ISSUES TO ADDRESS...

• What is the difference in atomic arrangement between crystalline and noncrystalline solids?

• How are crystallographic directions and planes named?

• Under what circumstances does a material property vary with the measurement direction?
Energy and Packing

- Non dense, random packing
- Dense, ordered packing

Dense, ordered packed structures tend to have lower energies.
Materials and Packing

Crystalline materials...
- atoms pack in periodic, 3D arrays
- typical of: - metals
  - many ceramics
  - some polymers

Noncrystalline materials...
- atoms have no periodic packing
- occurs for: - complex structures
  - rapid cooling

"Amorphous" = Noncrystalline

Adapted from Fig. 3.11(a), Callister & Rethwisch 9e.

Adapted from Fig. 3.11(b), Callister & Rethwisch 9e.
Single vs Polycrystals

• Single Crystals
  - Properties vary with direction: **anisotropic**.
  - Example: the modulus of elasticity \( E \) in BCC iron:

\[
E \text{(diagonal)} = 273 \text{ GPa}
\]

\[
E \text{(edge)} = 125 \text{ GPa}
\]

• Polycrystals
  - Properties may/may not vary with direction.
  - If grains are randomly oriented: **isotropic**. \( E_{\text{poly iron}} = 210 \text{ GPa} \)
  - If grains are **textured**, anisotropic.


Adapted from Fig. 6.19(b), *Callister & Rethwisch 9e*. [Fig. 6.19(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC (now the National Institute of Standards and Technology, Gaithersburg, MD).]
Crystal Systems

**Unit cell:** smallest repetitive volume which contains the complete lattice pattern of a crystal.

- **7 crystal systems**
- **14 crystal lattices**

$a$, $b$, and $c$ are the lattice constants
Polymorphism

- Two or more distinct crystal structures for the same material (allotropy/polymorphism)

Titanium
- $\alpha$, $\beta$-Ti

Carbon
- Diamond, graphite

Iron system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>1538</td>
</tr>
<tr>
<td>BCC</td>
<td>1394</td>
</tr>
<tr>
<td>FCC</td>
<td>912</td>
</tr>
<tr>
<td>BCC</td>
<td></td>
</tr>
</tbody>
</table>
Introduction To Materials Science, Chapter 3, The structure of crystalline solids

**Single Crystals and Polycrystalline Materials**

**Single crystal:** atoms are in a repeating or periodic array over the entire extent of the material

**Polycrystalline material:** comprised of many small crystals or grains. The grains have different crystallographic orientation. There exist atomic mismatch within the regions where grains meet. These regions are called **grain boundaries.**
Introduction To Materials Science, Chapter 3, The structure of crystalline solids
Polycrystalline Materials

Atomistic model of a nanocrystalline solid by Mo Li, JHU
Point Coordinates

Point coordinates for unit cell center are
\[ \frac{a}{2}, \frac{b}{2}, \frac{c}{2} \quad \frac{1}{2} \frac{1}{2} \frac{1}{2} \]

Point coordinates for unit cell corner are 111

Translation: integer multiple of lattice constants \( \rightarrow \) identical position in another unit cell
Crystallographic Directions

Algorithm

1. Determine coordinates of vector tail, pt. 1: \(x_1, y_1, \text{ and } z_1\); and vector head, pt. 2: \(x_2, y_2, \text{ and } z_2\).
2. Tail point coordinates subtracted from head point coordinates.
3. Normalize coordinate differences in terms of lattice parameters \(a, b, \text{ and } c\):
   \[
   \frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}
   \]
4. Adjust to smallest integer values
5. Enclose in square brackets, no commas

ex:
pt. 1  \(x_1 = 0, \ y_1 = 0, \ z_1 = 0\)
pt. 2  \(x_2 = a, \ y_2 = 0, \ z_2 = c/2\)

\[
\begin{array}{ccc}
\frac{a - 0}{a} & \frac{0 - 0}{b} & \frac{c/2 - 0}{c}
\end{array}
\]

\[
=> \ 1, 0, 1/2 \quad => \ 2, 0, 1
\]

\[
=> [201]
\]
Crystallographic Directions

Example 2:

pt. 1 \( x_1 = a, \ y_1 = b/2, \ z_1 = 0 \)

pt. 2 \( x_2 = -a, \ y_2 = b, \ z_2 = c \)

\[
\begin{align*}
-a - a & b - b/2 & c - 0 \\
a & b & c
\end{align*}
\]

\( \Rightarrow -2, 1/2, 1 \)

Multiplying by 2 to eliminate the fraction

\(-4, 1, 2 \Rightarrow [\bar{4}12] \) where the overbar represents a negative index

families of directions \(<uvw>\)
Drawing HCP Crystallographic Directions (i)

Algorithm (Miller-Bravais coordinates)

1. Remove brackets
2. Divide by largest integer so all values are \( \leq 1 \)
3. Multiply terms by appropriate unit cell dimension \( a \) (for \( a_1, a_2, \) and \( a_3 \) axes) or \( c \) (for \( z \)-axis) to produce projections
4. Construct vector by placing tail at origin and stepping off these projections to locate the head
Drawing HCP Crystallographic Directions (ii)

- Draw the $[\bar{1} \bar{2} 13]$ direction in a hexagonal unit cell.

**Algorithm**

<table>
<thead>
<tr>
<th></th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$Z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Remove brackets</td>
<td>-1</td>
<td>-2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>2. Divide by 3</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{2}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>1</td>
</tr>
<tr>
<td>3. Projections</td>
<td>$\frac{-a}{3}$</td>
<td>$\frac{-2a}{3}$</td>
<td>$\frac{a}{3}$</td>
<td>$c$</td>
</tr>
</tbody>
</table>

4. Construct Vector

- Start at point $o$
- Proceed $-a/3$ units along $a_1$ axis to point $p$
- $-2a/3$ units parallel to $a_2$ axis to point $q$
- $a/3$ units parallel to $a_3$ axis to point $r$
- $c$ units parallel to $z$ axis to point $s$

$[\bar{1} \bar{2} 13]$ direction represented by vector from point $o$ to point $s$
Determination of HCP Crystallographic Directions (ii)

Algorithm

1. Determine coordinates of vector tail, pt. 1: $x_1, y_1, \text{ & } z_1$; and vector head, pt. 2: $x_2, y_2, \text{ & } z_2$. in terms of three axis ($a_1, a_2, \text{ and } z$)
2. Tail point coordinates subtracted from head point coordinates and normalized by unit cell dimensions $a$ and $c$
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas, for three-axis coordinates $[u'v'w']$
5. Convert to four-axis Miller-Bravais lattice coordinates using equations below:
   \[
   u = \frac{1}{3} (2u - v) \quad \nu = \frac{1}{3} (2\nu - u) \\
   t = (u + \nu) \quad w = w
   \]
6. Adjust to smallest integer values and enclose in brackets $[uvtw]$
Determination of HCP Crystallographic Directions (ii)

Determine indices for green vector

<table>
<thead>
<tr>
<th>Example</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Tail location</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Head location</td>
<td>$a$</td>
<td>$a$</td>
<td>$0c$</td>
</tr>
<tr>
<td>2. Normalized</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3. Reduction</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4. Brackets</td>
<td></td>
<td></td>
<td>[110]</td>
</tr>
<tr>
<td>5. Convert to 4-axis parameters</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$u = \frac{1}{3} \cdot [(2)(1) (1)] = \frac{1}{3}$</td>
<td>$v = \frac{1}{3} \cdot [(2)(1) (1)] = \frac{1}{3}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t = \left(\frac{1}{3} + \frac{1}{3}\right) = \frac{2}{3}$</td>
<td>$w = 0$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6. Reduction & Brackets

$1/3, 1/3, -2/3, 0 \Rightarrow 1, 1, -2, 0 \Rightarrow [1\bar{1}20]$
Crystallographic Planes

Adapted from Fig. 3.7, *Callister & Rethwisch 9e.*
Crystallographic Planes

• Miller Indices: Reciprocals of the (three) axial intercepts for a plane, cleared of fractions & common multiples. All parallel planes have same Miller indices.

• Algorithm
  1. Read off intercepts of plane with axes in terms of $a$, $b$, $c$
  2. Take reciprocals of intercepts
  3. Reduce to smallest integer values
  4. Enclose in parentheses, no commas i.e., $(hkl)$
## Crystallographic Planes

### Example

1. **Intercepts**
   
<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>∞</td>
</tr>
</tbody>
</table>

2. **Reciprocals**
   
<table>
<thead>
<tr>
<th></th>
<th>1/1</th>
<th>1/1</th>
<th>1/∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

3. **Reduction**
   
   |   | 1   | 1   | 0   |

4. **Miller Indices**
   
   (110)

### Example

1. **Intercepts**
   
<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2</td>
<td>∞</td>
<td>∞</td>
</tr>
</tbody>
</table>

2. **Reciprocals**
   
<table>
<thead>
<tr>
<th></th>
<th>1/½</th>
<th>1/∞</th>
<th>1/∞</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3. **Reduction**
   
   |   | 2   | 0   | 0   |

4. **Miller Indices**
   
   (100)
Crystallographic Planes

example
1. Intercepts \( \frac{1}{2} \ 1 \ 3/4 \)
2. Reciprocals \( \frac{1}{\frac{1}{2}} \ 1/1 \ 1/\frac{3}{4} \)
3. Reduction \( 6 \ 3 \ 4 \)
4. Miller Indices \( (634) \)

Family of Planes \( \{hkl\} \)

Ex: \( \{100\} = (100), (010), (001), (\bar{1}00), (0\bar{1}0), (00\bar{1}) \)
Crystallographic Planes (HCP)

- In hexagonal unit cells the same idea is used

<table>
<thead>
<tr>
<th>Example</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Intercepts</td>
<td>1</td>
<td>$\infty$</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>2. Reciprocals</td>
<td>1</td>
<td>$1/\infty$</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3. Reduction</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4. Miller-Bravais Indices</td>
<td>(1011)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Adapted from Fig. 3.8, Callister & Rethwisch 9e.
Crystallographic Planes

• We want to examine the atomic packing of crystallographic planes
• Iron foil can be used as a catalyst. The atomic packing of the exposed planes is important.
  a) Draw (100) and (111) crystallographic planes for Fe.
  b) Calculate the planar density for each of these planes.
Summary

• Atoms may assemble into crystalline or amorphous structures.

• Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

• Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
Chapter 4: The Structure of Crystalline Solids

ISSUES TO ADDRESS...

• What are common crystal structures for metals and ceramics?

• What features of a metal’s/ceramic’s atomic structure determine its density?

• How do the crystal structures of ceramic materials differ from those for metals?
Metallic Crystal Structures

- Metals are usually (poly)crystalline; although formation of amorphous metals is possible by rapid cooling.

- As we learned in Chapter 2, the atomic bonding in metals is non-directional $\Rightarrow$ no restriction on numbers or positions of nearest-neighbor atoms $\Rightarrow$ large number of nearest neighbors and dense atomic packing.

- **Atom (hard sphere) radius, $R$,** defined by ion core radius - typically 0.1 - 0.2 nm.

- The most common types of unit cells are the face-centered cubic (FCC), the body-centered cubic (FCC) and the hexagonal close-packed (HCP).
Metallic Crystal Structures

• How can we stack metal atoms to minimize empty space?

2-dimensions

Now stack these 2-D layers to make 3-D structures
Metallic Crystal Structures

• Tend to be densely packed.

• Reasons for dense packing:
  - Typically, only one element is present, so all atomic radii are the same.
  - Metallic bonding is not directional.
  - Nearest neighbor distances tend to be small in order to lower bond energy.
  - Electron cloud shields cores from each other.

• Metals have the simplest crystal structures.

  We will examine three such structures...
Simple Cubic Structure (SC)

- Rare due to low packing density (only Po has this structure)
- Close-packed directions are cube edges.

- **Coordination # = 6**
  (# nearest neighbors)

Fig. 4.2, *Callister & Rethwisch 9e.*
Atomic Packing Factor (APF)

\[
\text{APF} = \frac{\text{Volume of atoms in unit cell} \ast}{\text{Volume of unit cell}}
\]

*assume hard spheres

- APF for a simple cubic structure = 0.52

Adapted from Fig. 4.2 (a), Callister & Rethwisch 9e.
Body Centered Cubic Structure (BCC)

• Atoms touch each other along cube diagonals.
  --Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

ex: Cr, W, Fe ($\alpha$), Tantalum, Molybdenum

• Coordination # = 8

2 atoms/unit cell: 1 center + 8 corners x 1/8

Adapted from Fig. 4.1, Callister & Rethwisch 9e.
Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68

Adapted from Fig. 4.1(a), Callister & Rethwisch 9e.

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

Close-packed directions:
length = \(4R = \sqrt{3}a\)
Face Centered Cubic Structure (FCC)

- Atoms touch each other along face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- Coordination # = 12

4 atoms/unit cell: 6 face x 1/2 + 8 corners x 1/8

Adapted from Fig. 3.1, Callister & Rethwisch 9e.
Atomic Packing Factor: FCC

• APF for a face-centered cubic structure = 0.74
  maximum achievable APF

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

Unit cell contains:
  \(6 \times \frac{1}{2} + 8 \times \frac{1}{8}\) = 4 atoms/unit cell

\[
\text{APF} = \frac{4}{3} \pi \left(\frac{\sqrt{2}a}{4}\right)^3
\]

Adapted from Fig. 3.1(a), Callister & Rethwisch 9e.
FCC Stacking Sequence

- ABCABC... Stacking Sequence
- 2D Projection
- FCC Unit Cell
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection
- 2D Projection

- Coordination # = 12
- APF = 0.74
- $c/a = 1.633$

- Adapted from Fig. 4.3(a), Callister & Rethwisch 9e.

6 atoms/unit cell
ex: Cd, Mg, Ti, Zn
Theoretical Density, $\rho$

Density = $\rho$ = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}

$$\rho = \frac{n A}{V_C N_A}$$

where

- $n$ = number of atoms/unit cell
- $A$ = atomic weight
- $V_C$ = Volume of unit cell = $a^3$ for cubic
- $N_A$ = Avogadro’s number
  - $= 6.022 \times 10^{23}$ atoms/mol
Theoretical Density, $\rho$

- Ex: Cr (BCC)

\[ A = 52.00 \text{ g/mol} \]

\[ R = 0.125 \text{ nm} \]

\[ n = 2 \text{ atoms/unit cell} \]

\[ a = 4R/\sqrt{3} = 0.2887 \text{ nm} \]

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

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

Adapted from Fig. 4.1(a), Callister & Rethwisch 9e.
Linear Density

- Linear Density of Atoms \( \equiv LD = \frac{\text{Number of atoms}}{\text{Unit length of direction vector}} \)

ex: linear density of Al in [110] direction

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

\[ LD = \frac{2}{\sqrt{2}a} = 3.5 \text{ nm}^{-1} \]

Adapted from Fig. 3.1(a), Callister & Rethwisch 9e.
Planar Density of (100) Iron

Solution: At $T < 912^\circ C$ iron has the BCC structure.

Radius of iron $R = 0.1241 \text{ nm}$

$\text{Planar Density} = \frac{1}{a^2} = \frac{1}{\left(\frac{4\sqrt{3}}{3} R\right)^2} = 12.1 \frac{\text{atoms}}{\text{nm}^2} = 1.2 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}$

Planar Density of (111) Iron

Solution (cont): (111) plane

1 atom in plane/ unit surface cell

\[
\text{Planar Density} = \frac{1 \text{ atom in plane}}{\text{area}} \times \frac{\text{area}}{2D \text{ repeat unit}} = \frac{16\sqrt{3}}{3} \frac{\text{atoms}}{\text{nm}^2} = 7.0 \frac{\text{atoms}}{\text{nm}^2} = 0.70 \times 10^{19} \frac{\text{atoms}}{\text{m}^2}
\]

\[
\text{area} = \sqrt{2} ah = \sqrt{3} a^2 = \sqrt{3} \left(\frac{4\sqrt{3}}{3} R\right)^2 = \frac{16\sqrt{3}}{3} R^2
\]

\[
h = \sqrt{2} a
\]

\(\text{atoms in plane}\)
\(\text{atoms above plane}\)
\(\text{atoms below plane}\)

2D repeat unit
Summary

• Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.

• We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).

• Interatomic bonding in ceramics is ionic and/or covalent.

• Ceramic crystal structures are based on:
  -- maintaining charge neutrality
  -- cation-anion radii ratios.

• Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).

• X-ray diffraction is used for crystal structure and interplanar spacing determinations.