0,0,0)\), \((\frac{2}{3},\frac{1}{3},\frac{1}{3})\); 2Zn at \((\frac{2}{3},\frac{1}{3},\frac{1}{8})\) & \((0,0,\frac{5}{8})\)
- 2ZnS in unit cell
- Coordination: 4:4 (tetrahedral)
COORDINATION ENVIRONMENTS

Zinc Blende

4 Nearest Neighbours (Tetrahedral)
12 Next Nearest Neighbours

Cuboctahedral → Anti-Cuboctahedral

Very different Next, Next-Nearest Neighbour Coordinations & beyond

Wurtzite

POLYHEDRAL REPRESENTATIONS

Zinc Blende

Vertex-linked tetrahedra only, but layers skewed in Wurtzite, & not in Blende

Wurtzite
• HCP I with Cd in Octahedral holes of alternate layers

**CdI$_2$**

**Comparison**

**CdI$_2$ vs NiAs**

- **Lattice:** Hexagonal - P
- **Motif:** Cd at (0,0,0); 2I at ($\frac{2}{3}, \frac{1}{3}, \frac{1}{4}$) & ($\frac{1}{3}, \frac{2}{3}, \frac{3}{4}$)
- **1CdI$_2$** in unit cell
- **Coordination:** Cd - 6 (Octahedral) : I - 3 (base pyramid)
NiAs
- Transition metals with chalcogens, As, Sb, Bi
e.g. Ti(S,Se,Te); Cr(S,Se,Te,Sb); Ni(S,Se,Te,As,Sb,Sn)

CdI$_2$
- Iodides of moderately polarising cations; bromides and chlorides of strongly polarising cations;
e.g. PbI$_2$, FeBr$_2$, VCl$_2$
- Hydroxides of many divalent cations
e.g. (Mg,Ni)(OH)$_2$
- Di-chalcogenides of many quadrivalent cations
e.g. TiS$_2$, ZrSe$_2$, CoTe$_2$
CdCl₂ (CCP equivalent of CdI₂)
Chlorides of moderately polarising cations
e.g. MgCl₂, MnCl₂
Di-sulfides of quadrivalent cations
e.g. TaS₂, NbS₂ (CdI₂ form as well)

Cs₂O has the anti-cadmium chloride structure

HCP CaF₂?
No structures are known with all Tetrahedral sites
(T⁺ and T⁻) filled in HCP
i.e. there is no HCP analogue of the Fluorite/Anti-Fluorite Structure
<table>
<thead>
<tr>
<th>Formula</th>
<th>Type and fraction of sites occupied</th>
<th>CCP</th>
<th>HCP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AB</strong></td>
<td>All octahedral</td>
<td>NaCl Rock Salt</td>
<td>NiAs Nickel Arsenide</td>
</tr>
<tr>
<td></td>
<td>Half tetrahedral (T+ or T-)</td>
<td>ZnS Zinc Blende</td>
<td>ZnS Wurtzite</td>
</tr>
<tr>
<td><strong>AB₂</strong></td>
<td>All tetrahedral</td>
<td>Na₂O Anti-Fluorite CaF₂ Fluorite</td>
<td>Not known</td>
</tr>
<tr>
<td><strong>AB₃</strong></td>
<td>All octahedral &amp; tetrahedral</td>
<td>Li₂Bi</td>
<td>Not known</td>
</tr>
<tr>
<td><strong>A₂B</strong></td>
<td>Half octahedral (Alternate layers full/empty)</td>
<td>CdCl₂ (Cadmium Chloride)</td>
<td>CdI₂ (Cadmium Iodide)</td>
</tr>
<tr>
<td></td>
<td>Half octahedral (Ordered framework arrangement)</td>
<td>TiO₂ (Anatase)</td>
<td>CaCl₂ TiO₂ (Rutile)</td>
</tr>
<tr>
<td><strong>A₃B</strong></td>
<td>Third octahedral Alternate layers 2/3 full/empty</td>
<td>YCl₃</td>
<td>BiI₃</td>
</tr>
</tbody>
</table>