Physics of Materials:
Bonding and Material Properties
On The basis of Geometry and Bonding (Intermolecular forces)

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Just as before:

How the atoms are arranged
& how they form bond

AFFECTS

Their PROPERTIES
and hence use

ATOMIC Structure Electron configurations	Primary & secondary BONDING

Atomic Structure (Freshman Chem.)

- atom – electrons – 9.11×10^{-31} kg (.000911x 10^{-27} kg)
  $\left.\begin{array}{l}\text{protons}\\ \text{neutrons}\end{array}\right\}$ 1.67×10^{-27} 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 6.023×10^{23} molecules or atoms

  1 amu/atom = 1g/mol

C	12.011
H	1.008 etc.

  Atomic Weight is rarely a whole number – it is a weighted average of all of the natural isotopes of an "Element"

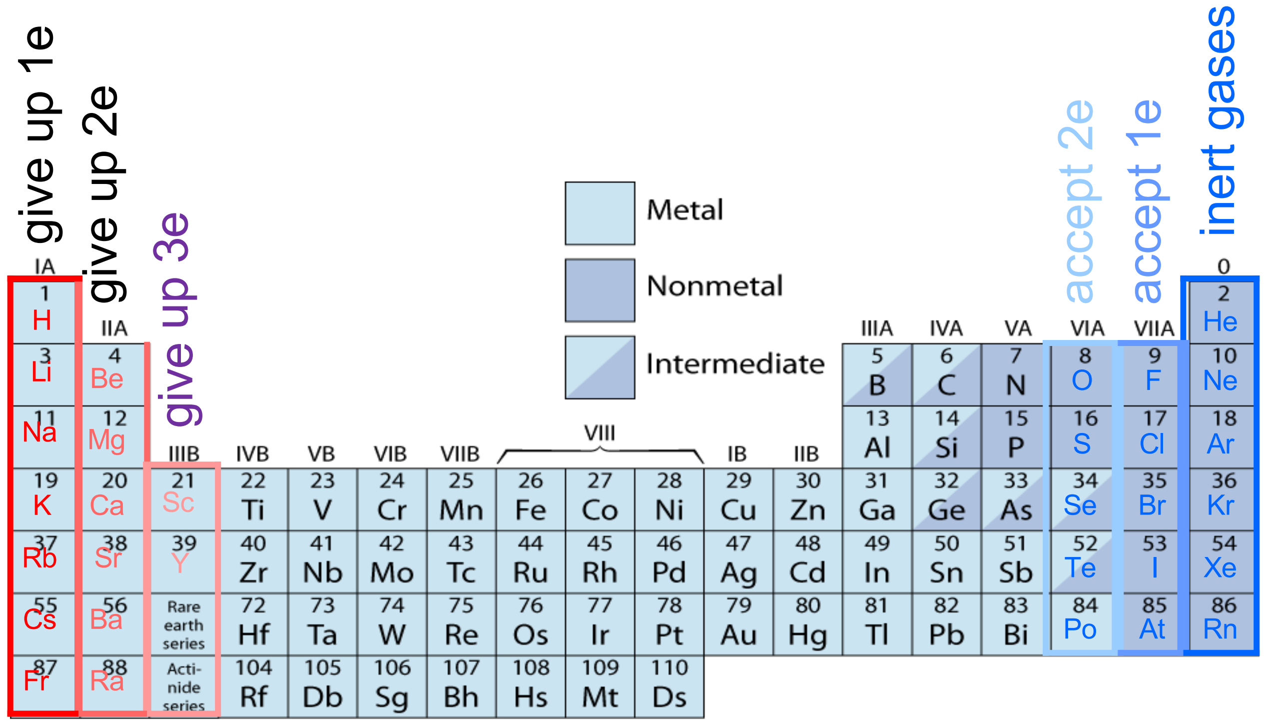
Structure of Matter – an Element

- ✓ Any material that is composed of only one type of atom is called a chemical element, a basic element, or just an element.
- ✓ Every element has a unique atomic structure.
- ✓ Scientists know of only about 118 basic elements at this time. (This number has a habit of changing!)
- ✓ All matter is composed of combinations of one or more of these elements.
- ✓ Ninety-eight of these basic elements occur naturally on or in the Earth (Hydrogen to Uraninum).
- ✓ These elements are pictured in the “Periodic Table”

Structure of Matter

- These outermost or Valence electrons determine all of the following properties concerning an element:
  1) Chemical
  2) Electrical
  3) Thermal
  4) Optical
  5) Magnetic

Matter (or elements) Bond as a result of their Valance states



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

Electronegative elements:
Readily acquire electrons to become - ions.

Molecular/Elemental Bonding

- Bonding is the result of the balance of the force of attraction and the force of repulsion of the electric nature of atoms (ions)
- Net Force between atoms: $F_N = F_A + F_R$ and at some equilibrium (stable) bond location of separation, $F_N = 0$ or $F_A = F_R$
- From Physics we like to talk about bonding energy where:

$$E = \int F dr = \int_{\infty}^{r} F dr$$

Bonding

Primary bonding:

Ionic (transfer of valence electrons)
Covalent (sharing of valence electrons, directional)
Metallic (delocalization of valence electrons)

Secondary or van der Waals Bonding:

(Common, but weaker than primary bonding)

Dipole-dipole
H-bonds
Polar molecule-induced dipole
Fluctuating dipole (weakest)

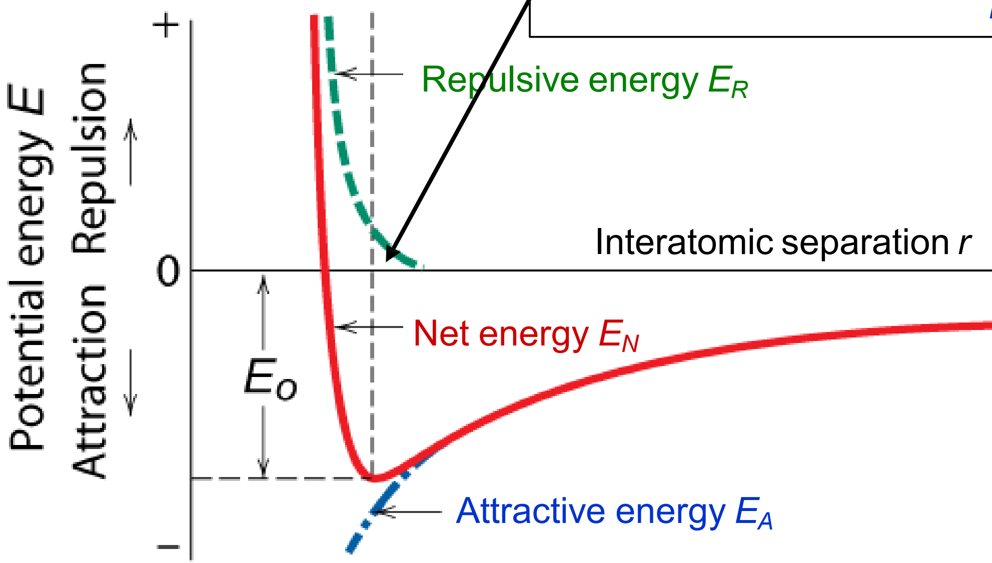
Bonding Energy

Equilibrium separation (r_0) is about .3 nm for many atoms

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

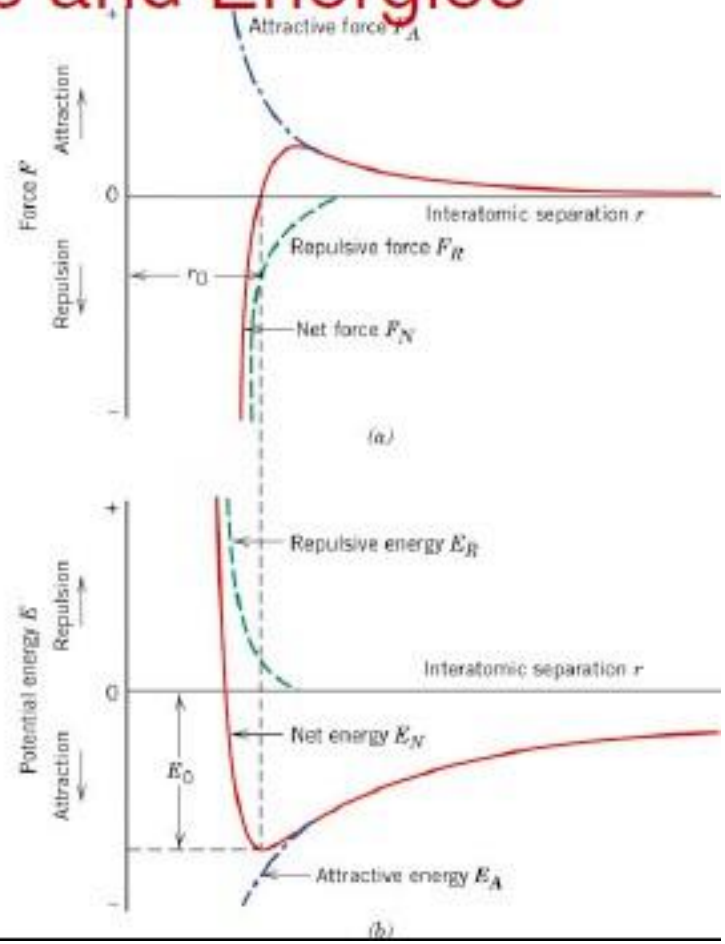
$$E_N = E_A + E_R = -\frac{A}{r} - \frac{B}{r^n}$$

n is 7-9 for most ionic pairs



Bonding Forces and Energies

- Considering the interaction between two isolated atoms as they are brought into close proximity from an infinite separation.
- At larger distances, the interactions are negligible.
- As the atoms approach, each exerts forces on the other.
  - Attractive
  - Repulsive
- Ultimately, the outer electron shells of the two atoms begin to overlap, and a strong repulsive force comes into play.



Bonding Energy, the Curve Shape, and Bonding Type

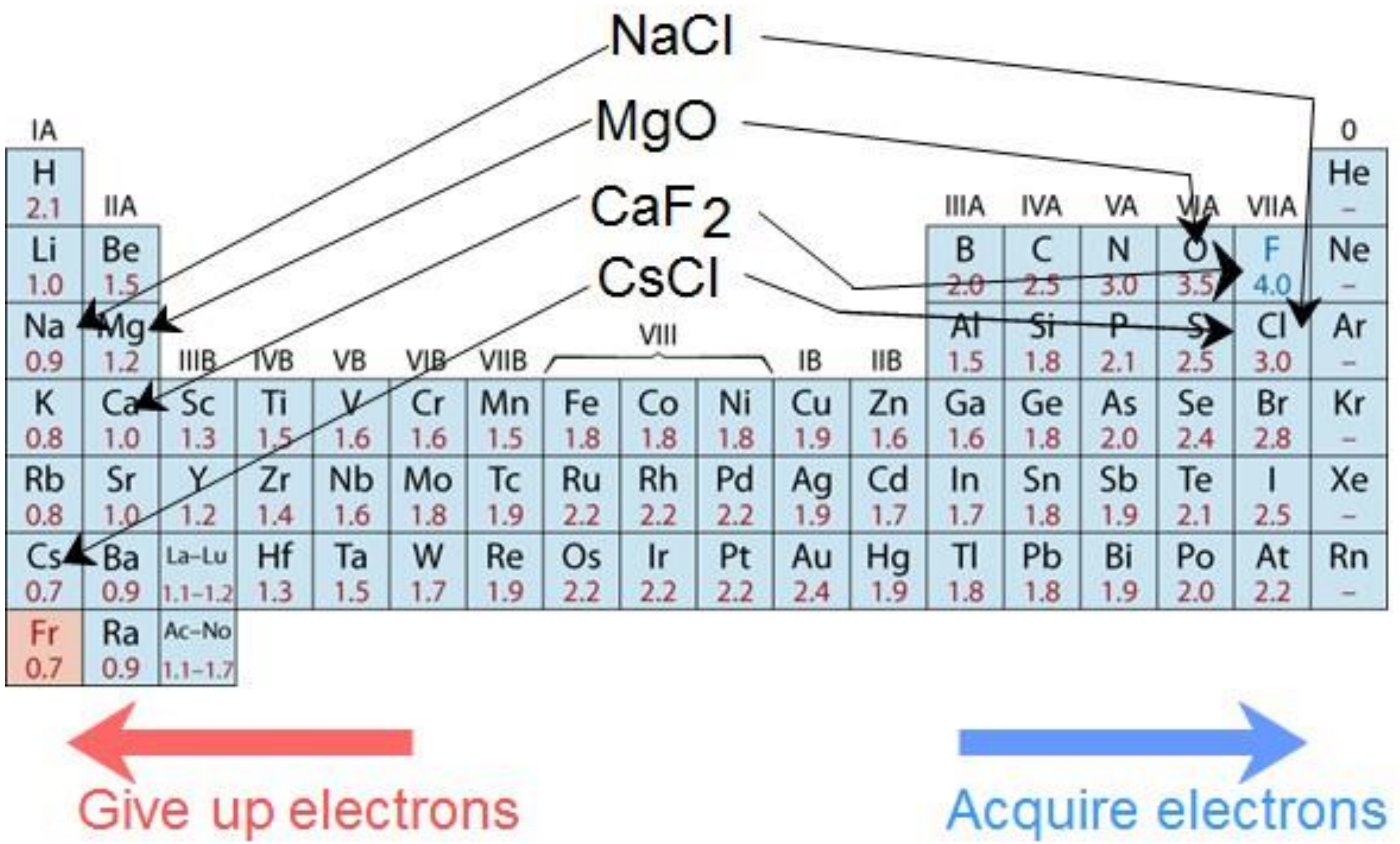
- Properties depend on shape, bonding type and values of curves: they vary for different materials.
- Bonding energy (minimum on curve) **is the energy that would be required to separate the two atoms to an infinite separation.**
- Modulus of elasticity depends on energy (force) versus distance curve: the slope at $r = r_0$ position on the curve will be quite steep for very stiff materials, slopes are shallower for more flexible materials.
- Coefficient of thermal expansion depends on E_0 versus r_0 curve: a deep and narrow trough correlates with a low coefficient of thermal expansion

Bonding Types of Interest:

- **Ionic Bonding**: Based on donation and acceptance of valance electrons between elements to create strong "ions" – CatIONs and AnIONs due to large electro-negativity differences
- **Covalent Bonding**: Based on the 'sharing' of valance electrons due to small electro negativity differences
- **Metallic Bonding**: All free electrons act as a moving 'cloud' or 'sea' to keep charged ion cores from flying apart in their 'stable' structure
- **secondary bonding**: van der wahl's attractive forces between molecules (with + to – 'ends')
  - This system of attraction takes place without valance electron participation in the whole
  - Valence Electrons participate in the bonding to build the molecules not in 'gluing' the molecules together

Ionic Bonding

- Predominant bonding in Ceramics



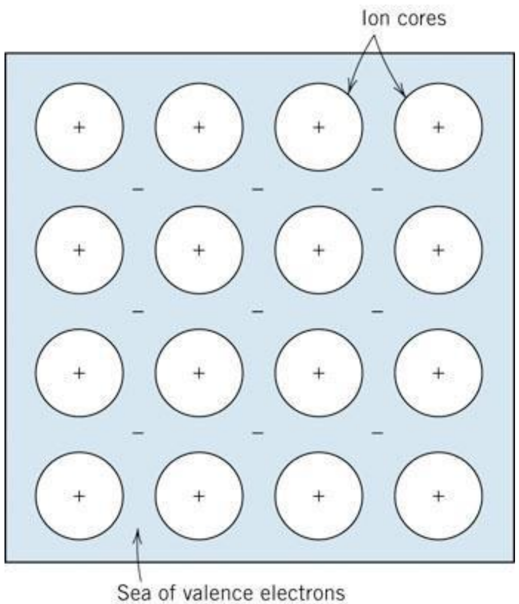
"Electro-negativity" Values for determining Ionic vs. Covalent Bond Character

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Give up electrons

Acquire electrons

Metallic Bonding:

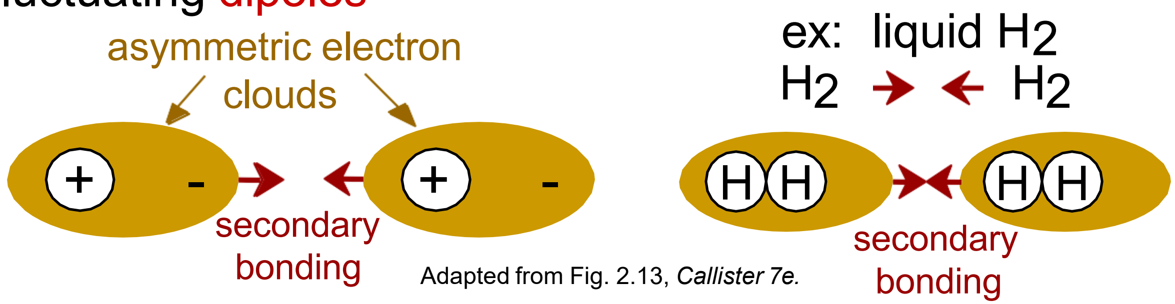


In a metallic bonded material, the valence electrons are “shared” among all of the ionic cores in the structure not just with nearest neighbors!

SECONDARY BONDING

Arises from interaction between “electric” dipoles

- Fluctuating dipoles

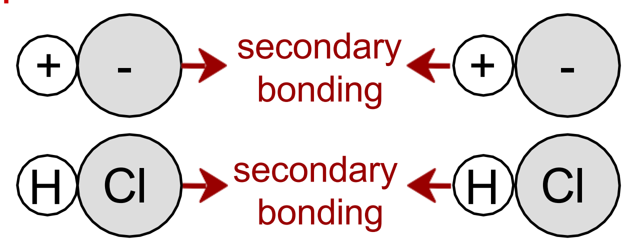


Adapted from Fig. 2.13, *Callister 7e.*

- Permanent dipoles-molecule induced

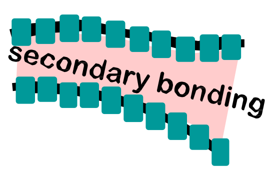
-general case:

-ex: liquid HCl



Adapted from Fig. 2.14, *Callister 7e.*

-ex: polymer



secondary bonding

Summary: Bonding

Type	Bond Energy	Comments
Ionic	Large!	Nondirectional (ceramics)
Covalent	Variable large-Diamond small-Bismuth	Directional (semiconductors, ceramics polymer chains)
Metallic	Variable large-Tungsten small-Mercury	Nondirectional (metals)
Secondary	smallest	Directional inter-chain (polymer) inter-molecular

Bonding and materials properties

- Materials with large bonding energies usually have high melting temperatures.

- There is a correlation between the magnitude of the bonding energy and the state of materials
  - Solids have large bonding energies
  - Liquids tend to have relatively lower energies

- The expansion/contraction during heating/cooling of materials is related to the shape of its E(r) curve.

- A deep and narrow 'trough,' which typically occurs for materials having large bonding energies, usually imply a low coefficient of thermal expansion.

Effect of Bonding on properties: a broad flavour

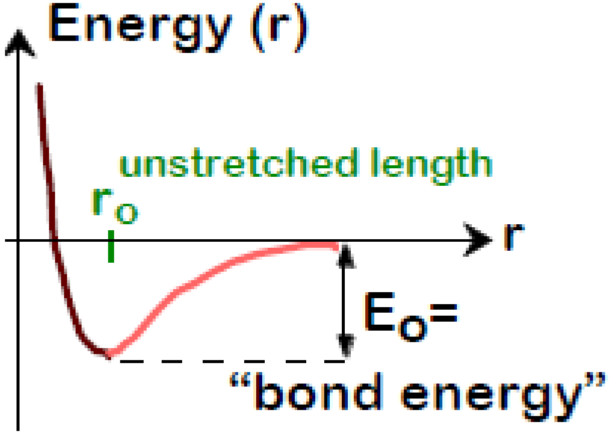
- ✓ Two important contributing factors to the properties of materials is the nature of bonding and the atomic structure.
- ✓ Both of these are a result of electron interactions and resulting distribution in the material.
- ✓ Bonding is an *'easily accessible term'* for the electromagnetic structure of an assemblage of atoms/molecules/ions. The interaction between atoms/molecules/ions may lead to a lowering of the energy of the system→ *the bonded state.*

Bond	Melting point	Hardness (Ductility)	Electrical Conductivity	Examples
Covalent	High	Hard (poor)	Usually Low	Diamond, Graphite, Ge, Si
Ionic	High	Hard (poor)	Low	NaCl, ZnS, CsCl
Metallic	Varies	Varies	High	Fe, Cu, Ag
Van der Waals	Low	Soft (poor)	Low	Ne, Ar, Kr
Hydrogen	Low	Soft (poor)	Usually Low	Ice

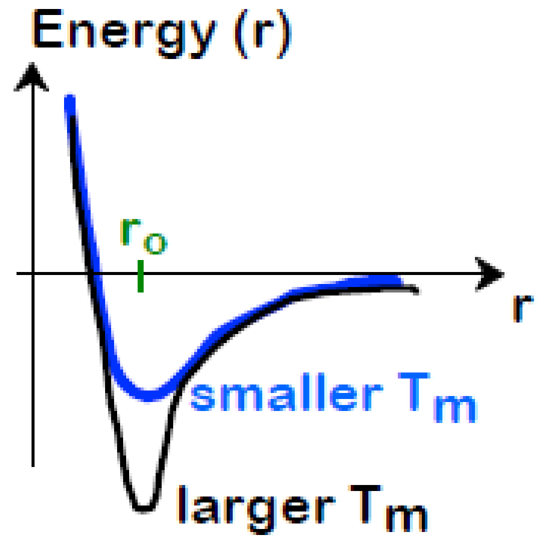
PROPERTIES FROM BONDING: T_M

- Bond length, r

- Bond energy, E_o



- Melting Temperature, T_m

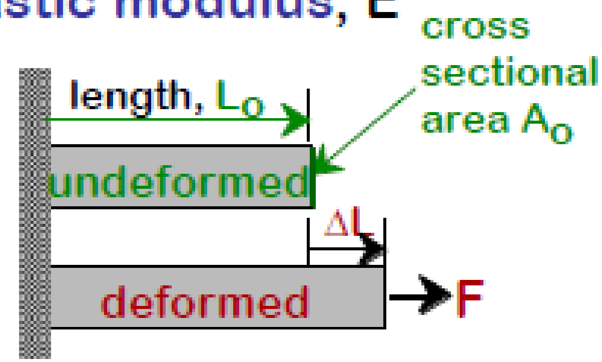


T_m is larger if E_o is larger.

From Callister 6e resource CD.

PROPERTIES FROM BONDING: E

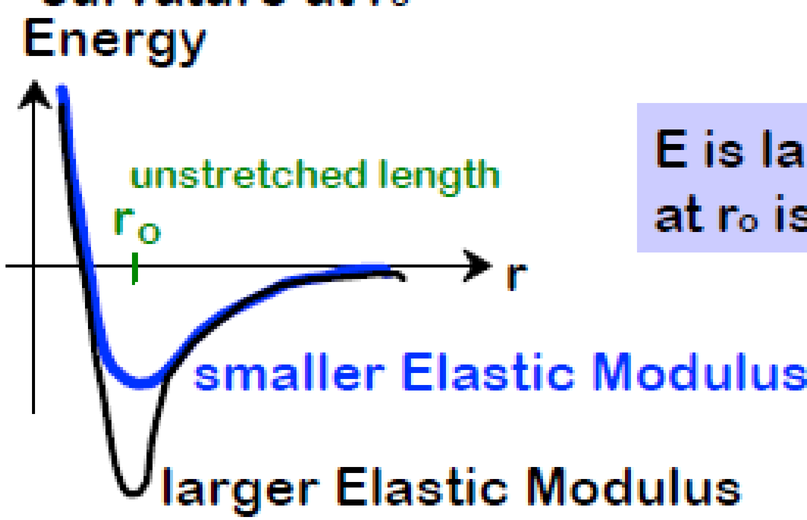
- Elastic modulus, E



Elastic modulus

$$\frac{F}{A_o} = E\,\frac{\Delta L}{L_o}$$

- E ~ curvature at r_o

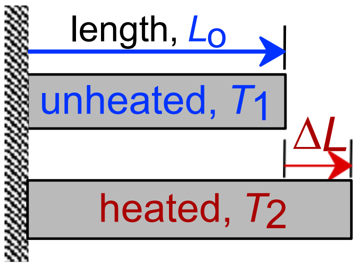


E is larger if curvature at r_o is larger.

From Callister 6e resource CD.

Properties From Bonding : α

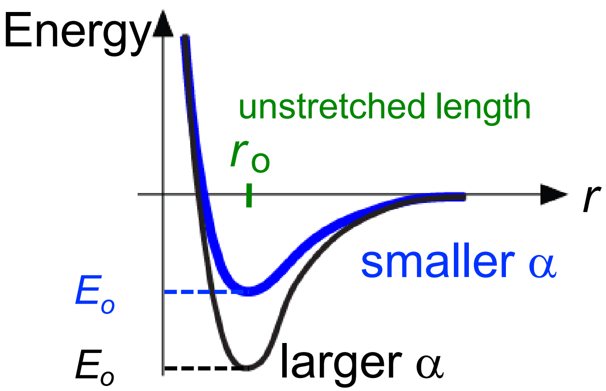
- Coefficient of thermal expansion, α



coeff. thermal expansion

$$\frac{\Delta L}{L_o} = \alpha\,(T_2 - T_1)$$

- α ~ symmetry at r_o



α is larger if E_o is smaller.

SUMMARY: BONDING and Materials' properties

Ceramics

(Ionic & covalent bonding):

Large bond energy

large T_m

large E

small α

Metals

(Metallic bonding):

Variable bond energy

moderate T_m

moderate E

moderate α

Polymers

(Covalent & Secondary):

Directional Properties

Secondary bonding dominates

small T

small E

large α