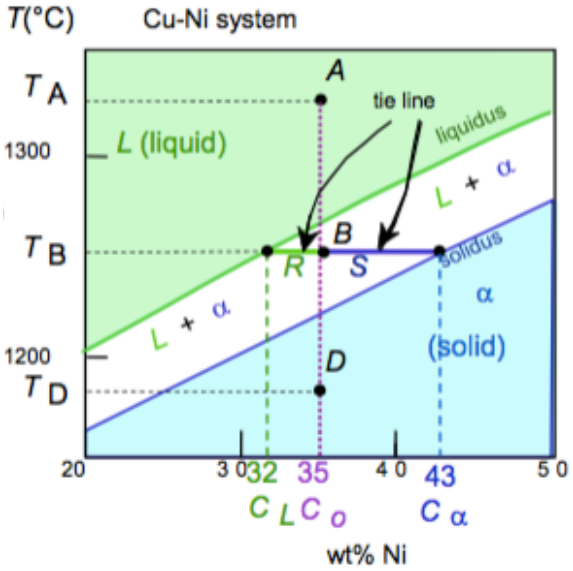
MECH 221 Final

Chapter 9
Phase Diagrams

- Phase diagrams give us information on:
  - Melting temperature
  - Casting
  - Composites and mixtures
- Many mechanical properties of materials are related to its microstructure
- Components:
  - The elements of compounds that are initially mixed
- Phases:
  - The physically and chemically distinct material regions that result
- Solubility limit:
  - Maximum amount of solute that can go into a solution
  - Maximum concentration for which only a single phase solution occurs
  - Both temperature and the initial concentration of the solution can change the number of phases present
- Equilibrium:
  - When a system is at equilibrium is is at the state of lowest free energy
  - Phase diagrams show us what phases are present at equilibrium or near-equilibrium conditions
- Alloys:
  - 2 metals – binary alloy
  - 3 metals – ternary alloy
  - 2 metals with similar crystal structures, size and valence usually provide good solubility
- Phase Diagrams:
  - If we know T and C_0, then we know the number and types of each phases present
  - If we know T and C_0, then we know the composition of each phase
  - If we know T and C_0, then we know the amount (wt %) of each phase
  - Use the level rule to calculate the amount of each phase present
  - Liquidus:
    - Line, above which only liquid is present

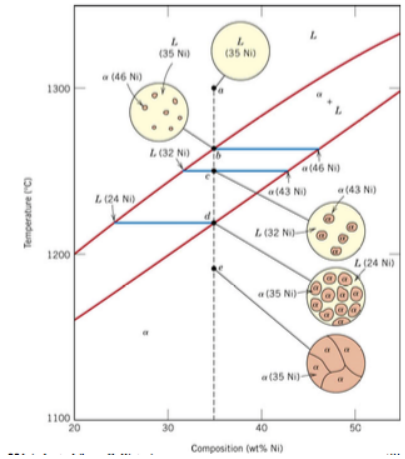
$$W_L = \frac{S}{R+S}$$

$$W_\alpha = \frac{R}{R+S}$$



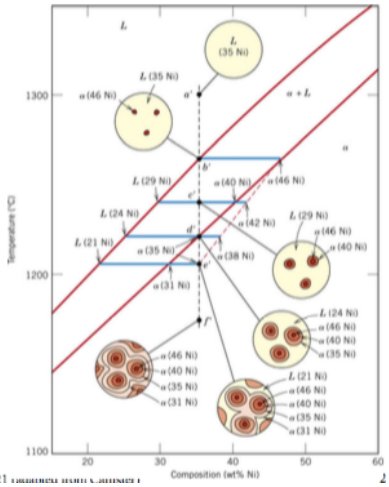
- Solidus:
  - Line, below which only solid is present
- Tie-line:
  - Horizontal line going across a phase region

- Mechanical Properties:
  - Alloying increases tensile strength and decreases ductility
- Cooling and Solidification of Alloys:
  - Solid State Diffusion:
    - When allowed to cool for a very long time diffusion can properly take place
  - Cored Microstructure Segregation:
    - If alloys are cooled too quickly, there is insufficient time and energy for complete diffusion

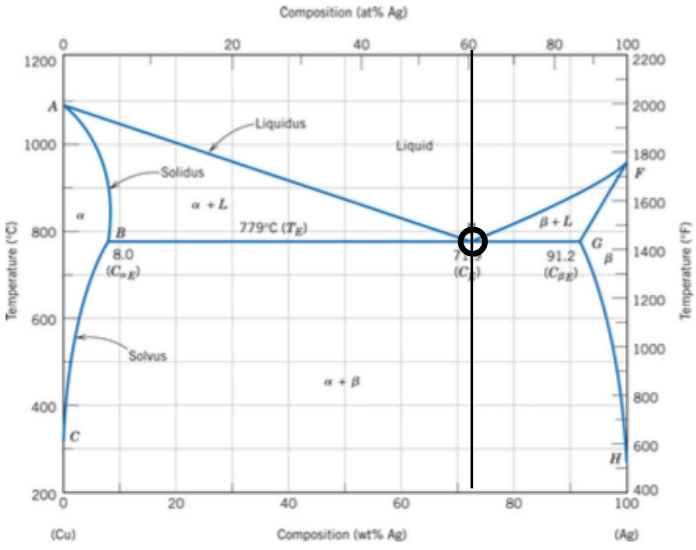


Equilibrium Cooling

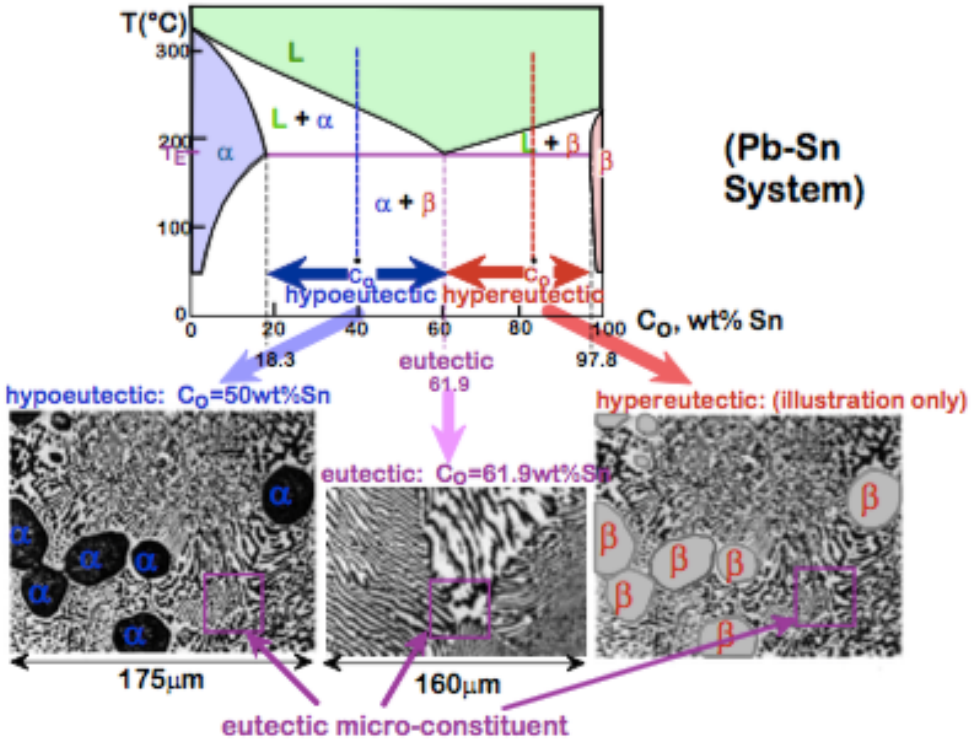
Non-Equilibrium Cooling



- Binary Alloy Systems:
  - Components have limited solid solubility
  - 3 single phase regions:
    - Liquid
    - α (solid 1)
    - β (solid 2)
  - 3 two-phase regions:
    - L + α
    - L + β
    - α + β
- Eutectic:
  - Important reaction occurs at eutectic composition as it cools through the eutectic temperature
  - $L \rightarrow \alpha + \beta$
  - $C_O = C_E$
    - Eutectic microstructure - alternating layers of α and β crystals



- Hypoeutectic and Hypereutectic:



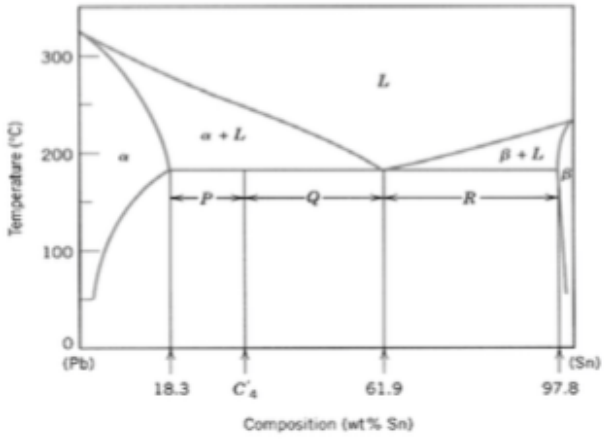
- Micro-constituents:
  - Eutectic is made up of two phases but a primary phase may also be present
  - In order to calculate amount of primary phase (micro-constituents) rather than total α, use Lever rule at eutectic temperature, as we have here:
    - Liquid + α' → α' + (α + β)

$$W_e = W_L = \frac{P}{P+Q}$$

$$W_{\alpha'} = \frac{Q}{P+Q}$$

$$W_{\alpha(Total)} = \frac{Q+R}{P+Q+R}$$

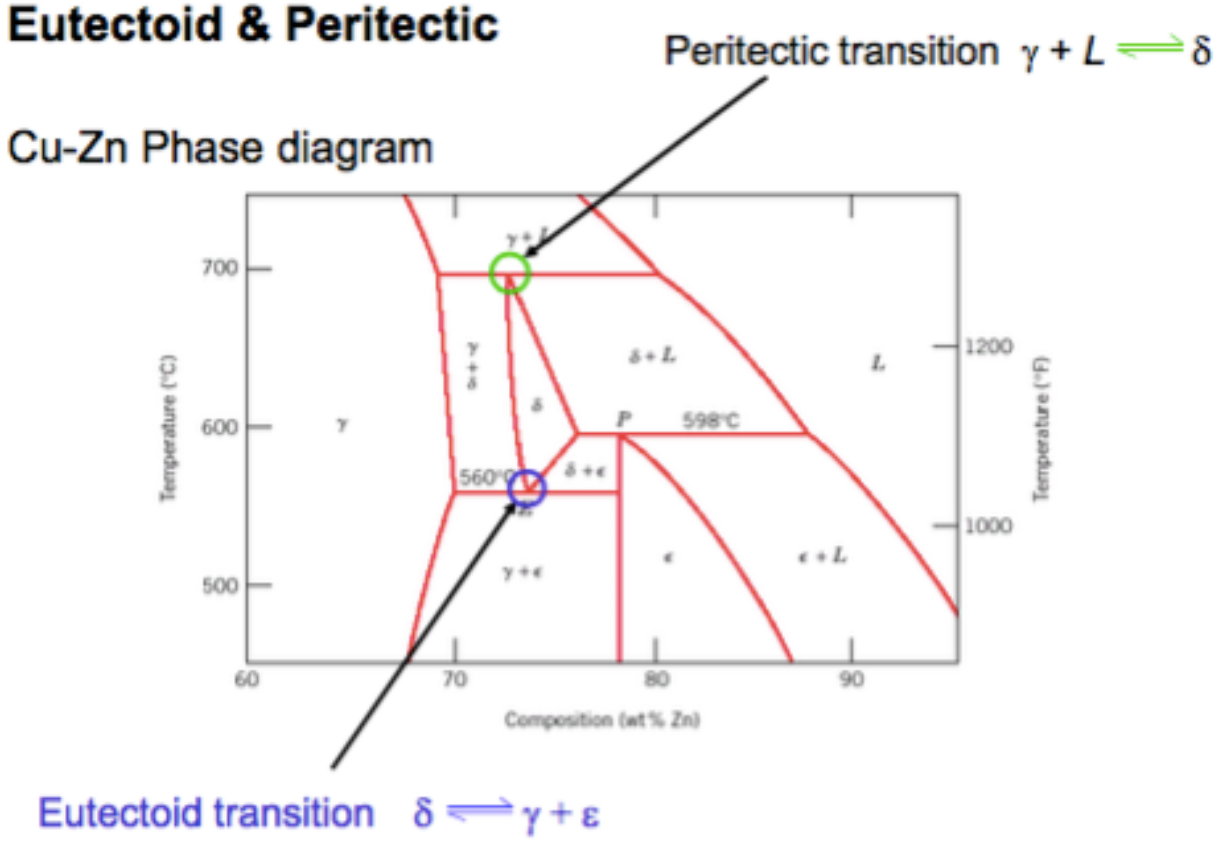
$$W_\beta = \frac{P}{P+Q+R}$$



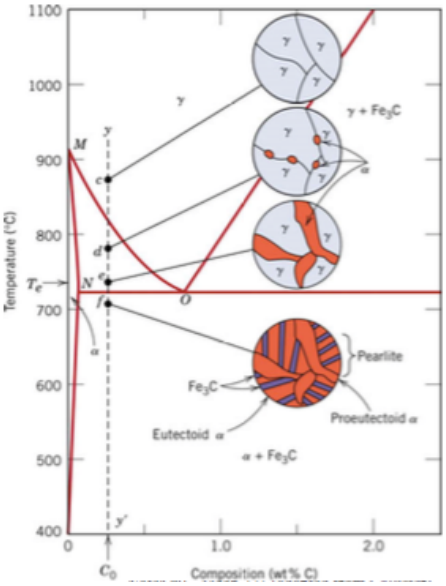
- To calculate amount of eutectic (α+β) use W_e
- To calculate amount of proeutectic α use $W_{\alpha'}$
- To calculate amount of Total α (I.e α_e + α') use W_α
- To calculate amount of β use W_β

- Intermediate Phases and Compounds
  - The solid solutions at the sides of the phase diagrams are called terminal phases
  - Sometimes intermediate solid solutions are formed as well
  - Intermetallic compounds:
    - May also be formed at particular ratios of two metals or a metal and a non-metal
    - These compounds appear as vertical lines on the phase diagram
    - Therefore, the diagram can often be broken down into two eutectics
    - Some intermetallic compounds can exist over slight changes in composition
- Eutectoid and Peritectic
  - Eutectic:
    - Liquid in equilibrium with two solids
    - $L \rightarrow \alpha + \beta$
  - Eutectoid:
    - Solid in equilibrium with two solids
    - $S_2 \rightarrow S_1 + S_3$
  - Peritectic:
    - Liquid and solid in equilibrium with solid
    - $S_1 + L \rightarrow S_2$

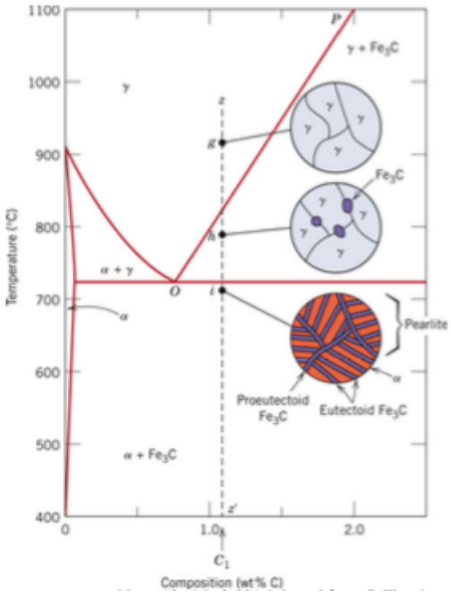
Eutectoid & Peritectic



- Iron-Iron Carbon System:
  - α - Ferrite
    - Interstitial solid solution of carbon in BCC iron
    - Maximum solubility is 0.022 wt %C at 727°C
  - γ - Austenite
    - Interstitial solid solution of carbon in FCC iron (polymorphic)
    - Maximum solubility is 2.08 wt %C at 1148°C and 0.76 wt %C at 727°C
  - Fe_3C - Cementite
    - Iron carbide, intermetallic compound
    - 93.3 wt %Fe + 6.7 wt %C
    - Hard and brittle
  - δ - Ferrite
    - Interstitial solid solution of carbon in BCC iron
    - "a" is larger that for α - Ferrite
  - Eutectic:
    - $L \rightarrow \gamma + Fe_3C$
    - 1147°C
  - Eutectoid:
    - $\gamma \rightarrow \alpha + Fe_3C$
    - 727°C
- Slow Cooling of Plain-Carbon Steels:
  - < 0.76 wt %C – Hypo-eutectoid steels
  - 0.76 wt %C – Eutectoid steel
  - > 0.76 wt %C – Hyper-eutectoid steels
- Eutectoid Steel:
  - A eutectoid steel heated in the γ region (austenitized) and then slow cooled below 727°C will go through the eutectoid reaction ($\gamma \rightarrow \alpha + Fe_3C$)
  - Pearlite is formed from this reaction
  - The microstructure will be 100% pearlite
- Pearlite:
  - Lamellar structure is formed
  - 88.9 % α
  - 11.1 % Fe_3C
  - Once formed there are no significant changes upon cooling
- Hypo-eutectoid Steels:
  - Have to heat to a higher temperature to get 100% γ
  - $\gamma \rightarrow$ 800°C $\rightarrow \gamma + \alpha'$ (Primary Ferrite)
  - $\gamma + \alpha' \rightarrow$ 727°C $\rightarrow \alpha' + (\alpha + Fe_3C)$ (Pearlite)
  - Below eutectoid temperature there are primary ferrite grains and pearlite

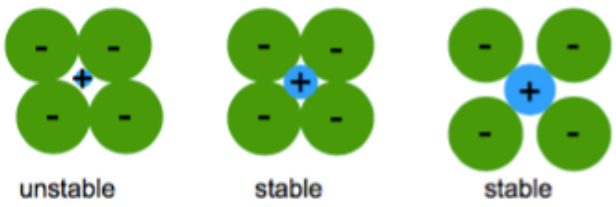


- Hyper-eutectoid Steels:
  - $\gamma \rightarrow 890°C \rightarrow \gamma + (Fe_3C)'$ (Primary Fe_3C)
  - $\gamma + Fe_3C \rightarrow 727°C \rightarrow \alpha + Fe_3C + (Fe_3C)'$
  - Below eutectoid temperature Fe_3C and pearlite
- Non-equilibrium Cooling:
  - If steel is cooled at faster rates, other behaviors may occur
    - Phase changes may occur at different concentrations or may vary microstructure
    - May get phases at room temperature which are not on the phase diagram

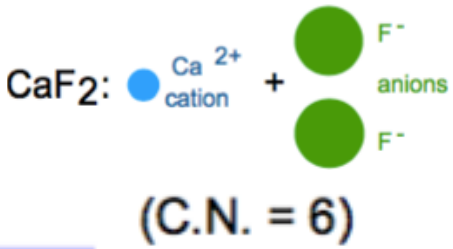


Chapter 12
Structures and Properties of Ceramics

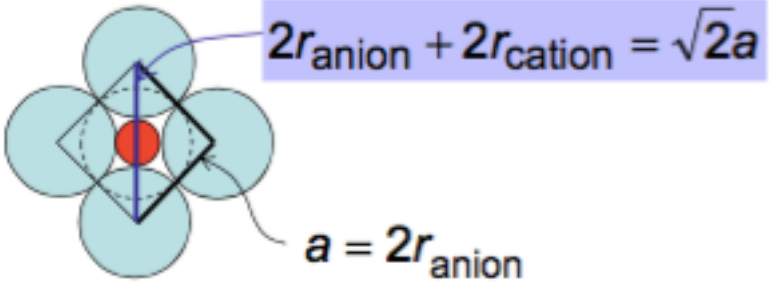
- Many applications:
  - Optical (transparency) opto-electronic
  - Electronic (sensors, superconductors)
  - Thermo-mechanical (engine materials)
- Ceramics:
  - Compounds of metals and non-metals.
  - Bonding is ionic or covalent, or a mixture of both
  - Generally, they are hard and brittle – low toughness and ductility
  - They are good electrical insulators and good thermal insulators because they have no valence electrons
  - They have high melting points
- Crystal Structures:
  - Ceramics usually have two types of ion species, so crystal structures are made up of both ions
  - Must satisfy charge neutrality
  - Must satisfy size and coordination number requirements
  - Standard type of crystal structures (AX)
  - More complex structures (A_mX_p)
  - Even more complex ($A_mB_nX_p$)
- Factors that determine Crystal Structure:
  - Relative size of ions:
    - Formation of stable structures
    - Maximize the number of oppositely charged ion neighbors



- Maintenance of Charge Neutrality:
  - Net charge in a ceramic should be zero
  - Reflected in its chemical formula



- Computation of Minimum Cation-Anion Radius Ratio:
  - Determine minimum r_{cation}/r_{anion}

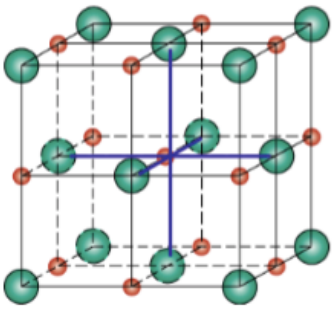


$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion} \qquad r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414$$

- Coordination Number and Ionic Radii:
  - Coordination number:
    - The number of adjacent atoms (or ions) surrounding a reference atom (or ion) without overlap
    - As the atom size increases, it becomes possible to pack more and more atoms around it
    - For like sized atoms, CN = 12
- Rock Salt Structure:
  - NaCl

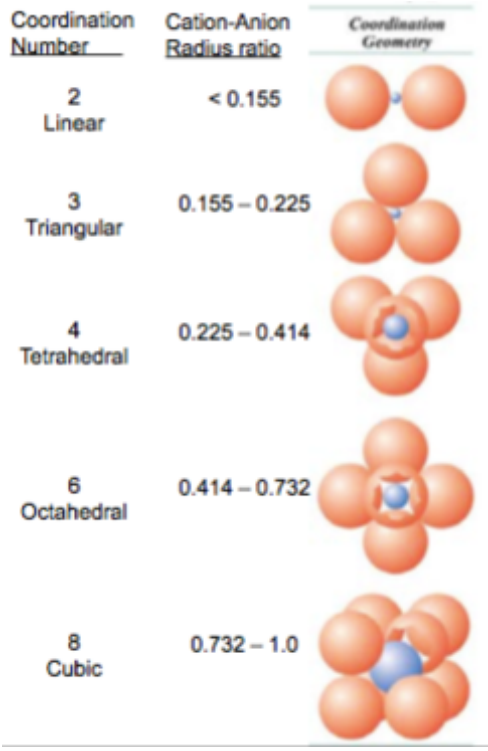


Na+ r_{Na} = 0.102 nm

Cl− r_{Cl} = 0.181 nm

r_{Na}/r_{Cl} = 0.564

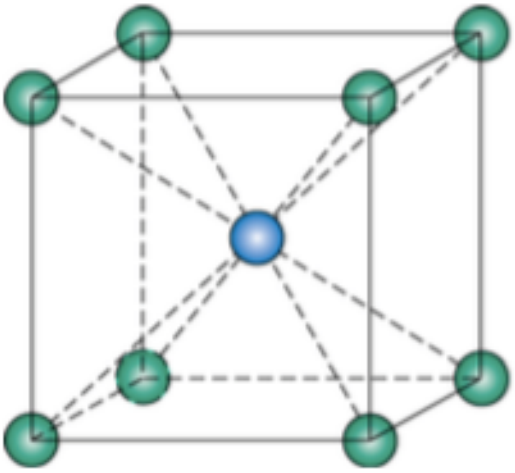
∴ cations (Na^+) prefer octahedral sites

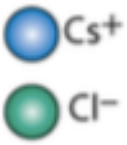


- MgO and FeO also have the salt structure

- AX Crystal Structures:

Cesium Chloride structure:





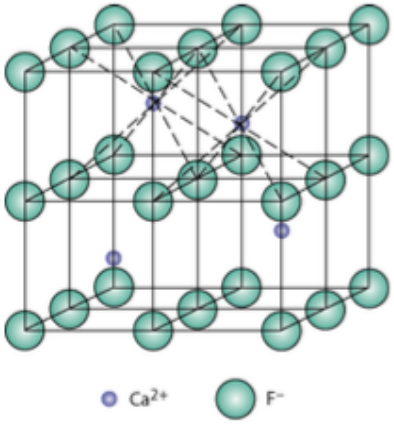
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

∴ Since 0.732 < 0.939 < 1.0, cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

- AX_2 Crystal Structures:
  - Cations in cubic sites

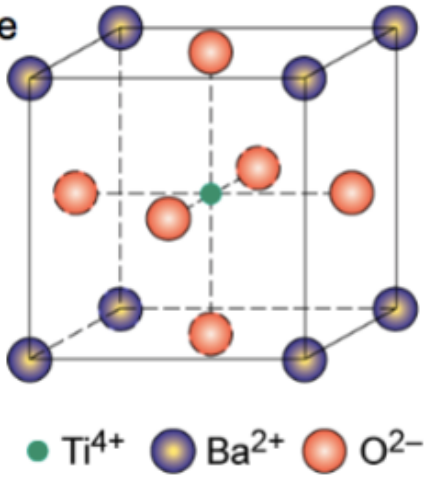
Fluorite structure



- ABX_3 Crystal Structure:

- Perovskite structure

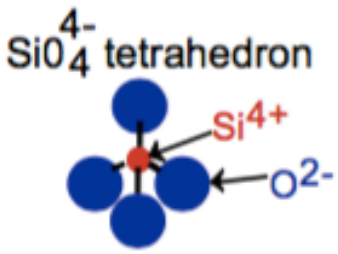
Ex: complex oxide
$BaTiO_3$

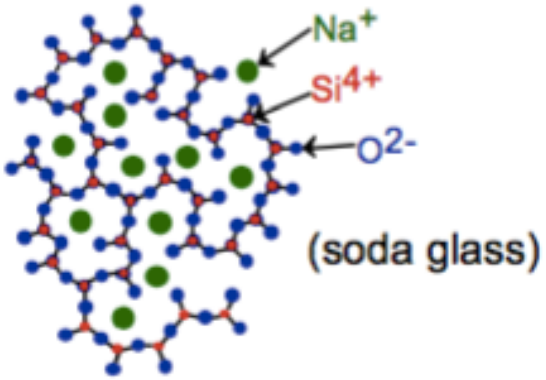


- Silicate Ceramics:
  - Most common elements on earth are Si and O
  - SiO_2 (silica) crystal forms are quartz, crystobalite and tridymite
  - The strong Si-O bonds lead to a high melting temperature (1710°C) for this material

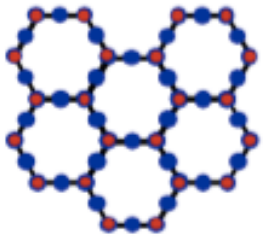
- Silicates:
  - Bonding of adjacent SiO_4^{4-} accomplished by the sharing of common corners, edges, or faces
  - Presence of cations such as Ca^{2+}, Mg^{2+}, and Al^{3+}
    - Maintain charge neutrality
    - Ionically bond SiO_4^{4-} to one another
- Glass Structure:
  - Glass is non-crystalline (amorphous)
  - Fused silica is SiO_2 to which no impurities have been added
  - Other common glasses contain ions such as Na^+, Ca^{2+}, Al^{3+}, and B^{3+}

- Basic Unit:





- Quartz is crystalline SiO_2:



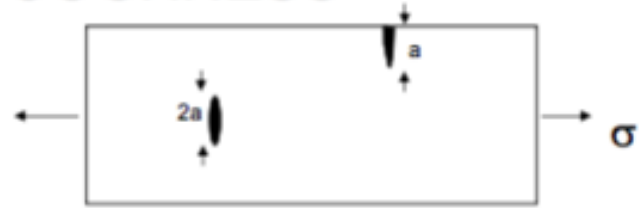
- Layered Silicates:
  - Layered silicates such as clays, mica, and talc:
    - SiO_4 tetrahedra connected together to form 2-D plane
  - A net negative charge is associated with each unit
  - Negative charge balanced by adjacent plane rich on positively charged cations
- Carbon:
  - Polymorphic
    - Diamond
    - Graphite
    - Fullerenes
  - Diamond
    - (ZnS) type structure
    - Strong covalent bonds
    - Hardest known material

        - Very low electrical conductivity
        - Very low thermal conductivity
        - Optically transparent
        - Used as:
            - Gemstones
            - Industrial cutting and grinding
            - Diamond thin films
    - Graphite
        - Layered crystal structure
            - In-plane covalent bonding (strong)
            - Between sheets – van der Waals (weak)
            - High electrical conductivity in plane
            - Relatively good strength, chemical stability
            - Good thermal shock
            - Easily machined
        - Used for:
            - Heating elements, electrodes, crucibles, insulators
            - Electrical contacts, air purifiers
    - Fullerenes
        - Hollow spherical cluster of 60 Carbon atoms
            - Buckyball – Buckminster-fullerene
            - Discrete molecules rather than network
        - Also nanotubes – tubular fullerenes
        - Doping gives interesting properties (nano-electronics and nano-structures)
- Point Defects in Ceramics:
    - Vacancies:
        - Vacancies exist in ceramics for both cations and anions
    - Interstitials:
        - Exists for cations
        - Not normally observed for anions because anions are large relative to the interstitial sites
    - Frenkel Defect:
        - A cation vacancy – cation interstitial pair
    - Shottky Defect:
        - A paired set of cation and anion vacancies
- Imperfections in Ceramics:
    - Electro neutrality (charge balance) must be maintained when impurities are present
- Mechanical Properties of Ceramics:
    - Ceramics are brittle
    - Tensile strengths usually very low
        - Formation and propagation of cracks
    - Compressive strengths usually very high
    - High hardness
    - Due to very small flaws/defects/cracks the strength of the ceramics is lowered

- Reduce the number of pores and pore size to increase strength and stiffness

FRACTURE -TOUGHNESS

$$K_{1c} = Y\sigma_f\sqrt{\pi a}$$



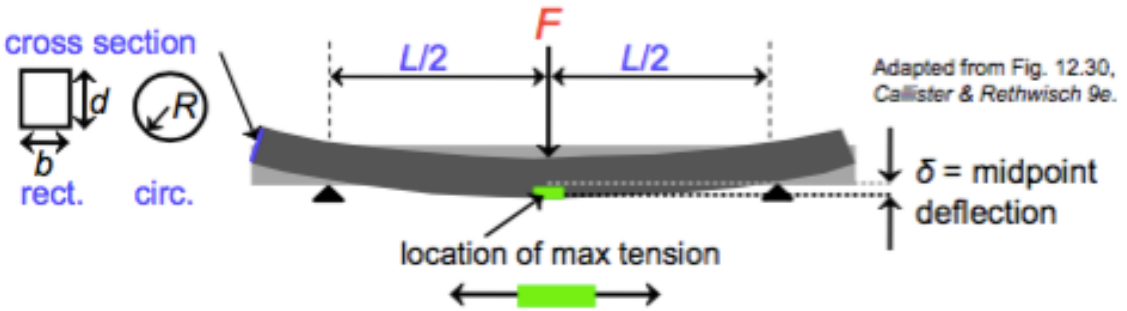
- Y = a dimensionless constant (usually ≈ 1)
- σ_f = fracture stress (MPa)
- *a* = half the size of the internal flaw (m).
- K_{1c} = Plane strain fracture toughness (for most ceramics is less than 10 MPa.$m^{1/2}$

- If the stress/crack size combination is such that RHS >LHS then fracture occurs.
- So to improve strength of ceramics increase K_{1c} or decrease crack size "a"

- Stress-Strain Behavior:
  - Tensile samples are very expensive and difficult to make and test. Use flexural bending tests instead to measure Flexural Strength
    - 3-point bending
    - 4-point bending
  - Values higher than for tensile test
  - Compressive strengths usually very high
  - Ceramic whiskers and fibers have tensile strength of up to 7000MPa
  - Whiskers are very small, thus largest defect cannot be very big
  - Elastic behavior is usually minimal (like metals)
  - Plastic deformation – dislocations can be present in ceramics but,
    - In ionic crystals very few slip systems and charge neutrality problems
    - In covalent crystals, strong bonding, limited slip systems and complex dislocations
  - Dislocations cannot form easily at room temperature
  - No elastic deformation

- Flexural Tests:

- 3-point bend test to measure room-*T* flexural strength.



- Flexural strength:

$$\sigma_{fs} = \frac{3F_f L}{2bd^2} \quad \text{(rect. cross section)}$$

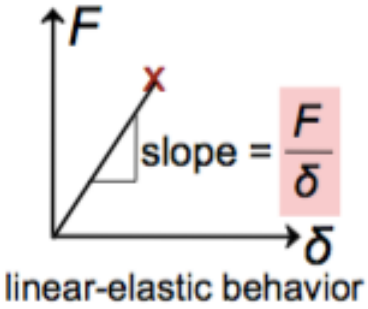
$$\sigma_{fs} = \frac{F_f L}{\pi R^3} \quad \text{(circ. cross section)}$$

- Typical values:

Material	σ_{fs} (MPa)	E(GPa)
Si nitride	250-1000	304
Si carbide	100-820	345
Al oxide	275-700	393
glass (soda-lime)	69	69

Data from Table 12.5, Callister & Rethwisch 9e.

- Determine elastic modulus according to:

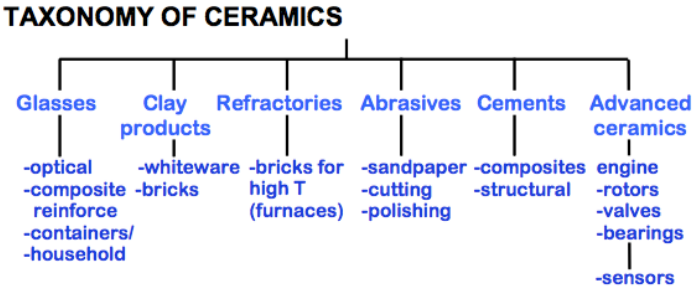


$$E = \frac{F}{\delta}\frac{L^3}{4bd^3} \quad \text{(rect. cross section)}$$

$$E = \frac{F}{\delta}\frac{L^3}{12\pi R^4} \quad \text{(circ. cross section)}$$

WILEY

Chapter 13
Applications and Processing of Ceramics



- Most metal components are made by
  - Directly molding them into final shape
  - Cast metal bars/slabs into shape
- Ceramics cannot be easily melted and are difficult to contain
- Ceramics cannot be plastically deformed into shape easily (brittle)
- Ceramics are usually hard materials and machining them is slow and expensive

- Properties:
  - The melting temperature for glass is moderate, but large for other ceramics
  - Low toughness, ductility, large moduli and creep resist
- Applications:
  - High temperature, wear resistant, novel uses from charge neutrality
- Fabrication:
  - Some glasses can be easily formed
  - Other ceramics can not be formed or cast
- Refractories:
  - Need a material to use in high temperature furnaces
  - Consider Silica (SiO_2) – Alumina (Al_2O_3) system
- Die Blanks:
  - Need wear resistant properties
  - 4 micrometer polycrystalline diamond particles that are sintered on to a cemented tungsten carbide substrate
  - polycrystalline diamond helps control fracture and gives uniform hardness in all directions
- Cutting Tools:
  - Tools:
    - For grinding glass, tungsten, carbide, ceramics
    - For cutting Si wafers
    - For oil drilling
  - Solutions:
    - Manufactured single crystal or polycrystalline diamonds in a metal or resin matrix
    - Optical coatings
    - Polycrystalline diamonds resharpen by micro fracturing along crystalline planes
- Sensors:
  - Principle:
    - Make diffusion of ions fast for rapid response
  - Approach:
    - Add Ca impurity to increase O^{2-} vacancies and diffusion
  - Operation:
    - Voltage difference produced when O^{2-} ions diffuse between external and reference gases
- Modern Ceramics:
  - Heat-resistant structural materials
  - Heat engine components
  - Turbine engine
  - Wear-resistant materials
  - Cutting tools
  - Emission control catalyst carriers
  - Nuclear
  - Electronics
  - Sensors

- Medical and Bioengineering
- Optical materials

- Glasses:
  - Optical transparency
  - Relatively easy manufacturing
  - Hard at room temperature
  - Vacuum tight
  - Chemically resistant
  - Glasses do not solidify at one temperature like crystalline materials
  - They increase in viscosity as temperature drops – considered as "super-cooled liquids"
  - They do not show sudden change in volume on solidifying
  - Gradual shrinking as temperature decreases with a change in slope at T_g – glass transition temperature
  - Below T_g we have a glass (solid)
- Ceramic Fabrication Methods:
  - Glass Forming

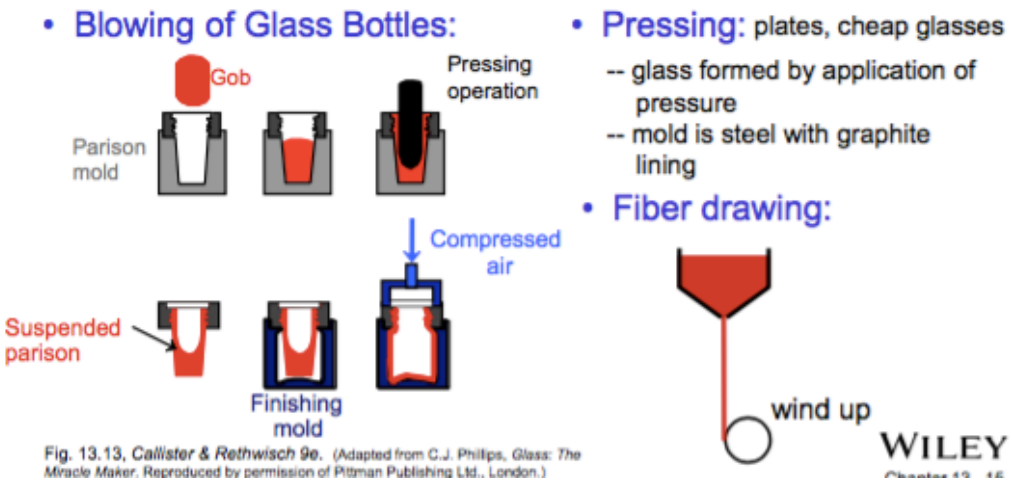
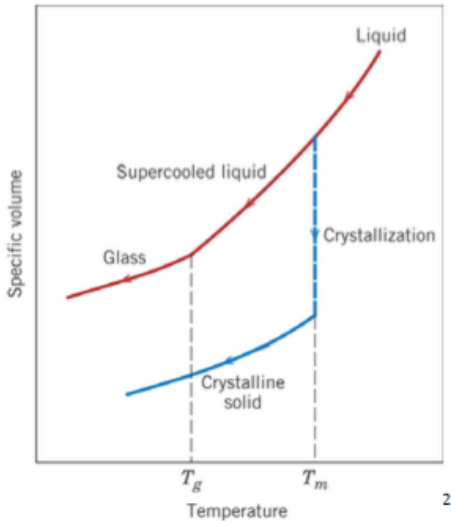


Fig. 13.13, *Callister & Rethwisch 9e.* (Adapted from C.J. Phillips, *Glass: The Miracle Maker*. Reproduced by permission of Pitman Publishing Ltd., London.)

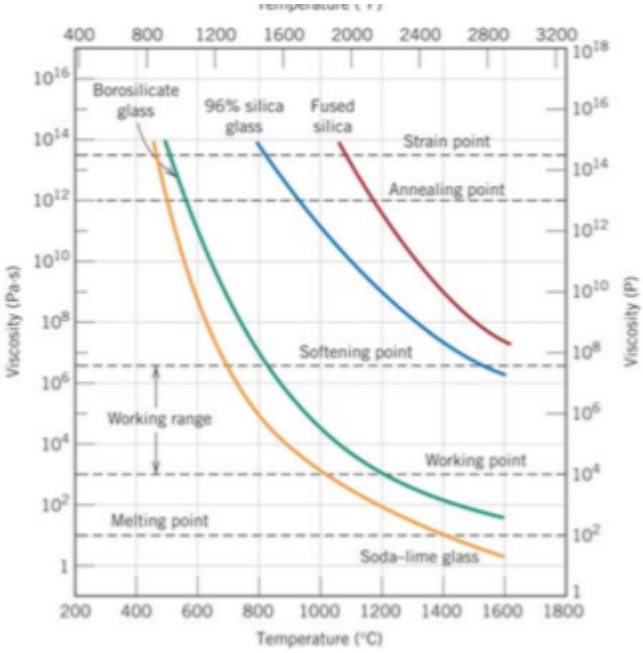
• **Specific volume** (≈1/ρ) **vs Temperature (T):**



• **Crystalline materials:**
- crystallize at melting temp, T_m
- have abrupt change in specific vol. at T_m

• **Glasses:**
- do not crystallize
- spec. vol. varies smoothly with T
- Glass transition temp, T_g

- Glass Viscosity:
  - Melting point:
    - Temperature at which viscosity is 10 Pa-s (100P)
    - The glass is fluid enough to be considered liquid
  - Working point:
    - Temperature at which the viscosity is 10^3 Pa-s (10^4P)
    - The glass is easily deformed at this viscosity
  - Softening point:
    - Temperature at which the viscosity is 4 x 10^6 Pa-s (4 x 10^7P)
    - Maximum temperature at which a glass piece may be handled without causing significant dimensional alterations
  - Annealing point:
    - Temperature at which the viscosity is 10^{12} Pa-s (10^{13}P)
    - At this temperature, atomic diffusion is sufficiently rapid that any residual stresses may be removed within about 15 minutes
  - Strain point:
    - Temperature at which the viscosity becomes 3 x 10^{13} Pa-s (3 x 10^{14}P)
    - For temperatures below strain point, fracture will occur before the onset of plastic deformation
    - The glass transition temperature will be above the strain point
- Viscosity:
  - Relates shear stress and velocity gradient
  - Has units of Pa-s
  - Viscosity decreases with increasing temperature
  - Impurities lower the temperature required to have deformations



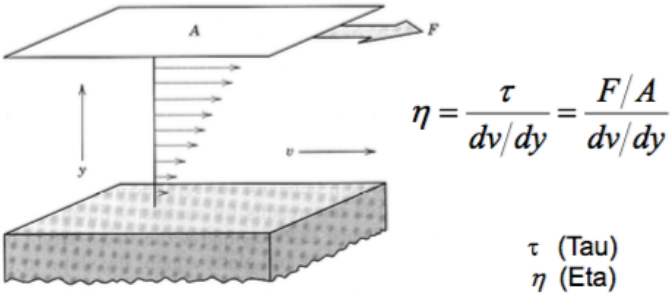


FIGURE 13.30 Representation of the viscous flow of a liquid or fluid glass in response to an applied shear force.

- Glass Forming:
  - Depending on composition and process, select an appropriate temperature
  - Working range is usually between softening and working points
  - Soda-lime glass is most common
  - Because optical clarity is usually important, processing has to remove impurities
  - Main forming routes use “heat, shape, cool”:
    - Pressing: plates, dishes
    - Blowing: jars, bottles, light bulbs
    - Fiber drawing: rods, tubes, plates, large fibers
    - Fiber forming: thin glass fibers

- Sheet Glass Forming:
  - Continuous casting:
    - Sheets are formed by floating the molten glass on a pool of molten tin

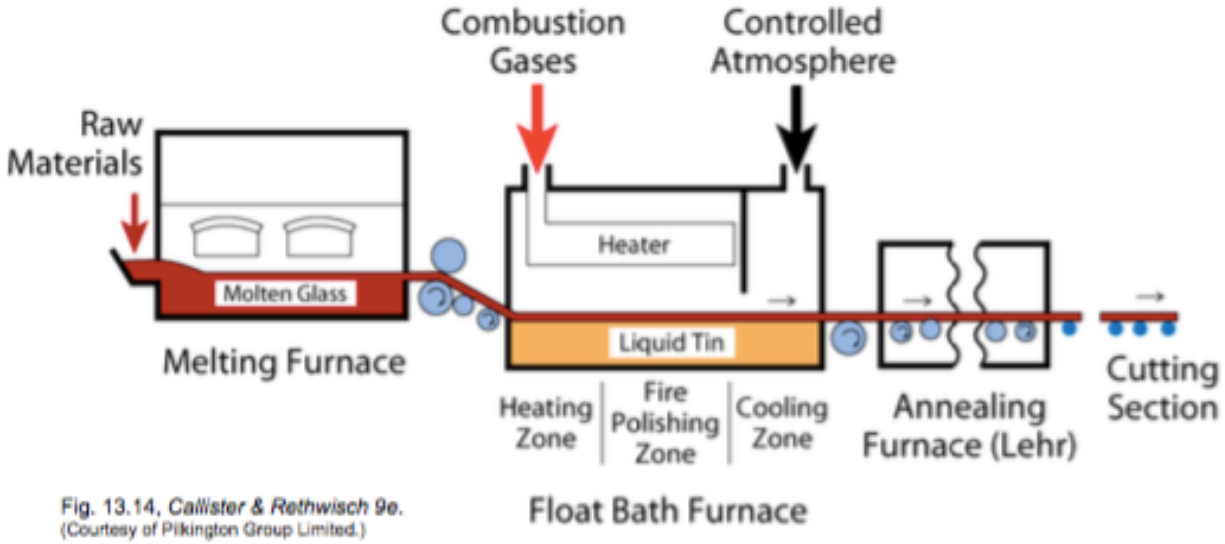
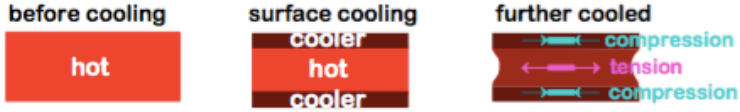


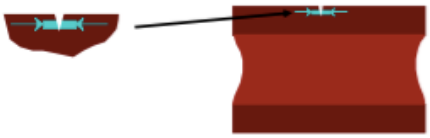
Fig. 13.14, *Callister & Rethwisch 9e.*
(Courtesy of Pilkington Group Limited.)

- Annealing:
  - Internal stress can build up when cooling glasses
  - Can cause spontaneous fracture in worst cases
  - Avoid this by slow cooling
  - Remove or diminish by reheating and slow cooling
- Tempered and Toughened Glass:
  - Glass tempering deliberately introduces residual stresses
  - Involves rapid surface cooling of hot glass
    - Surface contracts and hardens
    - Inside stays warm and soft
    - Inside cools and shrinks, and tries to pull surface (which is already rigid) inwards
    - This puts the surface into compression and the interior into tension
  - In order to break glass, you have to overcome the compressive forces in the surface layer first
  - Therefore, you need a higher tensile stress at the surface so glass is stronger and more resilient to fracture
  - This is not the same as laminate glass

- **Annealing:**
  --removes internal stress caused by uneven cooling.
- **Tempering:**
  --puts surface of glass part into compression
  --suppresses growth of cracks from surface scratches.
  --sequence:



--Result: surface crack growth is suppressed.



- Chemical Toughening
  - Replace surface Na^+ ions in soda-lime glass with larger K^+ ions by soaking it in a hot salt bath
  - When cooled, larger K^+ ions induce compressive stress at surface, tensile at center
- Glass Ceramics:
  - Some glass compositions can be "devitrified" (de-glassify) by heat-treatment to produce a crystalline material called a "glass-ceramic"
  - So use glass-forming to make shape of component and then devitrify to glass-ceramic which has better strength, thermal shock resistance, and better thermal conductivity than the glass
- Particulate Forming

Hydroplastic forming:

- Mill (grind) and screen constituents: desired particle size
- Extrude this mass (e.g., into a brick)

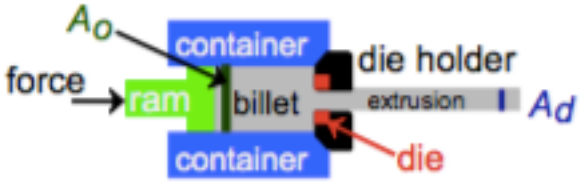


Fig. 11.9 (c), *Callister & Rethwisch 9e.*

- Dry and fire the formed piece

Slip casting:

- Mill (grind) and screen constituents: desired particle size
- Mix with water and other constituents to form slip
- Slip casting operation

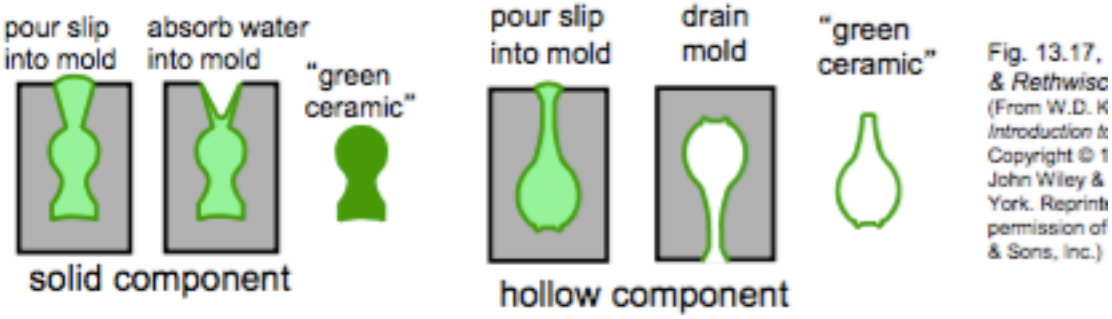
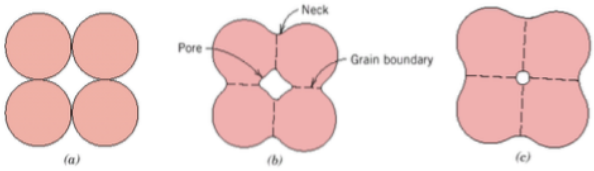


Fig. 13.17, *& Rethwisc* (From W.D. K *Introduction t* Copyright © 1 John Wiley & York. Reprint permission of & Sons, Inc.)

- Dry and fire the cast piece

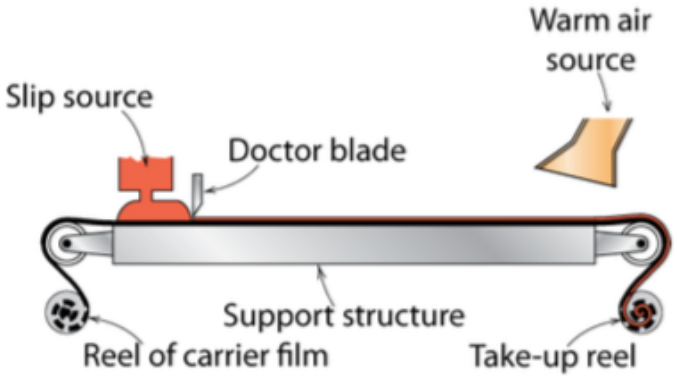
- Fabrication Techniques:
  - Melting points of most ceramics are very high, therefore impractical to melt and cast
  - Instead form compacts from powders
  - Ceramic powder:
    - Fine powder of the order of microns (10^{-6}m) plus additives
  - Formed by pressing, slip-casting or extrusion
  - Fired or sintered:
    - Heated to high temperatures (below T_M) for some time t
- Typical Porcelain Composition
  - 50% clay
  - 25% filler – for example quartz
  - 25% fluxing agent
- Drying and Firing:
  - Drying:
    - As water is removed, interparticle spacing decrease and shrinkage occurs
    - Drying too fast causes the sample to warp or crack due to non-uniform shrinkage

  - Firing:
    - Heat treatment between 900°C - 1400°C
    - Vitrification:
      - Liquid glass forms from clay and flux
      - Forms between SiO_2 particles
      - Flux lowers melting temperature
  - Sintering:
    - Useful for both clay and non-clay compositions
    - Procedure:
      - Grind to produce ceramic and/or glass particles
      - Inject into mold
      - Press at elevated temperatures to reduce pore size
- Powder Pressing:
  - Uniaxial compression
    - Compacted in a single direction
  - Isostatic (hydrostatic) compression
    - Pressure applied by fluid – powder in rubber envelope
  - Hot pressing
    - Pressure and heat



- Sintering:
  - Powder touches – forms neck and gradually neck thickens
  - Add processing aids to help form neck
  - Little or no plastic deformation

- Tape Casting:
  - Thin sheets of green ceramic cast as flexible tape
  - Used for integrated circuits and capacitors
  - Cast from liquid slip (ceramic and organic solvent)

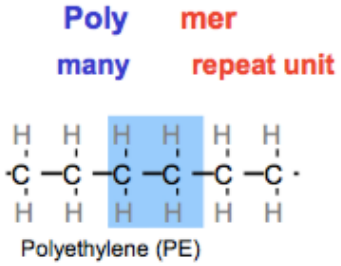


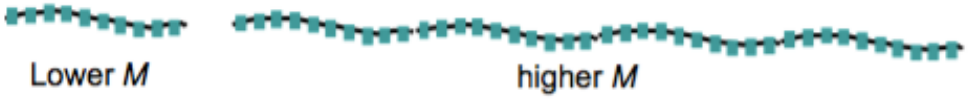
- Cementation:
  - Hardening of a paste
  - Paste formed by mixing cement material with water
  - Formation of rigid structures having varied and complex shapes
  - Hardening process
    - Hydration – complex chemical reactions involving water and cement particles
- Refractories:
  - Materials used for producing and refining metals and glasses and other high temperature applications
  - Need to:
    - Withstand high temperatures without breaking
    - Remain unreactive/inert to contents
    - Provide thermal insulation
  - Silica / Acidic Refractories:
    - Silica, alumina and fireclay
  - Basic:
    - MgO – Magnesite often used in steel-making
  - Neutral:
    - Chromite, chromite-magnesite
  - Special:
    - Carbon/graphite, zirconia, zircon

<u>Chapter 14</u>
<u>Polymers</u>

- Includes plastics and elastomers
- Commercial polymers:
  - Used in large quantities for their lightweight, corrosion-resistance and good formability
  - Usually low strength and stiffness
- Polymer Composition:
  - Most polymers are hydrocarbons – made of H and C
  - Saturated hydrocarbons:
    - Each carbon bonded to other atoms
- Unsaturated Hydrocarbons:
  - Double and triple bonds relatively stable – can from new bonds

        - Double bond – ethylene or ethene
        - Each C has 4 bonds, but only 3 atoms bound to each C
        - Triple bond – acetylene or ethyne
        - Each C has 4 bonds, but only 2 atoms bound to each C
- Hydrocarbon Molecules:
    - The basic building block of polymers is the hydrocarbon molecule
    - Each carbon atom wants to form 4 single bonds
    - If double or triple bonds form – stronger molecules
    - The double and triple bonds allow the molecule to join to something else under the right conditions
    - Other groups can be attached to the carbon atoms apart from H
    - The various polymers are made by taking varying proportions of hydrocarbons and end groups and assembling them together
    - Mers are the basic building unit
    - They are combined to form the polymer
- Isomerism:
    - Two compounds with the same chemical formula can have quite different structures
- Chemistry of Polymers:
    - Monomers can be joined to form polymers
    - Ethene monomers – polyethylene polymer
    - The repeating unit is the "mer" that makes up the polymer
- Molecular Mass:
    - Molecular weight or molar mass is the mass of a mole of polymer chains
    - Polymers are made up of many mers joined together
- Molecular Weight:
    - The mass of a mole of chains





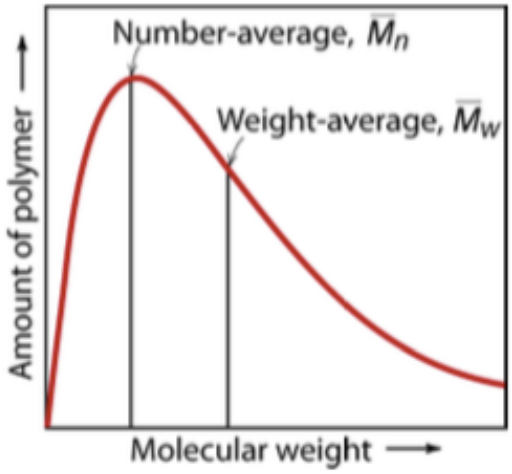
$$\overline{M}_n = \Sigma x_i M_i$$
$$\overline{M}_w = \Sigma w_i M_i$$

M_i is mean molecular weight of a size range

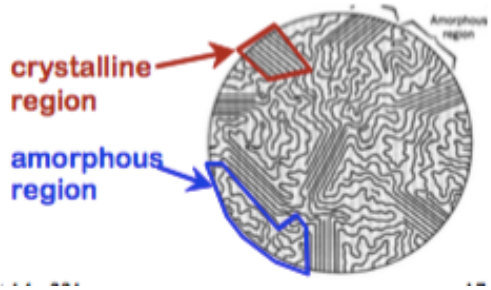
X_i is the fraction of the total number of chains

w_i is the weight fraction of the total weight of chains

$\overline{M}_w$ is more sensitive to higher molecular weights



- Tensile Strength
  - Often increases with M_w
  - Longer chains are anchored better
- Percent Crystallinity
  - Tensile strength and E often increase with percent crystallinity
  - Annealing causes crystalline regions to grow



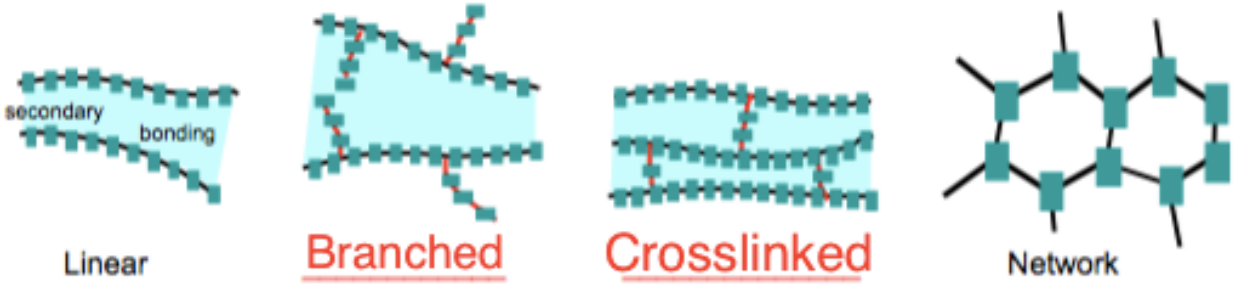
- Degree of Polymerization
  - DP = average number of repeat units per chain

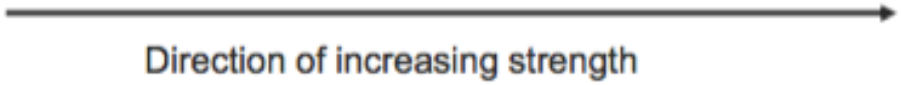
$$DP = \frac{\bar{M}_n}{\bar{m}}$$

where $\bar{m}$ = molecular weight of repeat unit

- Molecular Shape and Structure
  - Molecules are not strictly linear
  - Each bond can rotate to a range of configurations
  - Double bonds restrict rotation
  - Bulky side groups hinder rotation
  - Linear Polymers:
    - Mers joined end-to-end to form long chain
    - Many common polymers
  - Branched Polymers:
    - Side branches connected to main chain
    - Tends to reduce density
  - Crosslinked Polymers:
    - Adjacent linear chains have occasional covalent crosslinking
    - Many elastomers/rubbers have crosslinking
  - Network Polymers:
    - Trifunctional mers form 3-D networks
    - Thermosets

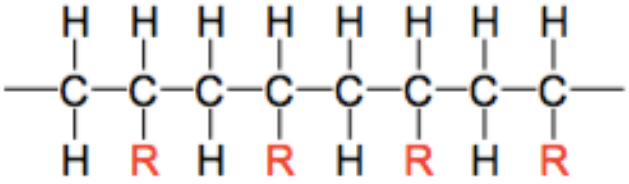
- Covalent chain configurations and strength:



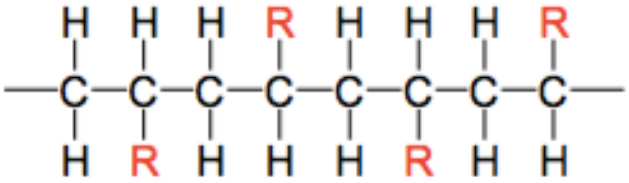


- Tacticity:

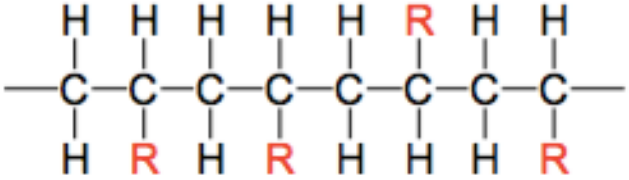
isotactic – all R groups on same side of chain



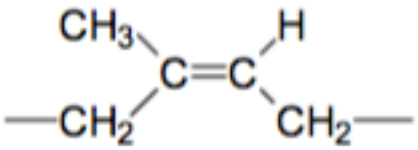
syndiotactic – R groups alternate sides



atactic – R groups random



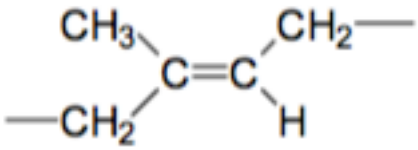
- cis/trans Iosmerism



cis

cis-isoprene
(natural rubber)

bulky groups on same side of chain



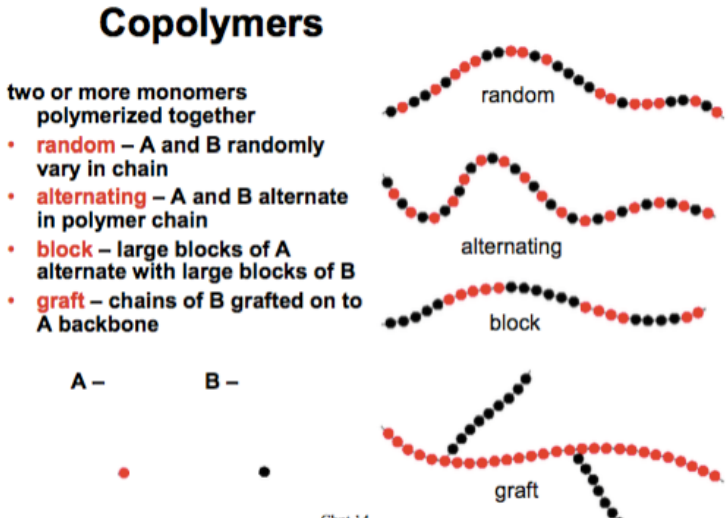
trans

trans-isoprene
(gutta percha)

bulky groups on opposite sides of chain

- Thermoplastics, Thermosets and Elastomers:
  - Thermoplastics:
    - Can be formed and shaped by viscous flow
    - Retain shape on cooling
    - Process can be repeated
    - Generally, consist of very long carbon chains with side groups of H, O, N
    - Carbon atoms are covalently bonded along chain
    - Chains are strong

        - Little cross linking
        - Ductile
        - Polyethylene, polypropylene, polycarbonate
    - Thermosets:
        - Thermosetting plastics are formed then cured or set by a chemical reaction
        - Cannot be remelted of reshaped by application of heat
        - Most consist of a rigid network of covalently bonded atoms
        - Other side groups O, N, H, will be present
        - Large cross linking (10% - 50%)
        - Hard and brittle
        - Vulcanized rubber, epoxies, polyester resin
    - Elastomers:
        - Very large elastic deformations, when loaded
        - Can be recovered on unloading
        - Up to 900% elongation possible
- Copolymers:
    - Homopolymers:
        - Chains of same repeating unit
    - Copolymers:
        - Two or more chemically different repeating units
    - Random copolymers:
        - Random arrangement of different mers
    - Alternating copolymers:
        - Ordered, unlike groups attract
    - Block copolymers:
        - Ordered, like groups attract
    - Graft copolymers:
        - Grafts of one type on another chain
- Polymer Crystallinity:
    - Crystals must contain the polymer chains in some way
    - Polymers are rarely 100% crystalline
- Partially Crystalline Thermoplastics:
    - Degree of crystallinity ranges from 5% to 95%



$$\% \, crystallinity = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} x100$$

Where:

ρ_s = Density of sample

ρ_a = Density of the completely amorphous polymer

ρ_c = Density of the completely crystalline polymer

%crystallinity depends on several factors:

Rate of cooling (faster cooling – less crystallinity)

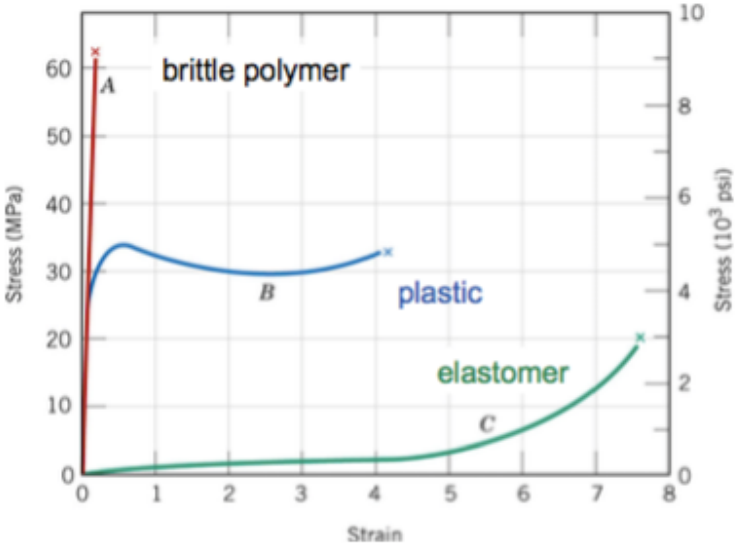
Chain configuration (simple structures – more crystallinity)
(Copolymers – less crystallinity)

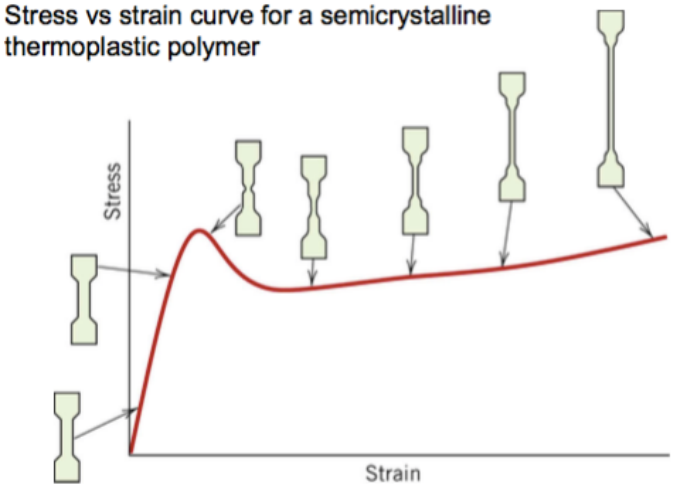
ATACTIC PP - Never crystallizes, softens ≈ 70°C

ISOTACTIC PP - Partially Crystalline $T_m \approx 176°C$!

Chapter 15
Plastics as Engineering Materials

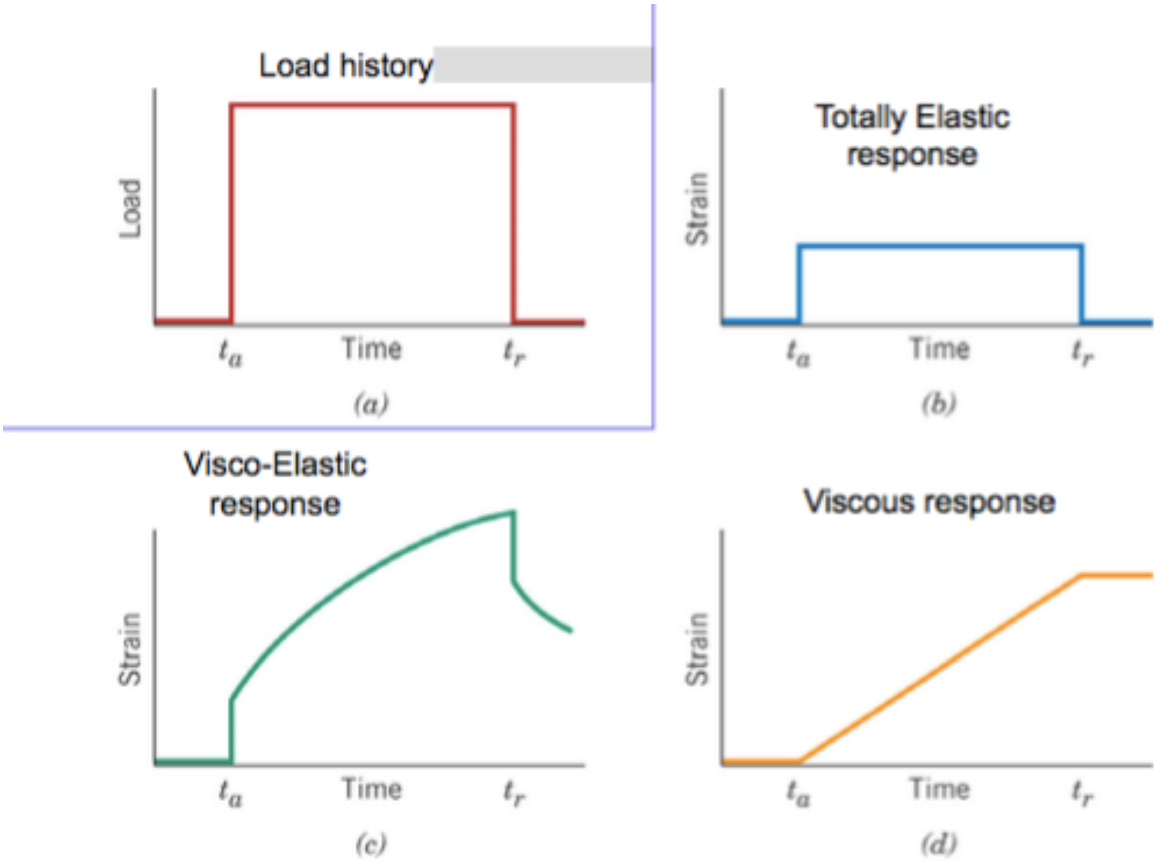
- Very low densities
- Excellent formability/molding
- Reduced number of part/forming and finishing operations
- Low cost
- Noise reduction
- Corrosion resistant
- Low friction
- Electrically insulating
- Tailored properties
- Behavior of Plastics:
    - Plastics exhibit a range of behaviors
    - Stress vs. Strain test used for many polymers, but results will also depend on
        - Temperature
        - Strain rate (speed of pulling)
        - Chemical environment
    - Three main types of behaviors:
        - Elastic – fracture
            - Brittle polymer
        - Elastic then plastic
            - Similar to metal
        - Totally elastic
            - Large recoverable strains, elastomers



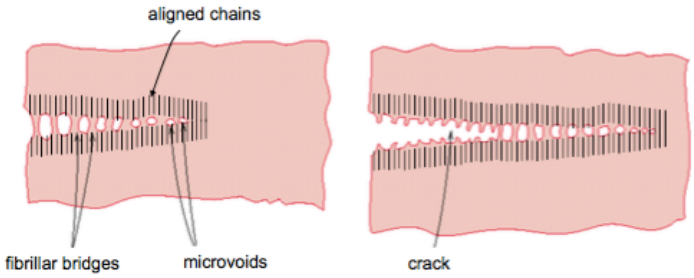


- Viscoelasticity:
    - Elastic:
        - Temporary deformation and recovery
        - Polymers below T_g

- Viscous:
  - Deformation is time dependent and not recoverable
  - Polymers at high temperatures
- Visco-Elastic:
  - At temperatures in between, polymers can behave as metals
  - Non-linear elastic behavior
- Chain slippage depends on rate of strain and time and temperature
- Fast-strain – no time for slippage, brittle failure
- Slow-strain – chain slippage, ductile



- Impact Strength:
  - Polymers are often ductile above their T_g and brittle below T_g
  - Temperature has a large effect
- Crazing During Fracture of Thermoplastic Polymers
  - Craze formation prior to cracking
  - During crazing, plastic deformation of spherulites, and formation of microvoids and fibrillar bridges



- Deformation of Semi-Crystalline Polymers:
  - Elastic:
    - This occurs by bond-stretching/bending in the chains
    - Recoverable
  - Plastic:
    - Amorphous regions elongate
    - Chains slide and rotate and move past each other
    - Tilting of crystalline regions
    - Blocks orient towards tensile axis
    - Non-recoverable unless heated
  - At upper yield point necking can occur
  - Alignment can occur in necked region leading to localized strengthening so continued deformation occurs preferentially in unnecked regions
- Deformation by Drawing:
  - Drawing:
    - Stretches the polymer prior to use
    - Aligns chains to the stretching direction
  - Results of Drawing:
    - Increases the elastic modulus in the stretching direction
    - Increases the tensile strength in the stretching direction
    - Decreases ductility
  - Annealing after Drawing:
    - Decrease alignment
    - Reverses effects of drawing
  - Compare to cold working in metals
- Factors Effecting Strength of Polymers:

$$TS = TS_{\infty} - \frac{A}{M_n}$$

  - As chains get longer more entanglement of chains increases tensile strength
  - Degree of crystallinity
    - Affects degree of intermolecular secondary bonding
    - Closer packing of chains, therefore more secondary bonds between chains
    - Stronger, stiffer, denser
    - Increase tensile modulus and strength
    - Increases brittleness
  - C-C chain alignment by drawing
    - Aligns chains by pulling material
    - Increases modulus and strength by large amounts
  - Heat-treating
    - For undrawn materials annealing of semi-crystalline polymers leads to increase in tensile modulus and yield strength and decrease in ductility
    - For drawn materials can lead to shrinkage
- Deformation of Elastomers:
  - Ability to be deformed to large deformations and then elastically spring back to original form
  - Low modulus of elasticity, non-linear stress-strain
  - Tensile load causes partial straightening, untwisting, uncoiling of chains

- As straightening occurs, entropy decreases
- On unloading entropy increases by returning to more disordered state
- Elastomers increase in temperature as stretched and elastic modulus increases as temperature increases

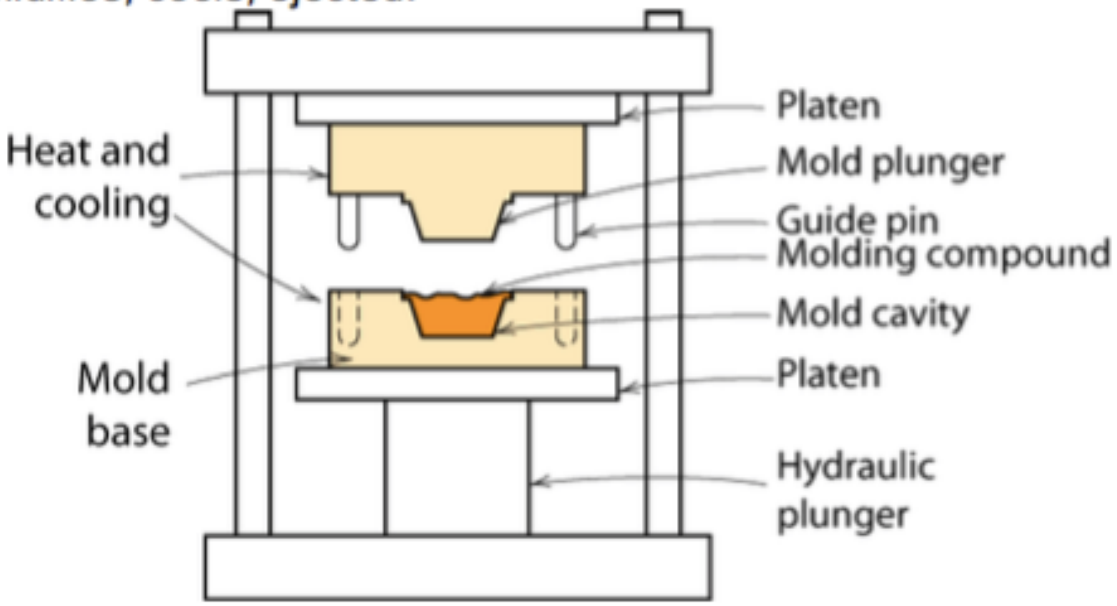
- Crystallization, Melting and Glass Transition
  - The degree of crystallinity affects the mechanical and thermal properties of the polymer
  - Crystalline regions of polymer will melt at T_m
  - Amorphous polymers or amorphous regions in semi crystalline polymers will not melt
  - They undergo glass transition at T_g
  - Below T_g:
    - Chains fairly immobile, cannot move easily, rigid material
  - Above T_g:
    - Chains more mobile, can flow past each other under load, rubbery
  - T_m and T_g are affected by:
    - Polymer chain structure
    - Molecular weight
    - Branching
    - Polar atoms, bulky side groups, unsaturated bonds
- Polymerization:
  - Addition polymerization:
    - Monomer is initiated
    - Propagation of reaction
    - Termination
  - Condensation (Step) polymerization:
    - Two different molecules come together to form repeat unit
    - Often by-product is formed
- Polymer additives:
  - Fillers:
    - Improve strength, abrasion resistance, toughness
  - Plasticizers:
    - Increases flexibility, toughness, lowers T_g
  - Stabilizers:
    - To prevent UV degradation, antioxidants
  - Lubricants:
    - Easier processing
  - Colorants:
    - Dyes or pigments to change color
  - Flame retardants:
    - Most polymers are flammable so additives introduced to reduce flammability of plastic products
- Processing of Plastics:
  - Thermoplastic:
    - Can be reversibly cooled and reheated (recycled)
    - Heat until soft, shape as desired, then cool

- Thermoset:
  - When heated forms a molecular network (chemical reaction)
  - Degrades when heated
  - A prepolymer molded into desired shape, then chemical reaction occurs
- Compression and Transfer Molding:
  - Plastic resin introduced into hot mold cavity
  - Upper part of mold closed, forces liquefied, resin to flow and fill mold
  - Continued heating cures thermoset – solidifies
  - Ejected and flash trimmed
  - Cheap, simple shapes, requires trimming

Processing Plastics – Compression Molding

Thermoplastic or thermoset

- polymer and additives placed in mold cavity
- mold heated and pressure applied
- fluid polymer assumes shape of mold
- solidifies, cools, ejected.

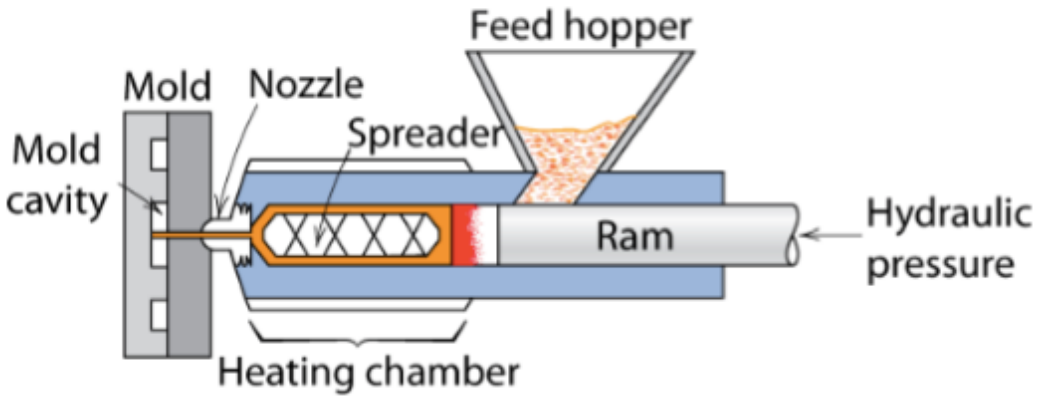


- Injection Molding:
  - Plastic granules are melted and mixed, injected into mold
  - High quality parts at high rates
  - Relatively low labor costs
  - Good surface finishes
  - Highly automated
  - Intricate shapes possible
  - High cost of machinery and also for molds
  - Close control of process parameters required for good product quality and throughout

Processing Plastics – Injection Molding

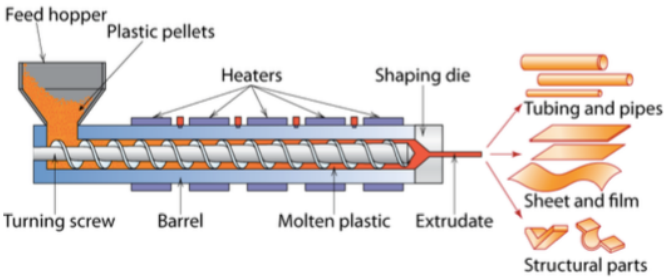
Thermoplastic & some thermosets

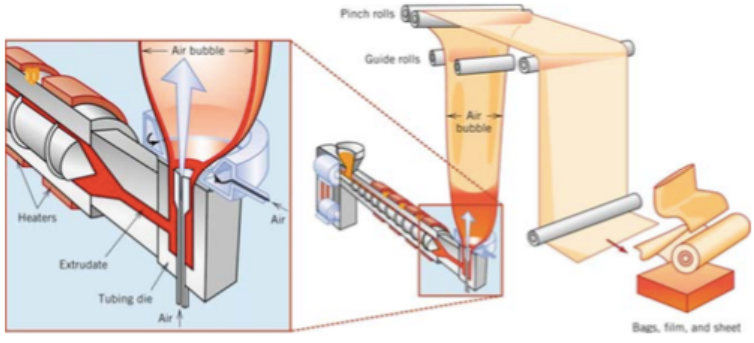
- when ram retracts, plastic pellets drop from hopper into barrel
- ram forces plastic into the heating chamber (around the spreader) where the plastic melts as it moves forward
- molten plastic is forced under pressure (injected) into the mold cavity where it assumes the shape of the mold, cools and solidifies, - ejected



- Extrusion:
  - Used for long continuous product
  - Melt pellets
  - Push melt through shaped die
  - Cool
  - Also used for homogenization, scrap recycling and mixing
- Blow Molding:
  - Heated tube/cylinder of plastic is pinched in a mold
  - Air is blown into tube until it conforms to sides
  - Mold is opened, part ejected

Processing Plastics – Extrusion





f15_26_pg568

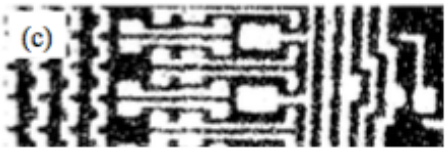
- Thermoforming:
  - Heated plastic sheet formed by pressing onto mold face
  - Mechanical, air or vacuum used for pressing

- Calendaring:
  - Molten plastic is squeezed between rolls
- Spinning:
  - Used to form fibers and filaments
- Casting:
  - Melt polymer and pour into mold

Chapter 18
Electrical Properties

- In SEM the electron beam causes the surface atoms to emit X-rays
- It is possible to filter all the rays but the ones from the atom of interest
- When these rays are projected on a cathode tube screen, they will generate white dots – dot map

A dot map showing location of Si (a semiconductor).
- *Si shows up as light regions.*



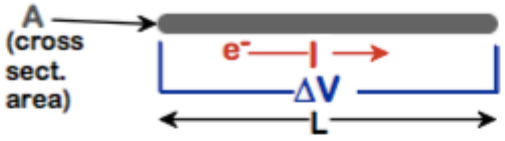
A dot map showing location of Al (a conductor).
- Al shows up as light regions.

2

- Electrical Conduction:
  - Ohm's Law:

$$V = IR$$

voltage drop (volts = J/C)
C = Coulomb
current (amps = C/s)
resistance (Ohms)



  - Resistivity, ρ:

-- a material property that is independent of sample size and geometry

$$\rho = \frac{RA}{\ell}$$

R: resistance
A: cross-sectional area of current flow
ℓ: current flow path length

  - Conductivity, σ

$$\sigma = \frac{1}{\rho}$$

WILI

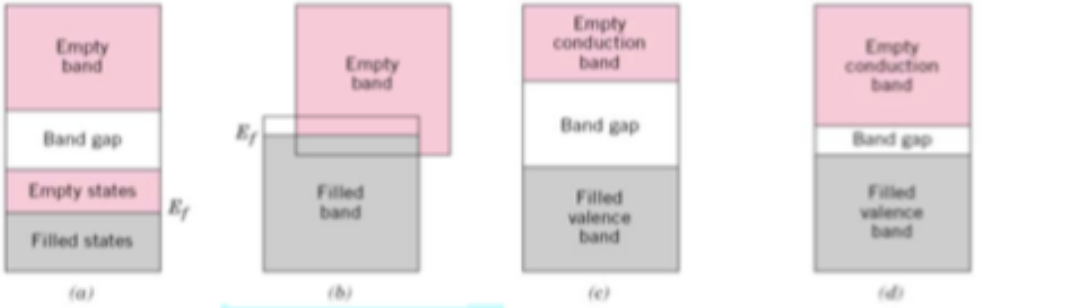
- Resistance (R) depends on sample geometry size
- Conductivity:
  - Solid materials exhibit a very wide range of electrical conductivity
  - Widest range compared to other physical properties
  - Materials can be classified according to their electrical conductivity

Conductivity values $(Ohm\text{-}m)^{-1}$ at room temp.

METALS	**conductors**	**CERAMICS**	
Silver	6.8×10^7	Soda-lime glass	10^{-10}
Copper	6.0×10^7	Concrete	10^{-9}
Iron	1.0×10^7	Aluminum oxide	$<10^{-13}$
SEMICONDUCTORS		**POLYMERS**	
Silicon	4×10^{-4}	Polystyrene	$<10^{-14}$
Germanium	2×10^0	Polyethylene	10^{-15}-10^{-17}
GaAs	10^{-6}		
	semiconductors		**insulators**

- Energy Band Structure in Solids:
  - The electrical properties of a solid material are a consequence of its electronic band structure
    - The arrangement of the outermost electron bands and the way in which they are filled with electrons

The various possible electron band structures in solids at 0 K:



metals such as copper, in which electron states are available above and adjacent to filled states, in the same band.

The electron band structure of metals such as magnesium, wherein there is an **overlap** of filled and empty outer bands.

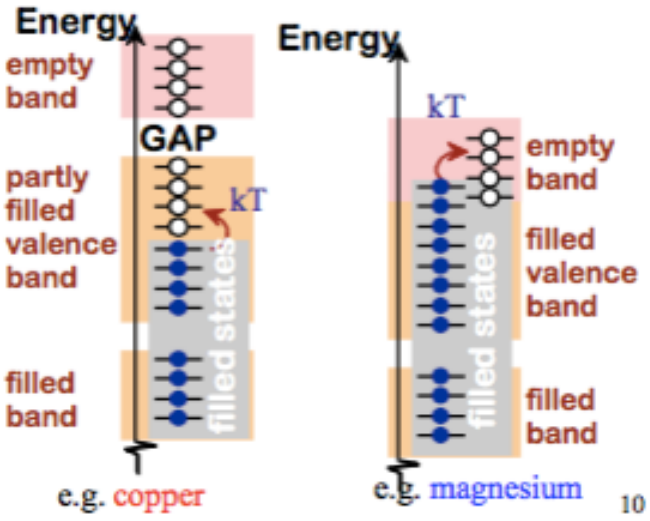
Insulators: the filled valence band is separated from the empty conduction band by a relatively **large** band gap (2 eV).

Semiconductors: same as for insulators except that the band gap is relatively **narrow** (2 eV).

- Conduction and Electron Transport:
  - Only electrons with energies greater than the Fermi energy E_f (free electrons) may be acted on and accelerated when the electric field is applied
    - Holes have energies less than E_f and also participate in electronic conduction
    - The electrical conductivity depends on the number of free electrons and holes

- **Metals:**
  - Thermal energy (kT) puts many electrons into a higher energy state.

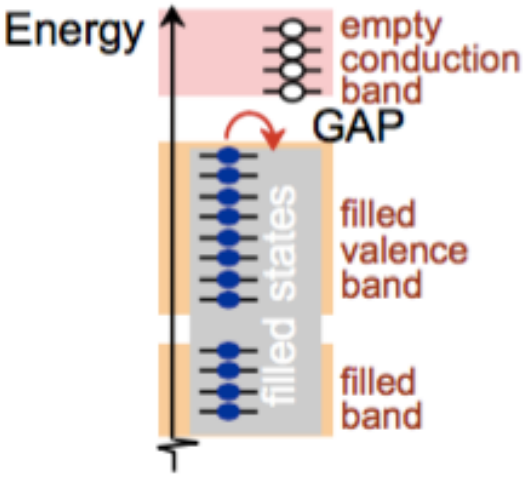
- **Energy States:**
  - for metals the nearby energy states are accessible by thermal fluctuations.

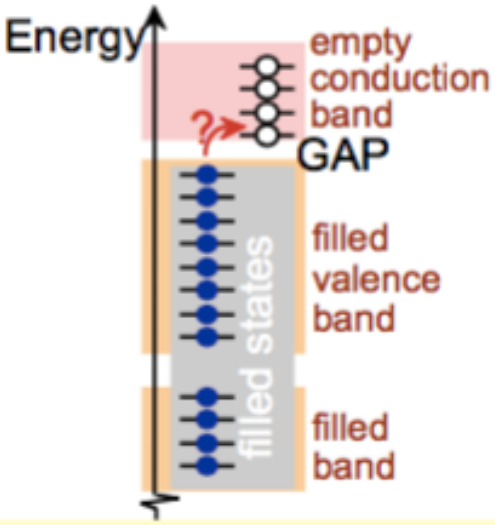


10

- **Insulators:**
  - -- wide band gap (> 2 eV)
  - -- few electrons excited across band gap

- **Semiconductors:**
  - -- narrow band gap (< 2 eV)
  - -- more electrons excited across band gap





The larger the band gap, the lower is the electrical conductivity at a given temp.

- Metals: Electron Mobility
  - Imperfections increase resistivity:
    - Grain boundaries

- Dislocations
- Impurity atoms
- Vacancies

  - These act to scatter electrons so that they take a less direct path
  - Resistivity increases with temperature, impurity concentration and %CW

$$\rho_{total} = \rho_{thermal} + \rho_{impurity} + \rho_{def}$$

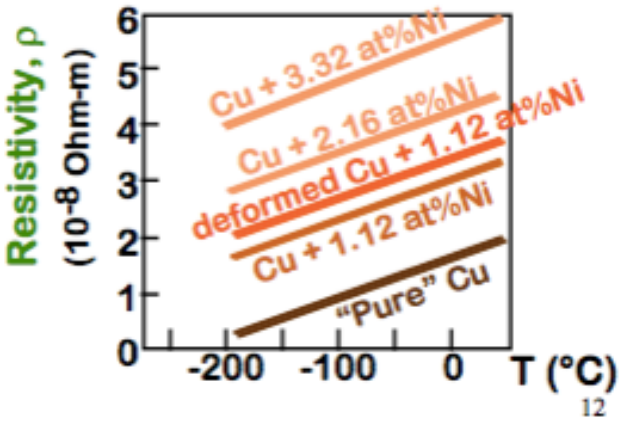
$$\rho_{thermal} = \rho_o + aT$$

Matthiessen's rule

Where ρ_o and a are constants for each metal.

T ↑ → vibration and lattice defects ↑ → electron scattering ↑

%CW ↑ → dislocation concentration ↑ → resistivity ↑



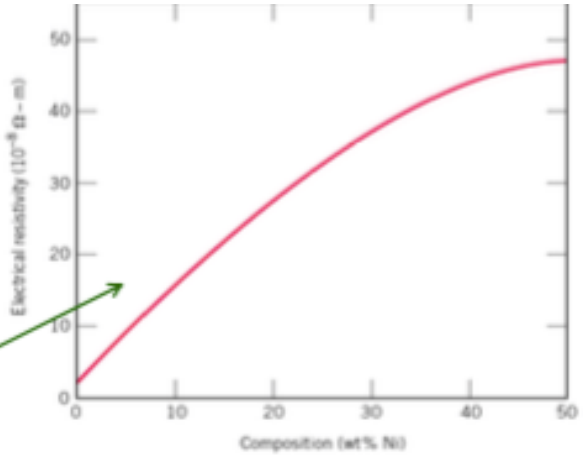
- Influence of Impurity:

$$\rho_{total} = \rho_{thermal} + \rho_{impurity} + \rho_{def}$$

$$\rho_{impurity} = Ac_i(1-c_i)$$

Where c_i is impurity concentration in atomic % and A is constant.

Ni atoms scatter the electrons → ρ ↑



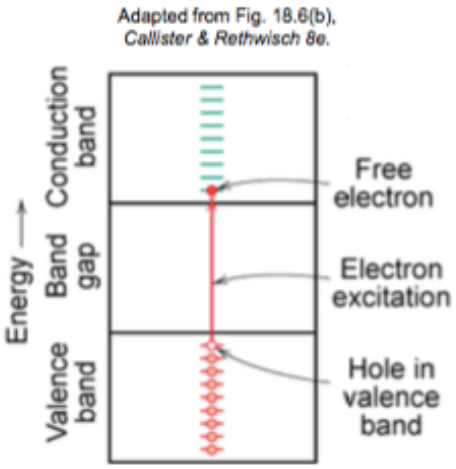
The effect of Ni impurity additions on the room temp. resistivity of Cu.

For a two phase alloy a rule of mixtures applies and the impurity reisistivity can be estimated as:

$$\rho_{impurity} = \rho_a V_a + \rho_\beta V_\beta$$

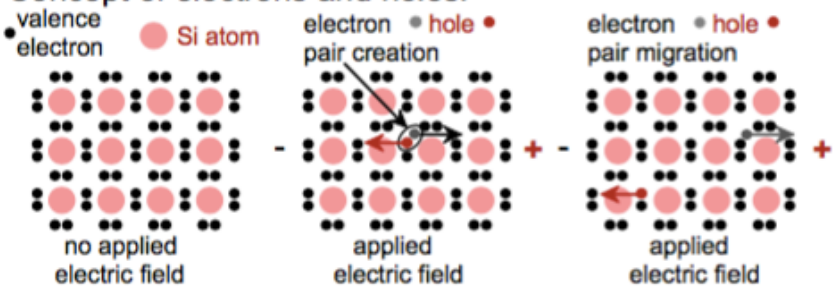
V's and ρ's are the volume fraction and individual resistivities for each phase.

- Charge Carriers in Insulators and Semiconductors:
  - Two types of electronic charge carriers
  - Free electron:
    - Negative charge
    - In conduction band
  - Hole:
    - Positive charge
    - Vacant electron state in the valence band
  - Move at different speeds – drift velocities
- Semiconductors:
  - As temperature increases, conductivity increases
  - Opposite to metals
  - For every electron excited into the conduction band there is left behind a missing electron – hole

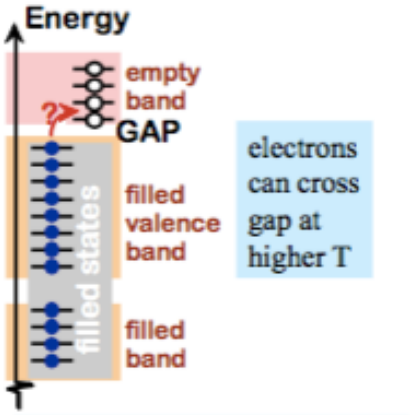


$$\sigma_{undoped} \propto e^{-E_{gap}/kT}$$

- Concept of electrons and holes:



Adapted from Fig. 18.11, Callister & Rethwisch 8e.



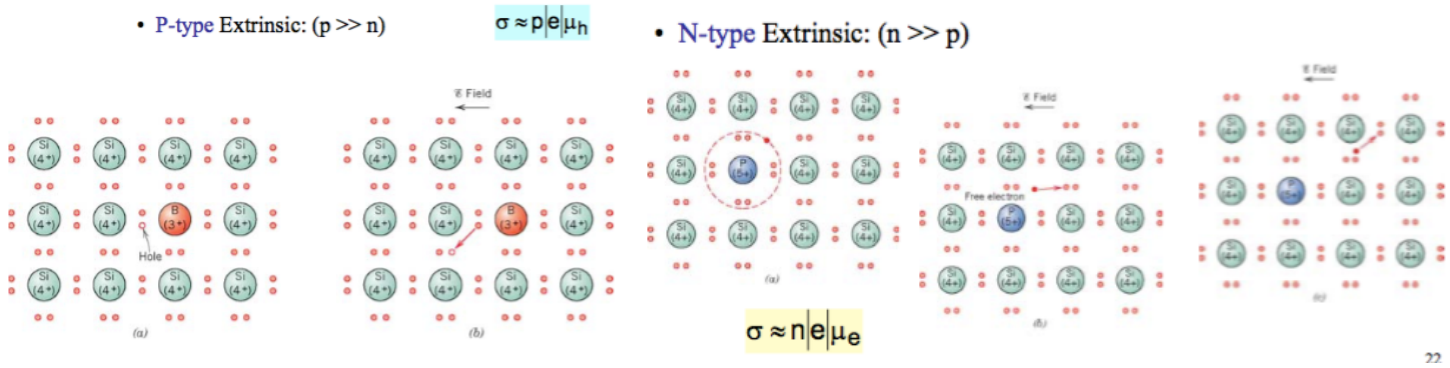
- Electrical Conductivity given by:

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

holes/m^3 — hole mobility — # electrons/m^3 — electron mobility

material	band gap (eV)
Si	1.11
Ge	0.67
GaP	2.25
CdS	2.40

- Intrinsic vs. Extrinsic Conduction:
  - Intrinsic:
    - Number of electrons = number of holes (n=p)
  - Extrinsic:
    - Number of electrons not equal to number of holes
    - Occurs when impurities are added with a different number of valence electrons than the host



- Summary:
  - Electrical resistance is:
    - A geometry and material dependent parameter
  - Electrical conductivity and resistivity are:
    - Material parameters and geometry independent
  - Conductors, semiconductors, and insulators
    - Different in whether there are accessible energy states for electrons
  - For metals, conductivity is increase by:
    - Reducing deformation
    - Reducing imperfections
    - Decreasing temperature
  - For pure semiconductors, conductivity is increase by:
    - Increasing temperature
    - Doping (adding B to Si (p-type) of P to Si (n-type))

Chapter 19
Thermal Properties

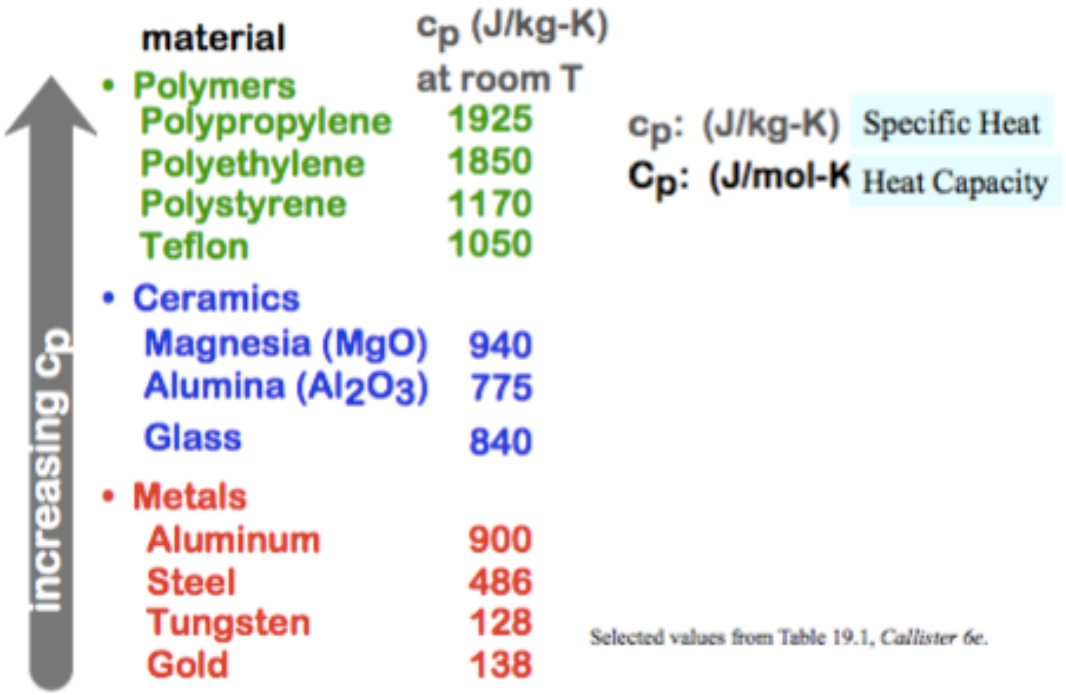
- Heat capacity:
  - The ability of a material to withstand heat
- Two ways to measure:
  - C_p – constant pressure
  - C_v – constant volume
  - C_p usually > C_v

• Heat capacity has units of : $\frac{J}{mol \cdot K}$

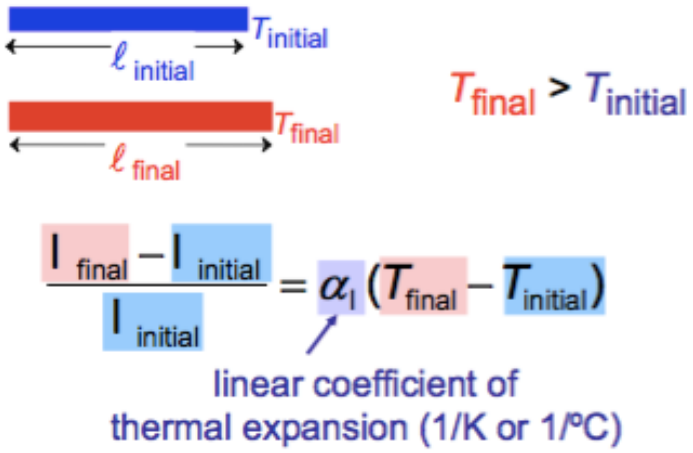
• Specific heat, c, has typical units of: $\frac{J}{kg \cdot K}$

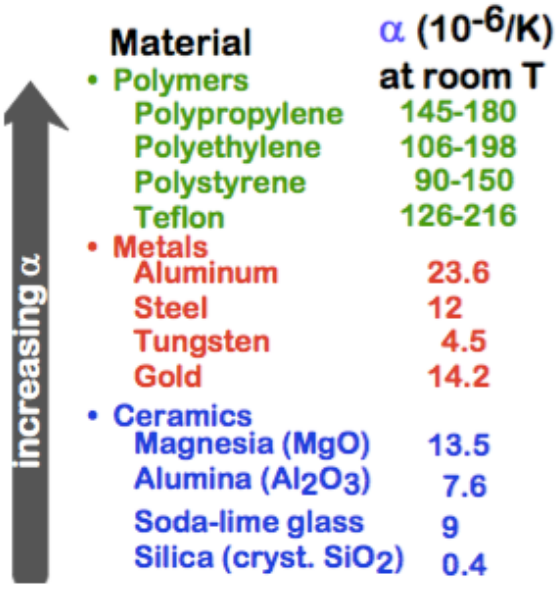
Mech 221 – Notes #19

- Heat capacity increases with temperature
- Reaches a limiting value of 3R
- R = 8.31 J/mol*K
- Atomic View:
  - Energy is stored as atomic vibrations
  - As T goes up, so does the average energy of atomic vibrations



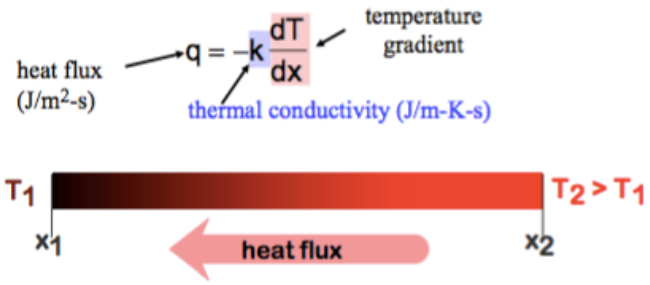
- Thermal Expansion:
  - Materials change length when temperature is changed

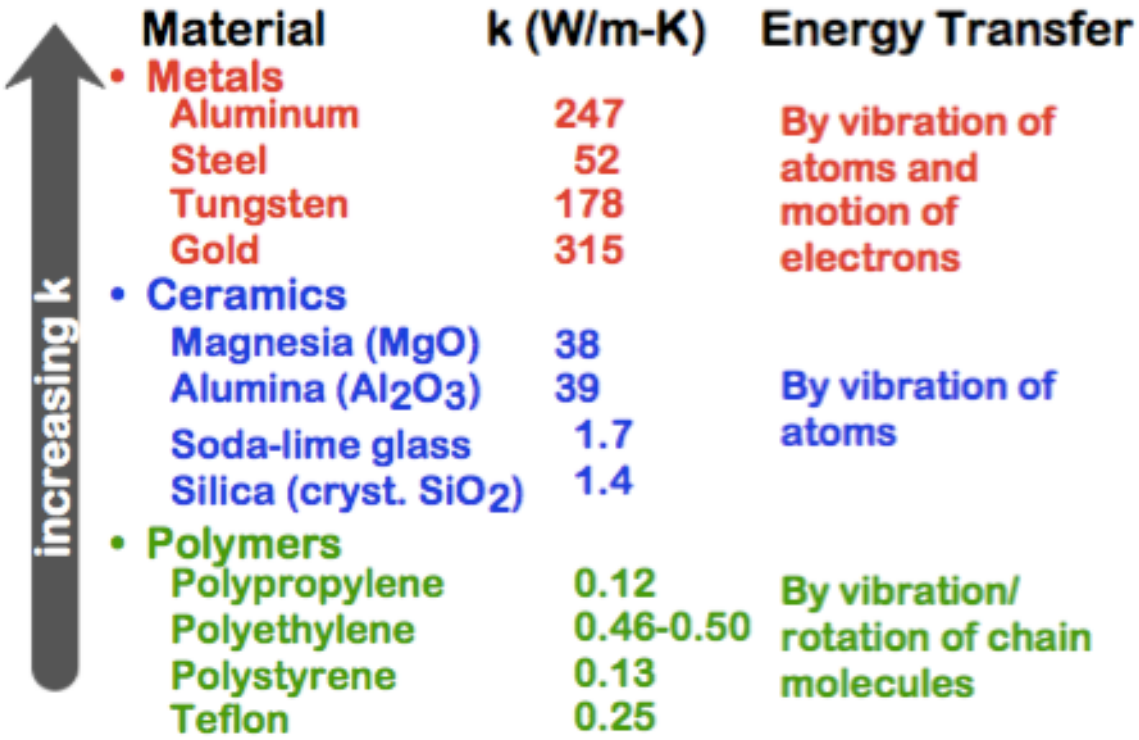




  - Polymers have more bonds, thus expand more

- Thermal Conductivity:
  - The ability of a material to transfer heat
  - Fourier's law
  - Atomic view:
    - Atomic vibrations in hotter region carry energy to cooler regions



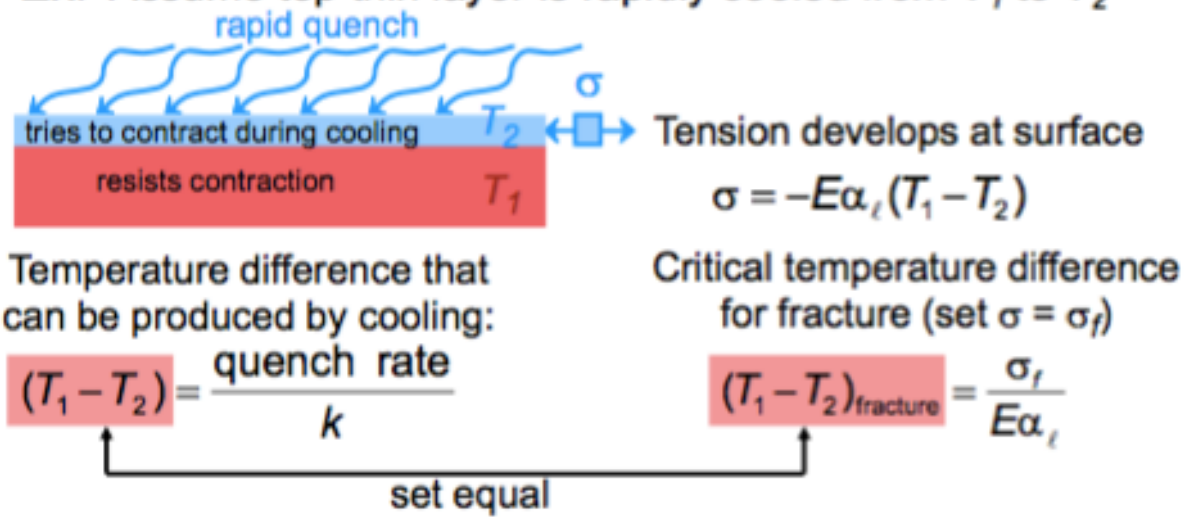


- Thermal Stresses:
  - Occur due to:
    - Continual thermal expansion and contraction
    - Temperature gradients that lead to differential dimensional changes

$$\text{Thermal stress} = \sigma = E\alpha_\ell (T_0 - T_f) = E\alpha_\ell \Delta T$$

- Thermal Shock Resistance:
  - Occurs due to rapid heating and cooling

- Ex: Assume top thin layer is rapidly cooled from T_1 to T_2



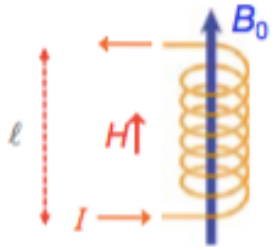
- $(\text{quench rate})_{\text{for fracture}} = \text{Thermal Shock Resistance } (TSR) \propto \frac{\sigma_f k}{E\alpha_\ell}$
- Large TSR when $\frac{\sigma_f k}{E\alpha_\ell}$ is large

- Summary:
  - A material responds to heat by:
    - Increased vibrational energy
    - Redistribution of this energy to achieve thermal equilibrium
  - Heat capacity:
    - Energy requires to increase a unit mass by a unit temperature
    - Polymers have the largest values
  - Coefficient of thermal expansion:
    - The stress-free strain induced by heating by a unit T
    - Polymers have the largest values
  - Thermal conductivity:
    - The ability of a material to transfer heat
    - Metals have the largest values
  - Thermal shock resistance:
    - The ability of a material to be rapidly cooled and not crack

Chapter 20
Magnetic Properties

- Generation of a Magnetic Field

- Created by current through a coil:



N = total number of turns
ℓ = coil length (m)
I = current (ampere)
H = applied magnetic field (ampere-turns/m)
B_0 = magnetic flux density in a vacuum (tesla)

- Computation of the applied magnetic field, H:

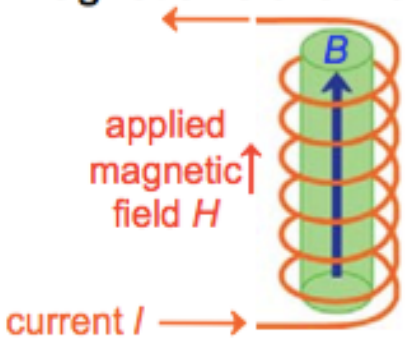
$$H = \frac{NI}{\ell}$$

- Computation of the magnetic flux density in a vacuum, B_0:

$$B_0 = \mu_0 H$$

μ_0: permeability of a vacuum (1.257×10^{-6} Henry/m)

- A magnetic field is induced in the material



B = Magnetic Induction (tesla) inside the material

$$B = \mu H$$

μ: permeability of a solid

- Relative permeability (dimensionless) $\mu_r = \frac{\mu}{\mu_0}$

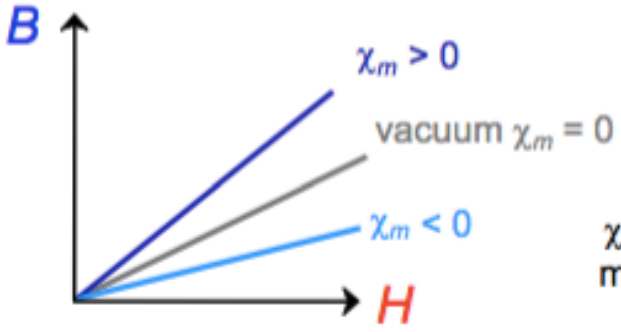
- Magnetization $M = \chi_m H$

  χ_m: Magnetic susceptibility (dimensionless)

- B in terms of H and M $B = \mu_0 H + \mu_0 M$
- Combining the above two equations:

$$B = \mu_0 H + \mu_0 \chi_m H$$
$$= (1 + \chi_m)\mu_0 H$$

μ_0: permeability of a vacuum: (1.26×10^{-6} Henry/m)

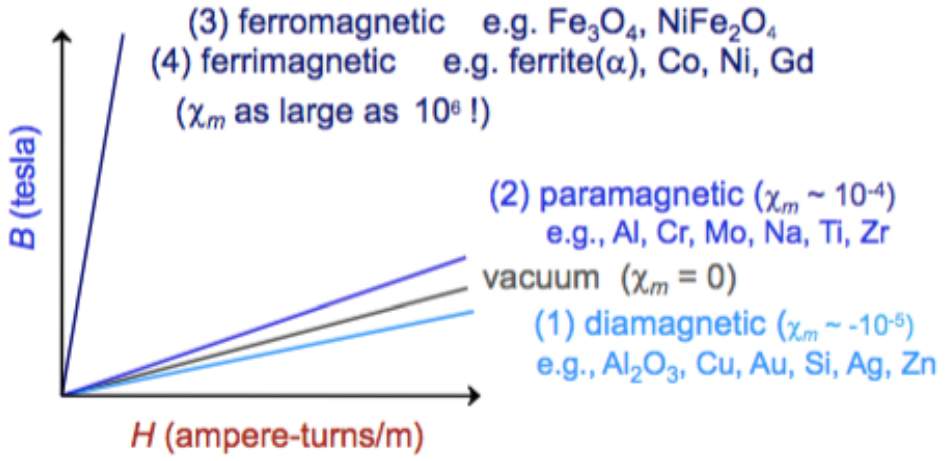


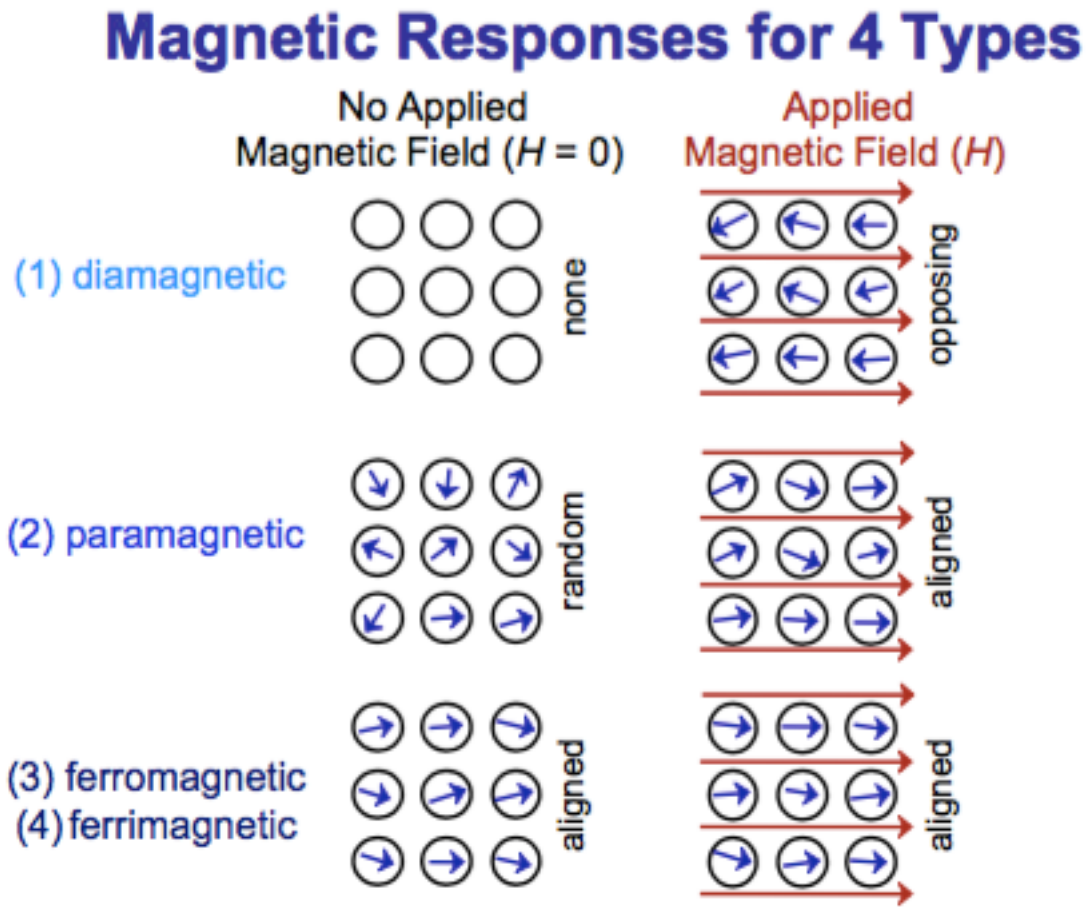
χ_m is a measure of a material's magnetic response relative to a vacuum

- Magnetic Moments:
  - Macroscopic properties are the result of electron magnetic moments
  - Moments come from:
    - Orbital motion around a nucleus
    - Spinning around an axis
- Types of Magnetism:

$$M = \chi_m H$$
$$\chi_m = \mu_r - 1$$

x_m is the magnetic _____. It measures the material's response to a magnetic field relative to a vacuum (*Dimensionless*)





- Summary:
  - A magnetic field is produced when a current flows through a wire coil
  - Magnetic induction (B)
    - An internal magnetic field is induced in a material that is situated within an external magnetic field (H)
    - Magnetic moments result from electron interactions with the applied magnetic field
  - Types of material responses to magnetic fields are:
    - Ferrimagnetic and ferromagnetic – large magnetic susceptibilities
    - Paramagnetic – small and positive magnetic susceptibilities
    - Diamagnetic – small and negative magnetic susceptibilities
  - Types of ferrimagnetic and ferromagnetic materials:
    - Hard – large coercivities
    - Soft – small coercivities
  - Magnetic storage media:
    - Particulate barium-ferrite in polymeric film (tape)
    - Thin film Co-Cr alloy (hard drive)

Chapter 21
Optical Properties

$c = 3 \times 10^8$ m/s

$c = \lambda\nu$

= wavelength*frequency

- Light has both particulate and wavelike characteristics

$$E = h\nu = \frac{hc}{\lambda}$$

E = energy of a photon

λ = wavelength of radiation

ν = frequency of radiation

h = Planck's constant (6.62×10^{-34} J·s)

c = speed of light in a vacuum (3.00×10^8 m/s)

- Summary:
  - When light (radiation) shines on a material, it may be:
    - Reflected, absorbed and/or transmitted
  - Optical classification:
    - Transparent, translucent, opaque
  - Metals:
    - Fine succession of energy states causes absorption and reflection
  - Non-metals:
    - May have full no or partial absorption
    - Color is determined by light wavelengths that are transmitted or re-emitted from electron transitions
    - Color may be changed by adding impurities which change the band gap magnitude
  - Refraction
    - Speed of transmitted light varies among materials
  - Applications:
    - Anti-reflective coatings for lenses
    - Fiber-optic communications
    - Lasers