BONDING AND PROPERTIES

ISSUES TO ADDRESS...

• What promotes bonding?

• What types of bonds are there?

• What properties are inferred from bonding?
Atomic Structure (Freshman Chem.)

- **atom** – electrons – $9.11 \times 10^{-31}$ kg
  - protons
  - neutrons
  \[
  \{ \text{protons, neutrons} \} \quad 1.67 \times 10^{-27} \text{ kg}
  \]

- atomic number = # of protons in nucleus of atom
  = # of electrons of neutral species

- A [=] **atomic mass unit** = amu = $1/12$ mass of $^{12}$C

  **Atomic wt** = wt of $6.023 \times 10^{23}$ molecules or atoms

  $1 \text{ amu/atom} = 1\text{g/mol}$

  C  12.011
  H  1.008 etc.
Atomic Structure

- Valence electrons determine all of the following properties:
  1. Chemical
  2. Electrical
  3. Thermal
  4. Optical
Electron Configurations

- **Valence electrons** – those in unfilled shells
- Filled shells more stable
- Valence electrons are most available for bonding and tend to control the chemical properties

- example: C (atomic number = 6)

\[ \begin{align*}
1s^2 & \quad 2s^2 2p^2 \\
\end{align*} \]

valence electrons
The Periodic Table

- Columns: Similar Valence Structure

Electropositive elements: Readily give up electrons to become + ions.

Electronegative elements: Readily acquire electrons to become - ions.

Adapted from Fig. 2.6, *Callister 7e.*
Ionic bond – metal + nonmetal

\[ \text{donates} \quad \text{accepts} \]

donates electrons accepts electrons

Dissimilar electronegativities

ex: MgO  
Mg \( 1s^2 2s^2 2p^6 3s^2 \)  
O \( 1s^2 2s^2 2p^4 \)

\[ \text{[Ne] } 3s^2 \quad \text{[Ne]} \]

\( \text{Mg}^{2+} \quad 1s^2 2s^2 2p^6 \)  
\( \text{O}^{2-} \quad 1s^2 2s^2 2p^6 \)  
\[ \text{[Ne]} \quad \text{[Ne]} \]
**Ionic Bonding**

- Occurs between + and - ions.
- Requires *electron transfer*.
- Large difference in electronegativity required.
- Example: NaCl

**Diagram:**

- Na (metal) unstable → Na (cation) stable
- Cl (nonmetal) unstable → Cl (anion) stable
- Electron transfers from Na to Cl
- Coulombic attraction

**Chemical Representation:**

- Na (metal)
- Cl (nonmetal)
- Na (cation)
- Cl (anion)
Ionic Bonding

- Energy – minimum energy most stable
  - Energy balance of attractive and repulsive terms

\[ E_N = E_A + E_R = -\frac{A}{r} - \frac{B}{r^n} \]

Adapted from Fig. 2.8(b), Callister 7e.
Examples: Ionic Bonding

- Predominant bonding in **Ceramics**

![Ionic Bonding Diagram]

Adapted from Fig. 2.7, *Callister 7e*. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.)
Covalent Bonding

- similar electronegativity $\therefore$ share electrons
- bonds determined by valence – $s$ & $p$ orbitals dominate bonding
- Example: CH$_4$

C: has 4 valence e\textsuperscript{\textminus}, needs 4 more
H: has 1 valence e\textsuperscript{\textminus}, needs 1 more

Electronegativities are comparable.

Adapted from Fig. 2.10, Callister 7e.
Metallic Bonding

- Occurs between Metallic elements
- Ion Cores (+) surrounded by delocalized electrons (-)
- High electrical and thermal conductivity from “free electrons”
Primary Bonding

- **Metallic Bond** -- delocalized as electron cloud

- **Ionic-Covalent Mixed Bonding**

  \[
  \text{% ionic character} = \left(1 - e^{-\frac{(X_A - X_B)^2}{4}}\right) \times (100\%)
  \]

  where $X_A$ & $X_B$ are Pauling electronegativities

  Ex: MgO

  \[
  X_{\text{Mg}} = 1.3 \\
  X_{\text{O}} = 3.5
  \]

  \[
  \text{% ionic character} = \left(1 - e^{-\frac{(3.5 - 1.3)^2}{4}}\right) \times (100\%) = 70.2\% \text{ ionic}
  \]
SECONDARY BONDING

Arises from interaction between dipoles

- Fluctuating dipoles
  - asymmetric electron clouds

- Permanent dipoles - molecule induced
  - general case:
  - ex: liquid HCl
  - ex: polymer

Adapted from Fig. 2.13, Callister 7e.

Adapted from Fig. 2.14, Callister 7e.
## Summary: Bonding

<table>
<thead>
<tr>
<th>Type</th>
<th>Bond Energy</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>Large!</td>
<td>Nondirectional <em>(ceramics)</em></td>
</tr>
<tr>
<td>Covalent</td>
<td>Variable</td>
<td>Directional <em>(semiconductors, ceramics, polymer chains)</em></td>
</tr>
<tr>
<td></td>
<td>large-Diamond</td>
<td></td>
</tr>
<tr>
<td></td>
<td>small-Bismuth</td>
<td></td>
</tr>
<tr>
<td>Metallic</td>
<td>Variable</td>
<td>Nondirectional <em>(metals)</em></td>
</tr>
<tr>
<td></td>
<td>large-Tungsten</td>
<td></td>
</tr>
<tr>
<td></td>
<td>small-Mercury</td>
<td></td>
</tr>
<tr>
<td>Secondary</td>
<td>smallest</td>
<td>Directional <em>(polymer)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>inter-chain <em>(polymer)</em></td>
</tr>
<tr>
<td></td>
<td></td>
<td>inter-molecular</td>
</tr>
</tbody>
</table>
Properties From Bonding: $T_m$

- Bond length, $r$

- Bond energy, $E_o$

- Melting Temperature, $T_m$

$T_m$ is larger if $E_o$ is larger.

$E_o = \text{"bond energy"}$

$r_o$ is the unstretched length.
Properties From Bonding: $\alpha$

- Coefficient of thermal expansion, $\alpha$

\[
\begin{align*}
\frac{\Delta L}{L_0} &= \alpha (T_2 - T_1) \\
\Delta L &= L_0 (T_2 - T_1)
\end{align*}
\]

- $\alpha \sim$ symmetry at $r_o$

$\alpha$ is larger if $E_o$ is smaller.
Summary: Primary Bonds

Ceramics
(Ionic & covalent bonding):

Large bond energy
large $T_m$
large $E$
small $\alpha$

Metals
(Metallic bonding):

Variable bond energy
moderate $T_m$
moderate $E$
moderate $\alpha$

Polymers
(Covalent & Secondary):

Directional Properties
Secondary bonding dominates
small $T_m$
small $E$
large $\alpha$
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?
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

---

**crystalline SiO$_2$**
Adapted from Fig. 3.22(a), Callister 7e.

**noncrystalline SiO$_2$**
Adapted from Fig. 3.22(b), Callister 7e.
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

Fig. 3.4, *Callister 7e.*
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

• 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)

(Courtesy P.M. Anderson)
Atomic Packing Factor (APF)

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

*assume hard spheres

• APF for a simple cubic structure = 0.52

Adapted from Fig. 3.23, Callister 7e.
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 (α), Tantalum, Molybdenum

- Coordination # = 8

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

(Courtesy P.M. Anderson)
Atomic Packing Factor: BCC

- APF for a body-centered cubic structure = 0.68

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

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

Adapted from Fig. 3.2(a), Callister 7e.
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

(Courtesy P.M. Anderson)
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

Adapted from Fig. 3.1(a), Callister 7e.
Hexagonal Close-Packed Structure (HCP)

- ABAB... Stacking Sequence
- 3D Projection
- Coordination # = 12
- APF = 0.74
- \( \frac{c}{a} = 1.633 \)
- 6 atoms/unit cell
  - ex: Cd, Mg, Ti, Zn

Adapted from Fig. 3.3(a), Callister 7e.
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

$n = \text{number of atoms/unit cell}$

$A = \text{atomic weight}$

$V_C = \text{Volume of unit cell} = a^3$ for cubic

$N_A = \text{Avogadro’s number}$

$= 6.023 \times 10^{23}$ atoms/mol
Theoretical Density, $\rho$

- Ex: Cr (BCC)
  - $A = 52.00 \text{ g/mol}$
  - $R = 0.125 \text{ nm}$
  - $n = 2$

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

$$\rho_{\text{theoretical}} = \frac{2 \times 52.00 \text{ g/mol}}{6.023 \times 10^{23} \text{ atoms/mol}}$$

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

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

Based on data in Table B1, Callister
*GFRE, CFRE, & AFRE are Glass, Carbon, & Aramid Fiber-Reinforced Epoxy composites (values based on 60% volume fraction of aligned fibers in an epoxy matrix).*

Data from Table B1, Callister 7e.
Crystals as Building Blocks

- Some engineering applications require single crystals:
  - diamond single crystals for abrasives
  - turbine blades

- Properties of crystalline materials often related to crystal structure.
  - Ex: Quartz fractures more easily along some crystal planes than others.

(Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.)

Fig. 8.33(c), Callister 7e.
(Fig. 8.33(c) courtesy of Pratt and Whitney).

(Courtesy P.M. Anderson)
Polycrystals

- Most engineering materials are polycrystals.

- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If grains are randomly oriented, overall component properties are not directional.
- Grain 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 5e*. (Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)
**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.

---

Data from Table 3.3, *Callister 7e*.  

Adapted from Fig. 4.14(b), *Callister 7e*.  
(Fig. 4.14(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].)
Polymorphism

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

  - Titanium
  - Carbon: $\alpha$, $\beta$-Ti
  - 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>

- $\delta$-Fe
- $\gamma$-Fe
- $\alpha$-Fe
Point Coordinates

Point coordinates for unit cell center are

\( a/2, b/2, c/2 \quad \frac{1}{2} \frac{1}{2} \frac{1}{2} \)

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. Vector repositioned (if necessary) to pass through origin.
2. Read off projections in terms of unit cell dimensions $a$, $b$, and $c$
3. Adjust to smallest integer values
4. Enclose in square brackets, no commas

$[uvw]$

ex: $1, 0, \frac{1}{2}$ => $2, 0, 1$ => $[201]$
-1, 1, 1 => $[\overline{111}]$ where overbar represents a negative index

families of directions $<uvw>$
Crystallographic Planes

Adapted from Fig. 3.9, Callister 7e.
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
   1
2. Reciprocals
   1/1 1/1 1/∞
   1
   1
   0
3. Reduction
   1
   1
   0
4. Miller Indices (110)

element

1. Intercepts
   1/2 ∞ ∞
2. Reciprocals
   1/1/2 1/∞ 1/∞
   2
   0
   0
3. Reduction
   2
   0
   0
4. Miller Indices (100)
Crystallographic Planes

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

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

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

• Atoms may assemble into crystalline or amorphous structures.

• 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).

• 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.
SUMMARY

• 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.

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