<u>BMEN E3010</u>
Biomedical Engineering I

Biomaterials:
Structure-Property Relationships

Prof. H.H. Lu

hhlu@columbia.edu

Department of Biomedical Engineering
Fu Foundation School of Engineering and Applied Science
Columbia University in the City of New York

Lecture - Structure-Function

- **Structure and Properties**
- **Bonding Energy in Solids**
  - Definitions
- **Interatomic Bonds (Primary vs. Secondary)**
  - Primary: Ionic, Covalent and Metallic bonding
  - Secondary bonding (van der Waals and hydrogen bonding)
- **Crystal structure**

Structure

- Arrangement of a material's internal components
- Relevant at several levels
  - Macrosopic (>1mm): Shape
    - visible to the eye
  - Microscopic (1µm-1mm): Grains
    - observable under microscope
  - Atomic (0.1-1nm): Unit Cells
    - organization of atoms or ions relative to one another
  - Subatomic (<0.1nm): Electron Structure
    - interaction of electrons with the nuclei

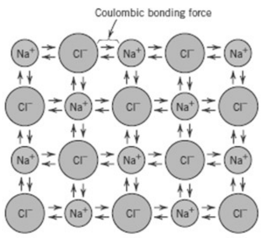
Physical Properties of Solids

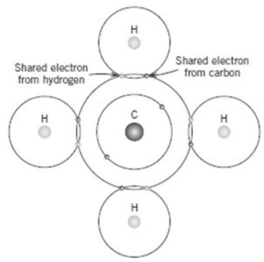
- Depends on type of atomic bond present
- Depends on bonding strength between atoms
- Depends on the resultant atomic structure
- Interaction between constituent ions
    - Bond length, angle, energy
    - Subatomic level
- Geometric arrangement of atoms or ion based on the bond parameters
    - Atomic level

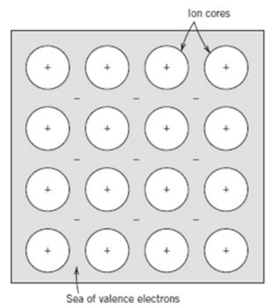
Primary Interatomic Bonds

- **Which bond is which?**

Ionic **Covalent** **Metallic**







- **Biomaterial: which bonds?**
  - **Polymer, Ceramic, Metal**

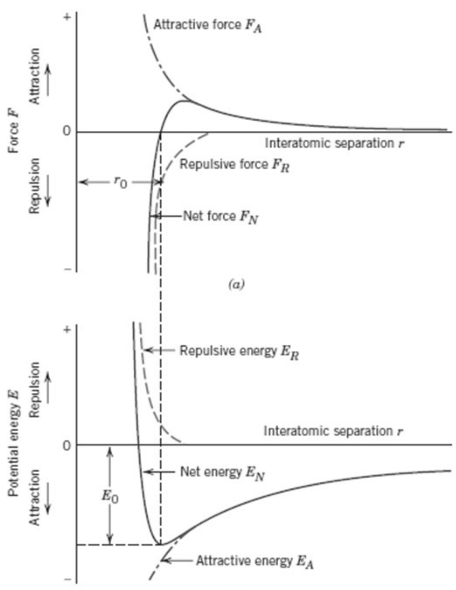


Figure 2.8 (*a*) The dependence of repulsive, attractive, and net forces on interatomic separation for two isolated atoms. (*b*) The dependence of repulsive, attractive, and net potential energies on interatomic separation for two isolated atoms.

$$F_A + F_R = 0$$

$$E = \int F\,dr$$

$$E_N = \int_\infty^r F_N\,dr = \int_\infty^r F_A\,dr + \int_\infty^r F_R\,dr = E_A + E_R$$

Interatomic Bonds

- Primary Bonds
  - Ionic (600-1500 kJ/mole)
  - Covalent (50-200 kJ/mole)
  - Metalic (68-850 kJ/mole)
- Secondary Bonds
  - Hydrogen (51 kJ/mole)
  - Van der Waal's forces (~20 kJ/mole)
- Type of primary bonds determines the manifested material properties
- Driving force for bond formation: *lower energy state*

Interatomic Bonding: Materials

- Metal – metallic bonding, non-directional
- Ceramic – ionic bonding, directional
- Polymer – covalent bonding, secondary bonding, directional

Structure-Property

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

Bonding Type	Substance	Bonding Energy kJ/mol	Bonding Energy eV/Atom, Ion, Molecule	Melting Temperature (°C)
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
Covalent	Si	450	4.7	1410
	C (diamond)	713	7.4	>3550
Metallic	Hg	68	0.7	−39
	Al	324	3.4	660
	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	−189
	Cl_2	31	0.32	−101
Hydrogen	NH_3	35	0.36	−78
	H_2O	51	0.52	0

Crystal Structure

- **3-D Organization of Atoms**
  - **Unit cell: atoms arranged in repeating units**
  - **Unit cells are repeated over a large distance to achieve long range order**
  - **Each atom is bond to its neighbor**
  - **Found commonly in metals, most ceramics and some polymers**
- **Crystalline vs. non-crystalline**
  - **Amorphous**
  - **some ceramics and most polymers**
  - ***e.g.* Glass**

Section 3.3 – Crystal Systems

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

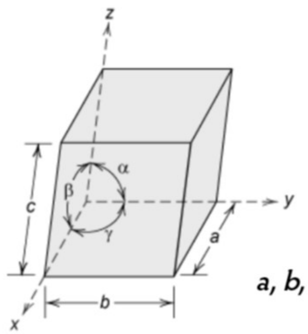


Fig. 3.4, *Callister 7e.*

7 crystal systems

14 crystal lattices

a, *b*, and *c* are the lattice constants

Unit Cells and Crystal Systems

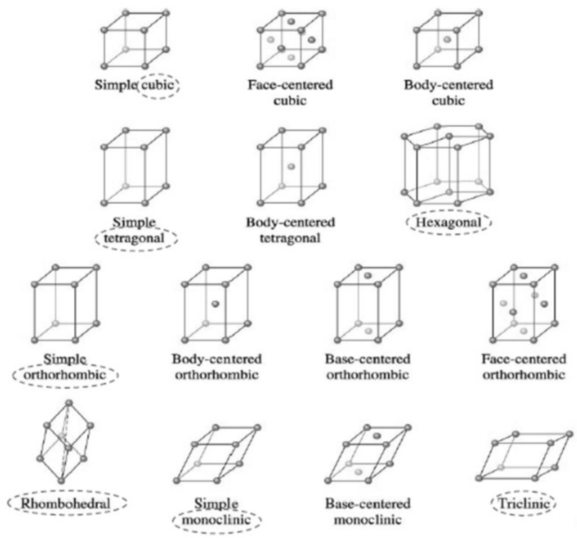
- **Components of Unit Cell**
  - **Axial length (a, b, c)**
    - **Represents distance between atoms**
  - **Interstitial angles (α, β, γ)**
    - α **is b/t b and c,** β **is b/t a and c,** γ **is b/t a and b**
  - **Direction of bonding**
  - **Atomic packing factor (APF)**

$$\mathrm{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}} = \frac{V_S}{V_C}$$

- **Atomic models**
  - **Assume that all atoms are spherical**
  - **Reduced sphere unit cell model**
  - **Atomic hard sphere unit cell model**

Fourteen Types of Bravais Lattices Grouped in Seven Crystal Systems

Bravais Lattices: describe the geometric arrangement of the lattice points



Chapter 1 - 41

Crystal Structure - Lattices

- **Seven (7) Crystal systems**
  - **Cubic, tetragonal, orthorhombic, triclinic, rhombohedral, hexagonal, monoclinic**
- **Fourteen (14) crystal lattices**
  - **Face centered cubic (FCC)**
  - **Body centered cubic (BCC)**
  - **Hexagonal close packed (HCP)**
- **For Biomaterials**
  - **Hexagonal – Titanium**
    - **$a=b \neq c$, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$**
  - **Cubic – Stainless steel, ceramics**
    - **$a=b=c$, $\alpha=\beta=\gamma=90^\circ$**
  - **Orthorhombic: ceramics and polymers (polyethylene)**
    - **$a \neq b \neq c$, $\alpha=\beta=\gamma=90^\circ$**

Crystal Structure: Metals

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.
[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

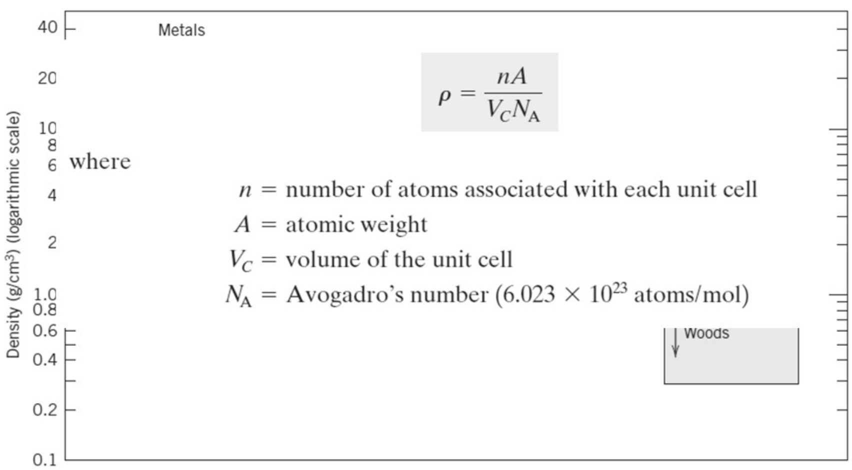
Material Properties

- **Bulk Properties**
  - **Mechanical**
  - **Electrical**
  - **Thermal**
  - **Chemical**
  - **Optical**
- **Surface Properties (< 1um)**
  - **Morphology (texture, roughness)**
  - **Charge and Chemical Composition**
  - **Surface tension/surface energy**

Property	**Response**	**Stimuli**
Mehanical (skin graft)	⟺	Force or Pressure
Electrical (pacemaker)	⟺	Electrical Field/Current flow
Chemical (hip implant)	⟺	Electrolyte containing environment/Saline
Optical (intraocular lens)	⟺	Light/electromagnetic stimuli/UV
Thermal (biosensors)	⟺	Temperature change (Fever)
Magnetic (Nanoparticles)	⟺	Magnetic field

Material Properties: Density

- **Theoretical Density**

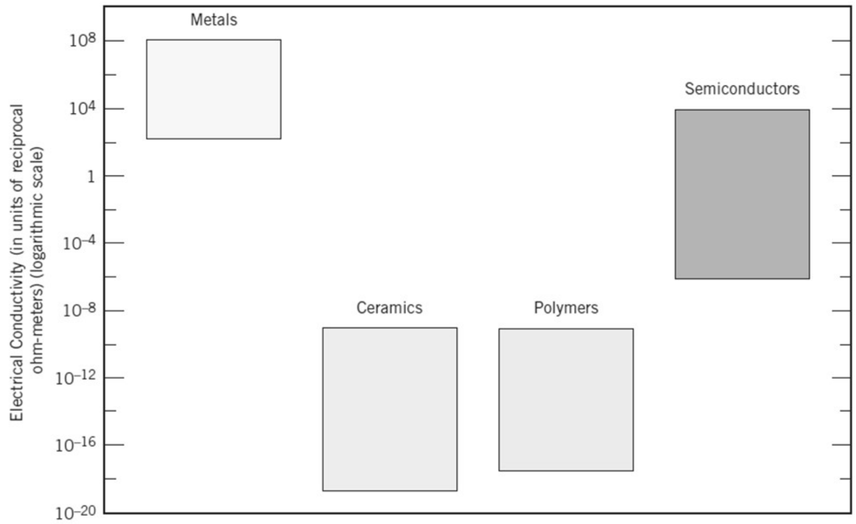


$$\rho = \frac{nA}{V_C N_A}$$

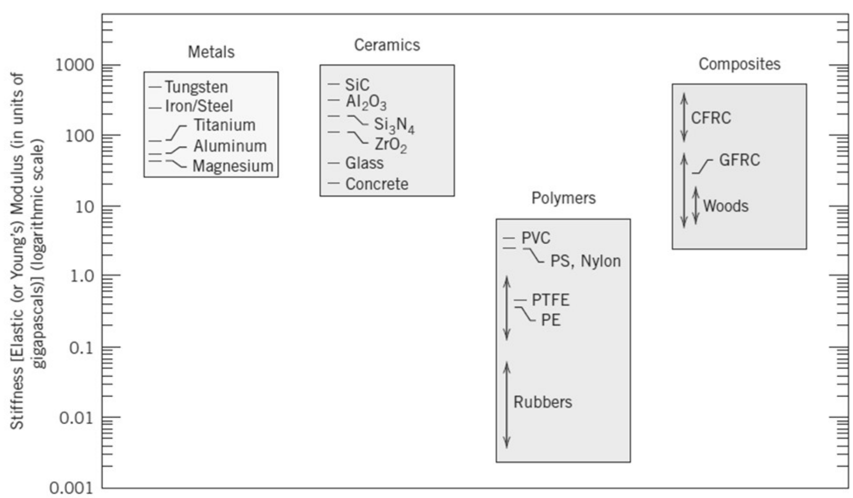
where

n = number of atoms associated with each unit cell
A = atomic weight
V_C = volume of the unit cell
N_A = Avogadro's number (6.023×10^{23} atoms/mol)

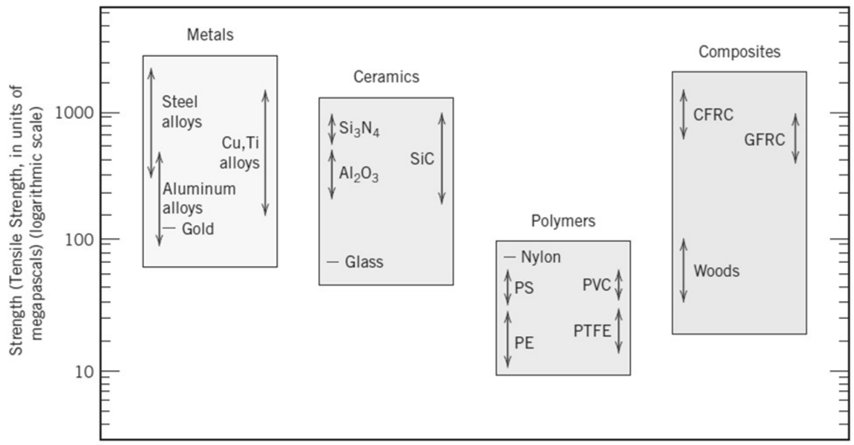
Electrical Conductivity



Mechanical Properties



Mechanical Properties



Mechanical Properties

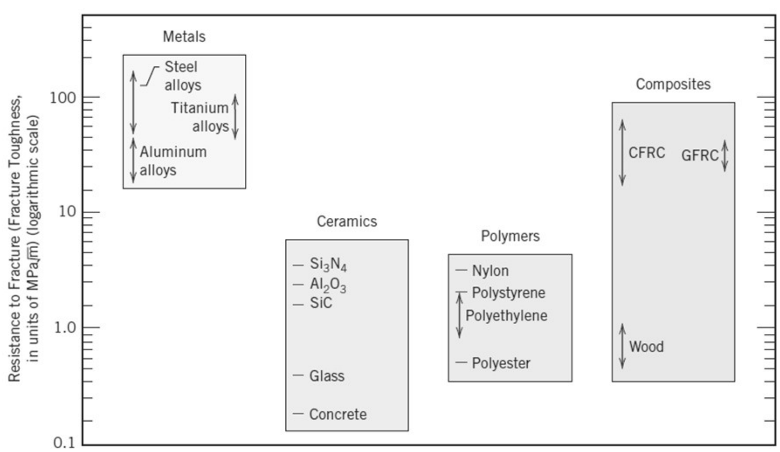


Figure 1.6 Bar-chart of room-temperature resistance to fracture (i.e., fracture toughness) for various metals, ceramics, polymers, and composite materials. (Reprinted from *Engineering Materials 1: An Introduction to Properties, Applications and Design,* third edition, M. F. Ashby and D. R. H. Jones, pages 177 and 178, Copyright 2005, with permission from Elsevier.)

Relevance to Biomaterials

- Bulk Properties
  - Mechanical properties
  - Electrical properties
  - Optical properties
- Surface Properties Controls
  - Protein adhesion and conformation
    - Race for the surface
    - Non-fouling surfaces
  - Cell-material interactions
    - Cell adhesion: surface textures
  - Electrolyte-material interactions
    - Corrosion

Property Considerations in Biomaterial Selection

- Mechanical Properties
  - Need to match that of native tissue
  - Porosity (%void volume)
    - Relevant for tissue ingrowth
    - Nutrient transport
    - vascularization
  - Compromise: porosity vs. mechanical properties
- Time-dependent changes in material properties
  - Modification by host environment
  - Reduction in intended function during service

The Materials Selection Process

1. Pick Application ⟶ Determine required Properties

   Properties: mechanical, electrical, thermal, magnetic, optical, deteriorative.

2. Properties ⟶ Identify candidate Material(s)

   Material: structure, composition.

3. Material ⟶ Identify required Processing

   Processing: changes *structure* and overall *shape*
   ex: casting, sintering, vapor deposition, doping forming, joining, annealing.