ISSUES TO ADDRESS...

• How do atoms assemble into solid structures? (for now, focus on metals)

• How does the density of a material depend on its structure?

• When do material properties vary with the sample (i.e., part) orientation?
Crystal Structure

• **Motivation**: Many of the properties of materials (especially mechanical) are determined by the arrangement of the atoms. This arrangement is called the material’s **crystal structure**.

• An important distinction…
  – **Atomic structure** relates to the number of protons and neutrons in the nucleus of an atom, as well as the number and probability distributions of the electrons.
  – **Crystal structure** pertains to the arrangement of atoms in the crystalline solid material.
• Atoms can be arranged either in a regular, periodic array (i.e., long-range order) or completely disordered (amorphous).

• We need a way to specify crystallographic directions and planes.

To illustrate the concept of crystal structure and lattice systems, we first identify a coordinate system \((x, y, z)\):

We can’t specify directions or planes without knowing what the reference system is.
What is the Unit Cell?

• The **unit cell** is the smallest group of atoms which can generate the entire crystal by translation.

**Definition:** the length of each unit cell axis is called a **lattice parameter**.

– In cubic systems, all three orthogonal lattice parameters are equal

• Lattice parameters are typically on the order of a few **Angstroms** (or a few tenths of a nanometer)
ENERGY AND PACKING

• Non dense, random packing

• Dense, regular packing

Dense, regular-packed structures tend to have lower energy.
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. 3.18(a), Callister 6e.

Adapted from Fig. 3.18(b), Callister 6e.
METALLIC CRYSTALS

• tend to be densely packed.
• have several 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.
• have the simplest crystal structures.

We will look at three such structures...
SIMPLE CUBIC STRUCTURE (SC)

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

In terms of the hard sphere model, we say the atoms are touching in the close-packed directions!

(Courtesy P.M. Anderson)
ATOMIC PACKING FACTOR

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

*assume hard spheres

• APF for a simple cubic structure = 0.52

Adapted from Fig. 3.19, Callister 6e.
BODY CENTERED CUBIC STRUCTURE (BCC)

• Close packed directions are cube diagonals.

--Note: All atoms are identical; the center atom is shaded differently only for ease of viewing.

(Courtesy P.M. Anderson)
ATOMIC PACKING FACTOR: BCC

• APF for a body-centered cubic structure = 0.68

Close-packed directions:
length = 4R
= $\sqrt{3} \ a$

Unit cell contains:
$1 + 8 \times 1/8$
= 2 atoms/unit cell

Adapted from Fig. 3.2, Callister 6e.

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

2 $\frac{4}{3} \pi \left(\frac{\sqrt{3}a}{4}\right)^3$

Unit cell volume
Atom volume

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FACE CENTERED CUBIC STRUCTURE (FCC)

• Close packed directions are face diagonals.
  --Note: All atoms are identical; the face-centered atoms are shaded differently only for ease of viewing.

• Coordination # = 12

(Courtesy P.M. Anderson)

Adapted from Fig. 3.1(a), *Callister 6e.*
ATOMIC PACKING FACTOR: FCC

• APF for a body-centered cubic structure = 0.74

Adapted from Fig. 3.1(a), Callister 6e.
FCC STACKING SEQUENCE

• ABCABC… Stacking Sequence
• 2D Projection

A sites
B sites
C sites

• FCC Unit Cell

close-packed plane of atoms
HEXAGONAL CLOSE-PACKED STRUCTURE (HCP)

- ABAB... Stacking Sequence
- 3D Projection
- 2D Projection
- Coordination # = 12
- APF = 0.74

Adapted from Fig. 3.3, Callister 6e.
THEORETICAL DENSITY, $\rho$

$\rho = \frac{nA}{V_c N_A}$

- # atoms/unit cell
- Atomic weight (g/mol)
- Volume/unit cell (cm$^3$/unit cell)
- Avogadro's number (6.023 x 10$^{23}$ atoms/mol)

Example: Copper

Data from Table inside front cover of Callister (see next slide):

- 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)

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

Result: theoretical $\rho_{Cu} = 8.89$ g/cm$^3$

Compare to actual: $\rho_{Cu} = 8.94$ g/cm$^3$
## Characteristics of Selected Elements at 20°C

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>At. Weight (amu)</th>
<th>Density (g/cm³)</th>
<th>Crystal Structure</th>
<th>Atomic radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>26.98</td>
<td>2.71</td>
<td>FCC</td>
<td>0.143</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>39.95</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>137.33</td>
<td>3.5</td>
<td>BCC</td>
<td>0.217</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>9.012</td>
<td>1.85</td>
<td>HCP</td>
<td>0.114</td>
</tr>
<tr>
<td>Boron</td>
<td>B</td>
<td>10.81</td>
<td>2.34</td>
<td>Rhomb</td>
<td>------</td>
</tr>
<tr>
<td>Bromine</td>
<td>Br</td>
<td>79.90</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>112.41</td>
<td>8.65</td>
<td>HCP</td>
<td>0.149</td>
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<tr>
<td>Calcium</td>
<td>Ca</td>
<td>40.08</td>
<td>1.55</td>
<td>FCC</td>
<td>0.197</td>
</tr>
<tr>
<td>Carbon</td>
<td>C</td>
<td>12.011</td>
<td>2.25</td>
<td>Hex</td>
<td>0.071</td>
</tr>
<tr>
<td>Cesium</td>
<td>Cs</td>
<td>132.91</td>
<td>1.87</td>
<td>BCC</td>
<td>0.265</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl</td>
<td>35.45</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>52.00</td>
<td>7.19</td>
<td>BCC</td>
<td>0.125</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>58.93</td>
<td>8.9</td>
<td>HCP</td>
<td>0.125</td>
</tr>
<tr>
<td><strong>Copper</strong></td>
<td>Cu</td>
<td><strong>63.55</strong></td>
<td><strong>8.94</strong></td>
<td><strong>FCC</strong></td>
<td><strong>0.128</strong></td>
</tr>
<tr>
<td>Flourine</td>
<td>F</td>
<td>19.00</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga</td>
<td>69.72</td>
<td>5.90</td>
<td>Ortho.</td>
<td>0.122</td>
</tr>
<tr>
<td>Germanium</td>
<td>Ge</td>
<td>72.59</td>
<td>5.32</td>
<td>Dia. cubic</td>
<td>0.122</td>
</tr>
<tr>
<td>Gold</td>
<td>Au</td>
<td>196.97</td>
<td>19.32</td>
<td>FCC</td>
<td>0.144</td>
</tr>
<tr>
<td>Helium</td>
<td>He</td>
<td>4.003</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H</td>
<td>1.008</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
</tbody>
</table>

Adapted from Table, "Characteristics of Selected Elements", inside front cover, *Callister 6e.*
Polymorphism and allotropy

Carbon is a good example of allotropy, it has 3 crystal structures with very different properties.
### Table 1.4 Crystalline allotropes of carbon. (\( \rho \) is the density and \( Y \) is the elastic modulus or Young’s modulus)

<table>
<thead>
<tr>
<th></th>
<th>Graphite</th>
<th>Diamond</th>
<th>Buckminsterfullerene Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Structure</strong></td>
<td>Covalent bonding within layers.</td>
<td>Covalently bonded network.</td>
<td>Covalently bonded ( C_{60} ) spheroidal molecules held in an FCC crystal structure by van der Waals bonding.</td>
</tr>
<tr>
<td></td>
<td>Van der Waals bonding between layers. Hexagonal unit cell.</td>
<td>Diamond crystal structure.</td>
<td></td>
</tr>
<tr>
<td><strong>Electrical and thermal properties</strong></td>
<td>Good electrical conductor. Thermal conductivity comparable to metals, five times more than silver or copper.</td>
<td>Very good electrical insulator. Excellent thermal conductor, about</td>
<td>Semiconductor. Compounds with alkali metals (e.g., ( K_3C_{60} )) exhibit superconductivity.</td>
</tr>
<tr>
<td><strong>Mechanical properties</strong></td>
<td>Lubricating agent. Machinable. Bulk graphite: ( Y \approx 27 \text{ GPa} ) ( \rho = 2.25 \text{ g cm}^{-3} )</td>
<td>The hardest material. ( Y = 827 \text{ GPa} ) ( \rho = 3.25 \text{ g cm}^{-3} )</td>
<td>Mechanically soft. ( Y \approx 18 \text{ GPa} ) ( \rho = 1.65 \text{ g cm}^{-3} )</td>
</tr>
<tr>
<td><strong>Comment</strong></td>
<td>Stable allotrope at atmospheric pressure</td>
<td>High-pressure allotrope.</td>
<td>Laboratory synthesized. Occurs in the soot of partial combustion.</td>
</tr>
<tr>
<td><strong>Uses, potential uses</strong></td>
<td>Metallurgical crucibles; welding electrodes, heating elements, electrical contacts, refractory applications.</td>
<td>Cutting tool applications. Diamond anvil. Diamond film coated drills, blades, bearings, etc. Jewelry. Heat conductor for ICs. Possible thin-film semiconductor devices, as the charge carrier mobilities are large.</td>
<td>Possible future semiconductor or superconductivity applications.</td>
</tr>
</tbody>
</table>


**MECH 221**

**PM Wood-Adams**

**Fall 2008**
DENSITIES OF MATERIAL CLASSES

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

Why?

**Metals** have...
- close-packing (metallic bonding)
- large atomic mass

**Ceramics** have...
- less dense packing (covalent bonding)
- often lighter elements

**Polymers** have...
- poor packing (often amorphous)
- lighter elements (C,H,O)

**Composites** have...
- intermediate values

Based on data in Table B1, Callister 6e.

*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).
Some engineering applications require single crystals:

- diamond single crystals for abrasives
- turbine blades

Crystal properties reveal features of atomic structure.

- Ex: Certain crystal planes in quartz fracture more easily than others.

(Courtesy P.M. Anderson)
Fluorite is a ceramic with a unit cell made up of 8 cubes.
POLYCRYSTALS

- Most engineering materials are polycrystals.

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If crystals are randomly oriented, overall component properties are not directional.
- Crystal sizes typically range from 1 nm to 2 cm (i.e., from a few to millions of atomic layers).

Adapted from Fig. K, color inset pages of Callister 6e. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)
Solidification of a polycrystalline material

(α)

(β)

(γ)

(δ)
**SINGLE VS POLYCRYSTALS**

- **Single Crystals**
  - Properties vary with direction: **anisotropic**.
  - Example: the modulus of elasticity (E) in BCC iron:
    - $E$ (diagonal) = 273 GPa
    - $E$ (edge) = 125 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. 4.12(b), *Callister 6e*. Fig. 4.12(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].)
X-RAYS TO CONFIRM CRYSTAL STRUCTURE

- Incoming X-rays **diffract** from crystal planes.

- Measurement of:
  - Critical angles, $\theta_c$
  - for X-rays provide atomic spacing, $d$.

Read more about this subject in the textbook. Learn how to use Bragg’s Law.
SCANNING TUNNELING MICROSCOPY

- Atoms can be arranged and imaged!

Carbon monoxide molecules arranged on a platinum (111) surface.

Iron atoms arranged on a copper (111) surface. These Kanji characters represent the word “atom”.

Photos produced from the work of C.P. Lutz, Zeppenfeld, and D.M. Eigler. Reprinted with permission from International Business Machines Corporation, copyright 1995.
DEMO: HEATING AND COOLING OF AN IRON WIRE

- Demonstrates "polymorphism" The same atoms can have more than one crystal structure.

<table>
<thead>
<tr>
<th>Temperature, C</th>
<th>BCC Stable</th>
<th>FCC Stable</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1536</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1391</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>914</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T_c 768</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The magnet falls off when cooled through the transition temperature.
SUMMARY

• Atoms may assemble into crystalline or amorphous 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).

• Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but properties are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.