Chapter 3: Packing Densities and Coordination

Learning Objectives

- How does atomic packing factor change with different atom types?
- How do you calculate the density of a material?

Relevant Reading for this Lecture...

- Pages 46-58.

Re-cap: Atomic Packing Factor (APF)

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APF = \frac{\text{Volume of atoms in unit cell} \times \pi (\frac{\sqrt{2}}{4} a)^3}{3 \text{ Volume of unit cell}}

Describes how efficiently atoms fill space within a given unit cell.*

Unit cell contains: 6 x 1/2 + 8 x 1/8 = 4 atoms/unit cell

APF = \frac{4}{3} \pi (\frac{\sqrt{2}}{4} a)^3

Close-packed directions:
length = 4R = \sqrt{2} a

* assume hard spheres

Adapted from Fig. 3.1(a), Callister 7e.
If the unit cell has different atoms – watch out!

*Ceramic Crystal Structures!

Watch Out! Different Atoms. Must Modify APF Equations.

Close-packed directions:
\[
\text{diagonal} = 2R_{\text{blue}} + 2R_{\text{red}} = \sqrt{3}a
\]

Must put in correct value for each atom type.

\[
\text{APF} = \frac{4}{3} \pi \left(\frac{a}{\sqrt{3}}\right)^3
\]

Adapted from Fig. 3.2(a), Callister 7e.
What if ions from the crystal structure?

Cesium chloride (CsCl) unit cell showing (a) ion positions and the two ions per lattice point and (b) full-size ions. Note that the Cs⁺−Cl⁻ pair associated with a given lattice point is not a molecule because the ionic bonding is non-directional and because a given Cs⁺ is equally bonded to eight adjacent Cl⁻, and vice versa.

Calculate the following: (1) The CN of CsCl (2) Ionic Packing Factor of CsCl

Recall from the last lecture $CN \rightarrow r/R = r^+/r^-$

What are the $r$'s for Cs⁺ and Cl⁻?

$r_{Cs^+} = 0.170 \text{ nm}$
$r_{Cl^-} = 0.181 \text{ nm}$

$r^+/r^- = 0.939$

These numbers came from inside cover of text book!

<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Ratio $r^+/r^-$</th>
<th>Coordination Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>$0.135 \approx 0.135$</td>
<td>O = O</td>
</tr>
<tr>
<td>4</td>
<td>$0.255 \approx 0.255$</td>
<td>O = O</td>
</tr>
<tr>
<td>6</td>
<td>$0.414 \approx 0.414$</td>
<td>O = O</td>
</tr>
<tr>
<td>8</td>
<td>$0.572 \approx 0.572$</td>
<td>O = O</td>
</tr>
</tbody>
</table>
Now calculate the Ionic Packing Factor of CsCl

For these ions, they touch along the body diagonal (make sure you know which direction the ‘hard spheres’ are touching)

\[
\text{IPF} = \frac{\text{[# of atoms/unit cell] [volume of a sphere]}}{\text{volume of unit cell}}
\]

One atom of Cs + One atom of Cl

\[
\frac{4}{3}\pi (r_{Cs}^3) + \frac{4}{3}\pi (r_{Cl}^3)
\]

\[
V_{Cs} + V_{Cl}
\]

\[
= 0.0454 \text{ nm}^3
\]

\[
\sqrt[3]{a} = 2r_{Cs} + 2r_{Cl}
\]

\[
a = 0.405 \text{ nm}
\]

\[
V = a^3 = 0.0664 \text{ nm}^3
\]

\[
\text{IPF} = 0.683
\]

For kicks, what if the ions touched along the edge length (not the body diagonal)?

\[
\frac{\text{[# of atoms/unit cell] [volume of a sphere]}}{\text{volume of unit cell}}
\]

One atom of Cs + One atom of Cl

\[
\frac{4}{3}\pi (r_{Cs}^3) + \frac{4}{3}\pi (r_{Cl}^3)
\]

\[
V_{Cs} + V_{Cl}
\]

\[
= 0.0454 \text{ nm}^3
\]

\[
\sqrt{a} = \frac{2r_{Cs} + 2r_{Cl}}{\sqrt{3}}
\]

\[
a = 0.405 \text{ nm}
\]

\[
V = a^3 = 0.0664 \text{ nm}^3
\]

\[
\text{IPF} = 0.683
\]

\[
\frac{\text{which } r?}{\text{average them?}}
\]

\[
r_{avg} = 0.176
\]

\[
\text{IPF} = 0.88 < 1.04
\]

\[
\text{Not possible! >100% packing!!!}
\]

It is critical that you identify the correct ‘hard sphere’ touching directions!
Let's do another example: Consider NaCl

What is the CN?
What is the IPF?

How do we determine CN?

Correct, \( \text{CN} \rightarrow r^+ / r^- \)

What are the \( r \)'s for Na\(^+\) and Cl\(^-\)?

\[
\begin{align*}
    r_{\text{Na}^+} &= 0.102 \text{ nm} \\
    r_{\text{Cl}^-} &= 0.181 \text{ nm}
\end{align*}
\]

\( r^+ / r^- = 0.564 \)

Not a very clear representation – let's expand it!

Do you see how the green spheres form a FCC structure?!

The blue spheres do the same thing, form a FCC structure

We have two interpenetrating FCC lattices
Commonly called a Rock Salt structure – structure seen in other materials including TiC, TaC, MgO, CaO, etc.
Calculate the IPF of NaCl

\[
\text{IPF} = \frac{\text{[# of atoms/unit cell] [volume of a sphere]}}{\text{volume of unit cell}}
\]

What type of unit cell do we have? Two FCC lattices – one for Na and one for Cl

4 atoms/Na FCC + 4 atoms/Cl FCC = 8 atoms/unit cell total

Four atoms of Na + Four atoms of Cl

\[
4 \times 4/3\pi(0.102 \text{ nm})^3 + 4 \times 4/3\pi(0.181 \text{ nm})^3 = 0.117 \text{ nm}^3
\]

What is the volume of the unit cell?

\[
a = 2r_{Na} + 2r_{Cl}
\]

\[
a = 0.566 \text{ nm}
\]

\[
V = a^3 = 0.181 \text{ nm}^3
\]

CORRECTION!

Though it looks like FCC symmetry, the face diagonal atoms don’t touch; but the edge atoms do touch!

Why? Cations and anions do not have the same size! Before we considered atoms of the same size.
Atoms can occupy ‘interstitial’ sites

F\textsuperscript{−} ions located at corners of a cube (at one-quarter of the distance along the body diagonal)

\begin{itemize}
  \item \textbf{Ca\textsuperscript{2+}}
  \item \textbf{F\textsuperscript{−}}
\end{itemize}

Unoccupied space in center can accommodate small atoms, e.g. He in UO\textsubscript{2} fuel rods

Fluorite (CaF\textsubscript{2}) unit cell showing (a) ion positions (b) full-size ions.

Structure: fluorite (CaF\textsubscript{2}) type
Bravais lattice: FCC
Ions/unit cell: 4Ca\textsuperscript{2+} + 8F\textsuperscript{−}
Typical ceramics: UO\textsubscript{2}, ThO\textsubscript{2}, TeO\textsubscript{2}

\textbf{CLASS ROOM EXAMPLE:}

Calculate the ionic packing factor for UO\textsubscript{2}, which has the CaF\textsubscript{2} structure

\begin{itemize}
  \item F\textsuperscript{−} ions located at corners of a cube (at one-quarter of the distance along the body diagonal)
  \item \textbf{Ca\textsuperscript{2+}}
  \item \textbf{F\textsuperscript{−}}
\end{itemize}

U and O ions touch along a portion of the body diagonal

Structure: fluorite (CaF\textsubscript{2}) type
Bravais lattice: fcc
Ions/unit cell: 4Ca\textsuperscript{2+} + 8F\textsuperscript{−}
Typical ceramics: UO\textsubscript{2}, ThO\textsubscript{2}, and TeO\textsubscript{2}
Calculate the ionic packing factor for UO₂, which has the CaF₂ structure.

This problem is tricky!

The face diagonal has a length of \( \sqrt{2}a \).

The body diagonal has a length of \( \sqrt{3}a \).

Along with the cell edge, they form a right triangle within the unit cell.

The Ca²⁺ and F⁻ ions touch a short distance along the body diagonal.

By the principle of similitude, this smaller triangle, measures as \( \frac{1}{4} \) the size of the large one.

Because of this, the length of the bond becomes:

\[
\frac{1}{4} \times \sqrt{3}a = R_{\text{Va}} + R_{\text{UO}} = 0.105 + 0.132 \text{ nm} = 0.548 \text{ nm}
\]

Now you can calculate \( a \) and the corresponding unit cell volume.

\[
IPF = \frac{V_{\text{ions in unit cell}}}{V_{\text{unit cell}}}
\]

Solving for \( a \) we get: \( a = 0.548 \text{ nm} \)

\[
V_{\text{unit cell}} = a^3 = (0.548 \text{ nm})^3 = 0.164 \text{ nm}^3
\]

\[
V_{\text{single ion}} = \frac{4}{3} \pi R^3
\]

\[
V_{\text{ions}} = 4 \times \frac{4}{3} \pi R_{\text{U}}^3 + 8 \times \frac{4}{3} \pi R_{\text{O}}^3 = \frac{16}{3} \pi (0.105)^3 + \frac{32}{3} \pi (0.132)^3 = 0.0965 \text{ nm}^3
\]

\[
IPF = \frac{V_{\text{ions}}}{V_{\text{unit cell}}} = \frac{0.0965 \text{ nm}^3}{0.164 \text{ nm}^3} = 0.588
\]
THEORETICAL DENSITY, $\rho$

Density = mass/volume

mass = number of atoms per unit cell $\times$ mass of each atom

mass of each atom = atomic weight / Avogadro's number

$$\rho = \frac{nA}{V_cN_A}$$

Volume/unit cell (cm$^3$/unit cell) $V_c$ $\times$ Avogadro's number (6.023 x 10$^{23}$ atoms/mol)

Example: Copper
- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius $R = 0.128$ nm (1 nm = 10$^{-7}$ cm)

$$V_c = a^3; \text{ For FCC, } a = 4R/\sqrt{2}; \quad V_c = 4.75 \times 10^{-23} \text{cm}^3$$

Result: theoretical $\rho_{\text{Cu}} = 8.89$ g/cm$^3$
Compare to actual: $\rho_{\text{Cu}} = 8.94$ g/cm$^3$ Why the difference?
Theoretical Density, $\rho$

- **Ex:** Cr (BCC)
  \[ A = 52.00 \text{ g/mol} \]
  \[ R = 0.125 \text{ nm} \]
  \[ n = 2 \]
  \[ a = 4R\sqrt{3} = 0.2887 \text{ nm} \]

\[ \rho = \frac{2 \times 52.00}{a^3 \times 6.023 \times 10^{23}} \]

\[ \rho_{\text{theoretical}} = 7.18 \text{ g/cm}^3 \]
\[ \rho_{\text{actual}} = 7.19 \text{ g/cm}^3 \]

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Densities of Material Classes

**In general**

\[ \rho_{\text{metals}} > \rho_{\text{ceramics}} > \rho_{\text{polymers}} \]

**Why?**

- **Metals** have...
  - close-packing (metallic bonding)
  - often large atomic masses
- **Ceramics** have...
  - less dense packing
  - often lighter elements
- **Polymers** have...
  - low packing density (often amorphous)
  - lighter elements (C,H,O)
- **Composites** have...
  - intermediate values

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Data from Table B1, Callister 7e.
Summary

• If there are different ions in the unit cell, APF/IPF equations must be modified! Find out which direction the ‘hard spheres’ touch

• The ionic packing factor can be calculated by

\[ IPF = \frac{V_{\text{ions in unit cell}}}{V_{\text{unit cell}}} \]

• Theoretical Density can be calculated by

\[ \rho = \frac{n}{V_c N_A} \]

### Notes

- \(\rho\): Theoretical Density (g/mol)
- \(n\): Number of atoms in the unit cell
- \(V_c\): Volume of the unit cell (cm³/unit cell)
- \(N_A\): Avogadro’s number (6.023 x 10²³ atoms/mol)