Chapter 2: Atomic Structure and Interatomic Bonding

Goals

– Define basic concepts (*refortify* your chemistry):
  - Filling of Atomic Energy Levels: Pauli Exclusion Principle
  - Atomic Orbitals (s-, p-, d-, and f- type electrons)
  - Types of Bonding between Atoms
  - The Periodic Table (and solid state structures)
  - Bond Energy Curves

– Describe how types of bonding affect Bond-Energy Curves.
– Describe how the Bond-Energy Curve describes macroscale properties.

Learning Objective

– Know, and be able to use, filling of atomic levels to get ionic electron configurations of atoms.
– Use the Bond-Energy Curve to describe qualitatively the difference types of materials and their macroscale properties.
– Know the origins of stress and strain, melting temperature, and thermal expansion.

How are Macroscopic Properties related to Bonding?

Chapter 2: R*efortify* your chemistry - Atomic scale structures.

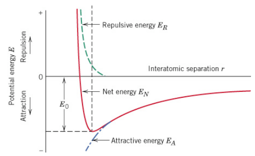
- Structure of atoms
  - A. Protons, neutrons, and electrons
  - B. Electron configurations: shells and subshells
  - C. Valence states
  - D. Atoms and the periodic table
- Types of bonding between atoms
  - A. Ionic bonding
  - B. Covalent bonding
  - C. Metallic bonding
  - D. Secondary bonds
    1. Permanent dipoles and the hydrogen bond
    2. Temporary dipoles and the van der Waals bond
- Influence of Bond Type on Engineering Properties
  - A. Brittle versus ductile behavior
  - B. Electrical conductivity
  - C. Melting temperature of polymers

How are Macroscopic Properties related to Bonding?

The Bond-Energy Curve

A. Dependence of potential energy on atomic spacing
  1. Long-range attraction versus short-range repulsion
  2. Superposition of attractive and repulsive potentials

B. The bond-energy curve and engineering properties
  1. Melting temperature
  2. Elastic modulus
  3. Thermal expansion coefficient



- How are macroscopic properties (mechanical, structural, thermal, electrical, optical, ...) most simply related to bonding?
- Are there directionality dependencies in materials response?
- Can point defects (i.e., vacancies or impurities) change such bonding related properties?

Atomic Structure and Periodic Table

Electrons

The behavior of electrons can be correctly described only by the theory of *quantum mechanics*, which for most of you have or will be covered in physics/ECE course.

For this class, we will simply borrow some of the major results of the theory so that we can adequately understand the behavior of electrons.

Notably, the Bohr model of the atom is incorrect as it does not describe the dual *particle* (e.g., photo-electric effect) and *wave* (e.g., electron diffraction) features of electron scattering.

Major Results from Quantum Mechanics

- Electrons sometimes behave like *particles.*
  - they can scatter off objects and they have momentum, p=h**k**/2π.
- but sometimes they behave like *waves.*
  - they don't exist uniquely at any given location, but are spread out in space.
  - they can interfere with each other, and even form standing waves in a cavity.
  - their energy and momentum depend on their wavelength.
- When orbiting an atomic nucleus, electrons are best described by energy waves with a specific amplitude and wavelength, and these specific values may be found by solving *Schrodinger's equation*.
- Solutions of Schrodinger's Eq. are catalogued in terms of *quantum numbers* (three integers, plus a fourth that is either 1/2 or -1/2).
- These quantum numbers are: ***n, l,*** and ***m,*** and ***spin*** (1/2 or -1/2).
  can be collected as set of integers and the e⁻ spin, e.g., **210(1/2)**

Electron Quantum Numbers

Principle, *n*: **Allowed values of *n* are 1, 2, 3…**
- Roughly associated with electron's energy
  - higher values of *n* mean larger (less favorable) energies.
- The value of *n* also tells how "far" from the nucleus the electron is
- *n* is also called the electron shell (*n*=1 is the first shell, etc.)

Angular momentum, *l*: **Allowed values of *l* are 0 to (*n*-1)**
- related to angular momentum of the electron in its orbit
- *l* is also called the electron orbital within a given shell
- Each value of *l* is assigned a letter of the alphabet:

l value	letter	Why?
0	s	sharp
1	p	principal
2	d	diffuse
3	f	fundamental

Magnetic, *m*: **Allowed values of *m* are -*l* to +*l* (2*l* + 1 distinct values)**

Spin, m_s: **Allowed values of m_s are -1/2 (spin-up) and +1/2 (spin-down)**.

Pauli Exclusion Principle: No two electrons in the same system can share the same four (n, l, m, m_s) quantum numbers!

Electron States

see, e.g., Table 2.1: The Pauli exclusion principle forces there to be only a certain number of electrons in each *shell* and *orbital*.

shell *n*	orbital (0 to *n*-1)	*m* values (*m* = -*l* to *l*)	*spin* ($m_s = \pm 1/2$)	# electrons in shell
1	0 (1*s*)	1	2	**2**
2	0 (2*s*)	1	2	1x2+3x2= **8**
	1 (2*p*)	3 ($2p_x$, …)	2	
3	0 (3*s*)	1	2	1x2+3x2+5x= **18**
	1 (3*p*)	3 ($3p_x$, …)	2	
	2 (3*d*)	5 ($3d_{xy}$, …)	2	
4	0 (4*s*)	1	2	1x2+3x2+5x2 +7x2= **32**
	1 (4*p*)	3 ($3p_x$, …)	2	
	2 (4*d*)	5 ($3d_{xy}$, …)	2	
	3 (4*f*)	7 ($4f_{xyz}$,…)	2	

s bonds

s-p bonds

s-p + d bonds

Quantum Mechanics: Hydrogen Atom (spherical 1-electron atom)

Schrödinger's Eq. for spherical atom is a separable differential eq.

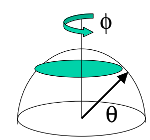
$$H\psi=(T+V)\psi=E\psi$$

choosing separable (spatial and angular) form for atom
where $\psi(r,\theta,\phi)=R_\ell(r)Y_{\ell m}(\theta,\phi)$

Radial PDE $$\left(-\frac{\hbar^2}{2\mu r^2}\right)\left(\frac{\partial^2}{\partial r^2}\right)(rR)+\left[\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}+V(r)\right](rR)=E(rR)$$

Angular PDE $$\Lambda^2 Y_{\ell m}=\ell(\ell+1)\hbar^2 Y_{\ell m}$$

$x=r\sin\theta\cos\phi$
$y=r\sin\theta\sin\phi$
$z=r\cos\theta$



$$Y_{\ell m}(\theta,\phi)=\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}\,P_{\ell m}(\theta)(-1)^m e^{im\phi}\quad(m\geq 0)$$

See P.W. Atkins, Molecular Q.M. 2nd Edition

Orbital shapes come from spherical harmonics, Y, given by Legendre polynomials, P, and $e^{im\phi}$.

Electrons have sharp energy states with diffuse orbits

Unlike Bohr model orbits are given probabilistically..

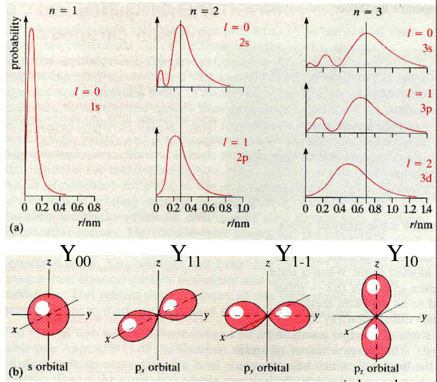
- For each (n, l, m, m_s) radial distribution is given by $|R_{nl}(r)|^2$, and electrons inhabit much more space around the nuclei.
- e.g., n - 1 tells # of nodes.
- The angular distribution is given by the shapes of the Y_{lm} dictated by the l and m.

$Y_{00} \sim 1.$

$Y_{10} \sim z = \cos\theta.$

$Y_{1\text{-}1} \sim y = \sin\phi\sin\theta.$

$Y_{11} \sim x = \sin\phi\cos\theta.$

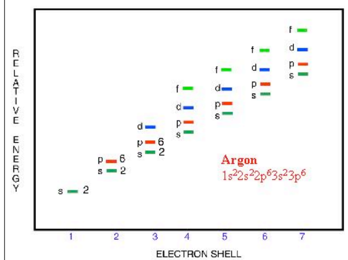


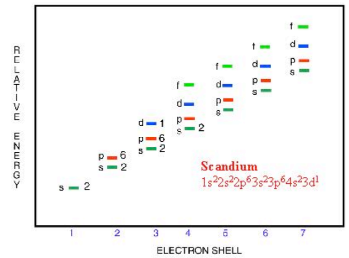
no ϕ dependence

Energy Shell Diagrams

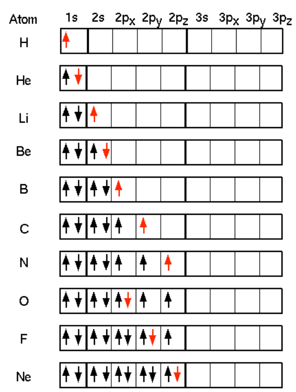
Note: *4s state* fills *before 3d state*, i.e. $(n+1)$-s state fills before n-d state, otherwise states fill according to increasing quantum numbers (n,l).

Note: a similar thing happens for *f* state also. It fills before some of the d-states.



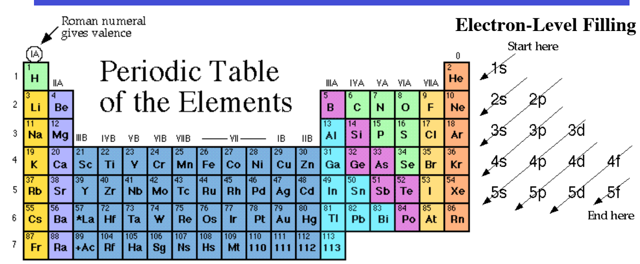


Periodic Table: Orbital Filling



⇐Example of Pauli Exclusion Principle no 2 electrons share the same quantum numbers for the same (n,l) at same E.

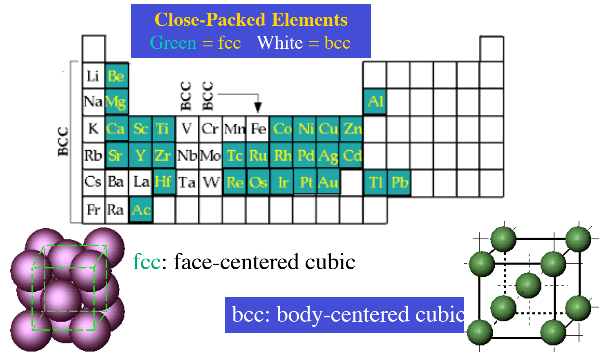
Periodic Table: Orbital Filling



- 4s is slightly lower in energy and fills first, but is removed first as it is less tightly bound (remove electron in higher lowest quantum levels first).
- Electrons in higher states, which resides farther from nuclei, come off first.

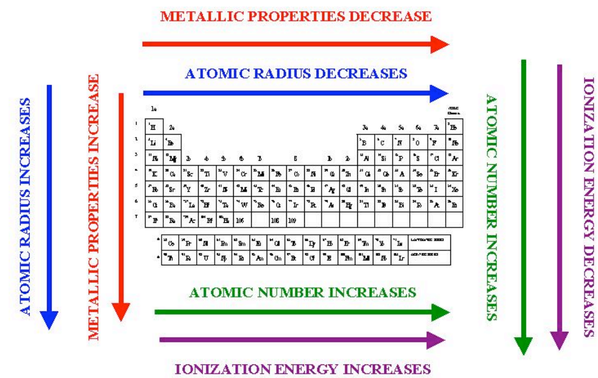
Consider Mn ($1s^22s^22p^63s^23p^63d^54s^2$), what is Mn^{2+} state?

Periodic Table: Close-Packed Structures

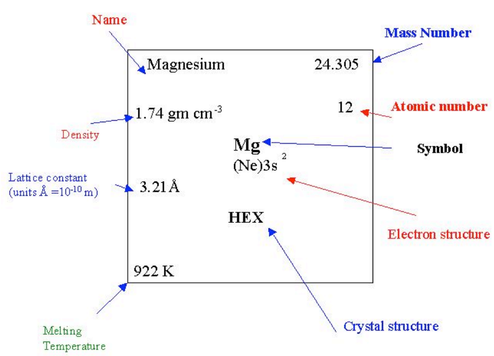


bcc Mn is metastable. Alpha-Mn has many atoms per cell.

Summary of Periodic Table Trends

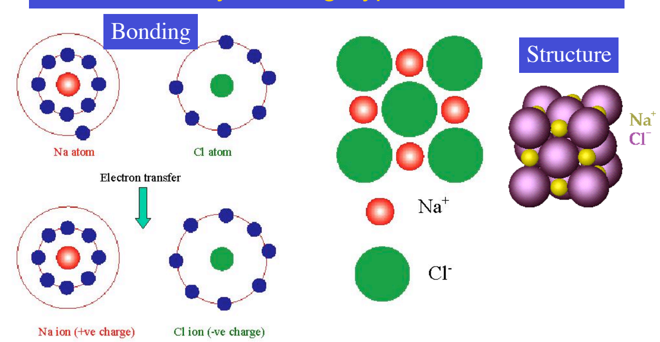


Periodic Table Information



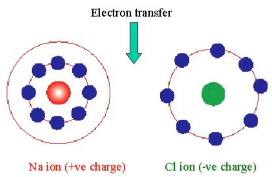
- **Avogadro's Number: 1 mole has 6.023 x 10^{23} atoms (or molecules).**
- **1 amu/atom (or molecule) = 1 g/mol (e.g. at. wt. of Fe is 55.85 amu/atom or g/mol)**

Primary Bonding Types: IONIC

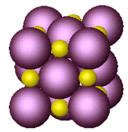


- Occurs for electronegative (positive) elements that can form **close-shell configurations**. Requires work to remove (add) e- from Na (to Cl-).
- Electronegativity plays a role here, e.g., H-F.

Primary Bonding Types: IONIC



Structure

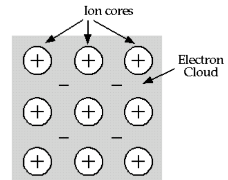


Why does becoming ionic change sizes of atoms?

Structure is determined by electrostatic *attraction* $E_A = -A/r$ (Coulomb's Law) and collapse is prevented by electronic and nuclear *repulsion* $E_R = +B/r^n$.

For closed-shell gases (Ar, Kr,…) n~12. Generally need quantum mechanics.

Primary Bonding Types: METALLIC



Metals share so-called *itinerant* electrons, or a "sea of electron" (electron-glue).

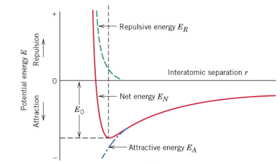
Itinerant electrons move (or "hop") about spending more time at an atom if they are more tightly bound, as with d-state, and less time if they are less bound, as with s-state.

Metallic bonds may be weak or strong

Bonding energies (E_0): range from
68 kJ/mol (0.7 eV/atom) for Hg
to 850 kJ/mol (8.8 eV/atom) for W.

Melting temperatures ($T_{melt} \sim E_0$):
-39 C for Hg and 3410 C for W.

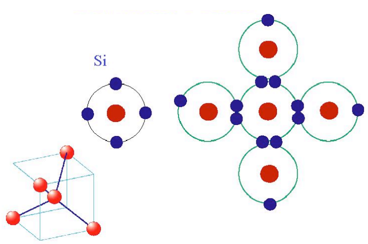
Stronger bonds lead to higher melting temperature:
atomic scale property ⇒ macroscale property.



Primary Bonding Types: COVALENT

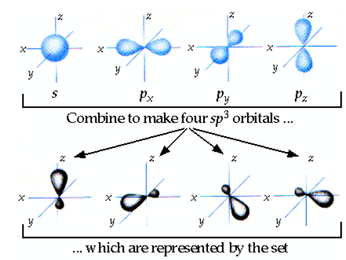
Covalent bonds share electrons amongst *adjacent* atoms.

For Si, the electronic filling is $3s^2 3p^2$.
- To fill up all the remaining p-states in bulk Si, 4 electrons are required.
- One way to due this is *promote* one of the *3s* electrons into a p-state, creating a sp^3 **hybrid** state, which has tetrahedral symmetry due to bond.



Primary Bonding Types: COVALENT

The sp^3 **hybrid** (109.5⁰) bonds shows directionality.



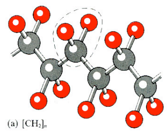
We start with 4 atomic states:
s, p_x, p_y, and p_z
and form linear combination to get estimate of molecular orbitals.

The sp^3 hybrids are higher in energy than separate s- and p- atom states (need promotion energy), but the molecule (solid) is lower in energy.

For sp^3 we still have 4 states to fill:
$s + p_x + p_y + p_z$
$s - p_x + p_y + p_z$
$s + p_x - p_y + p_z$
$s + p_x + p_y - p_z$

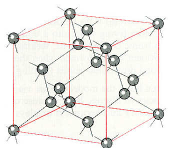
Sum together, they look like this!
Again, bonding determines structure, which also affects properties.

Structures from sp^3 hybrid tetrahedral bonds



(a) $[CH_2]_n$

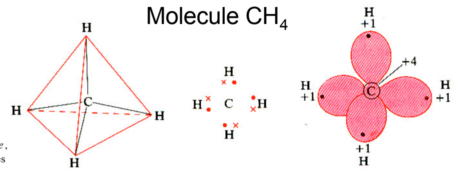
Polymers $[CH_2]_n$



(b) diamond

Diamond

Molecule CH_4



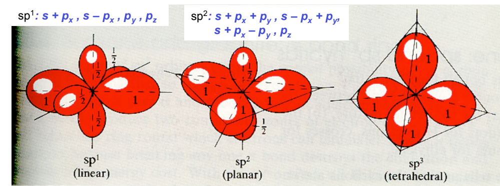
(a) tetrahedral shape (b) shared electrons (c) orbitals

Chapter 3 *Materials Principles and Practice*, Materials in Action Series, edited by Charles Newey and Graham Weaver.

Primary Bonding Types: COVALENT

The sp-hybrids can have 3 different shape, showing bond directionality.
(Numbers on orbitals indicate the fraction of electrons available in bonding lobe.)

sp^1: $s + p_x$, $s - p_x$, p_y, p_z sp^2: $s + p_x + p_y$, $s - p_x + p_y$, $s + p_x - p_y$, p_z



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- Bonds formed between atoms that have sp-hybrid orbitals are highly covalent (strong and directional) and are called *sigma* (for strong) bonds, with electron density on the line between the atoms.
- The ones out of the sigma-bond plane are called *pi* bonds, with no density on the line connecting the atoms.

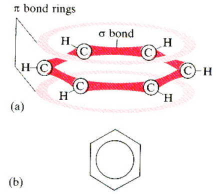
Primary Bonding Types: COVALENT

• Materials with *pi* bonds have less electrons (not as many shared) between the atoms compare to *sigma* bonds, and therefore are weaker bonds.

• Hence, the electrons are more mobile (i.e. delocalized), giving rise to the conduction in carbon-graphite, for example.

• Benzene (C_6H_6) has *sigma* sp^2 120^0 bonds in plane and *sigma* p_z orbitals out of plane.

• Acetylene (C_2H_4) has sp^1 180^0 bonds.



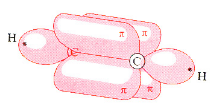


Figure 3.25 Acetylene molecule

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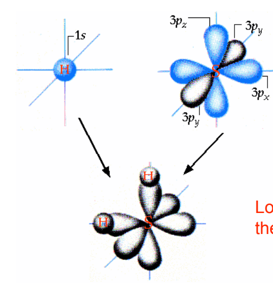
Primary Bonding Types: COVALENT

Of course, not all atoms with only s and p states form hybrids to get covalent bonds. *Hydrogen-Sulfide*, H_2S, does not need to promote hybrid orbitals to form a strong covalent bond.

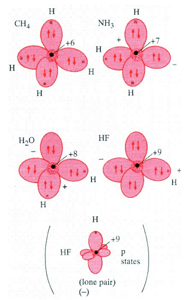


Lower energy bond configuration as there is no need to promote to hybrid.

Self-Assessment Questions

Types of Bonding Lead to Specific Charge Distributions and Polar Molecules

Consider the "Simple Molecules" H with C, N, O, and F:
Configurations are $1s^2\ 2s^2$ plus **$2p^2$** for C; **$2p^3$** for N; **$2p^4$** for O; **$2p^5$** for F.



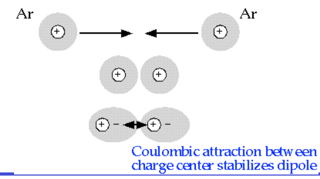
- If the 2s and 2p states form four sp^3 hydrids, what shape can be anticipated for the molecules? (You must consider how many H are needed for each case.)
- Can you identify the polar character of the molecule?
- How does this roughly explain that H_2O is bent at ~109.3^0?
- What is the effect of the increasing nuclear charge from C to F?
- Why is H-F different than others in shape?

Primary Bonding Types: Secondary (van der Waals)

Two types of Secondary: **induced dipolar** and **permanent dipole**.

- Induced dipolar interactions are weak and depend on molecular environment.
- They are typically caused by vibrational effects within the particular molecule and lead to interactions **between** molecules.
- Hence, they are **weak** secondary bonds to the stronger molecular bonds.

Example of Induced Dipole: Argon Gas
The positive nuclei repel one another and the electron cloud deforms in the neighboring atoms such that the two dipoles align and their is a weak attraction via dipolar forces, $1/r^4$.

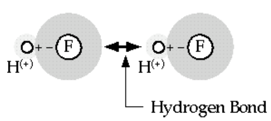


Primary Bonding Types: Secondary (van der Waals)

Example of Permanent Dipole: H-Cl Gas

The Cl has a large electronegativity (3.0) compared to H (2.1); hence, Cl grabs the electron away from H. (H-F and H_20 are other examples of this.)

Notably, such "Hydrogen bonds" with permanent dipoles lead to higher melting points and boiling temperatures, more than can be expected from their low molecular weights. Such bonds are crucial for polymer chemistry.



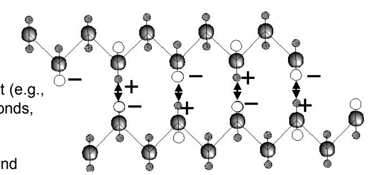
Primary Bonding Types: Secondary (van der Waals)

van der Waals Bonds lead to **induced dipole** interactions between, e.g. graphite layers, or polymer chains.

Hence, to strengthen bonds between such layered and chain molecules additional interactions must be made, as done in **Vulcanization of rubber** where sulfur atoms are bonded between rubber molecules (later).

Example: C_8H_{18} (Octane)
A molecular mass of 114, larger than most (e.g., Acetylene), has weaker **van der Waals** bonds, hence lower melting temperature.

In fact, **Octane** bonds are easy to break and form more stable bonds, giving off lots of energy; that's why it is used in gasoline.

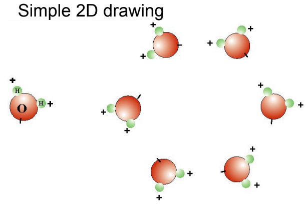


Primary Bonding Types: Secondary (van der Waals)

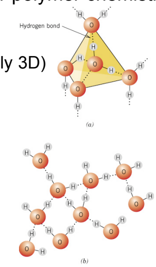
Example of Permanent Dipole: H_2O
Water is a *Polar Molecule* with a **Permanent Dipole Moment**.

Again, such "Hydrogen bonds" with permanent dipoles lead to higher melting points and boiling temperatures, more than can be expected from their low molecular weights. Such bonds are crucial for polymer chemistry.

Simple 2D drawing



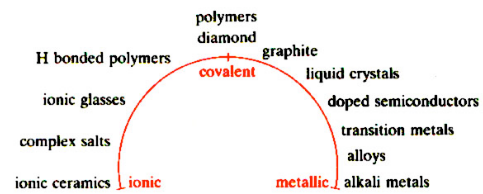
(really 3D)



Percent Ionicity: Ionic to metallic

Nature of the Bonds: Percent ionicity
(see text, where X is the electronegativity)

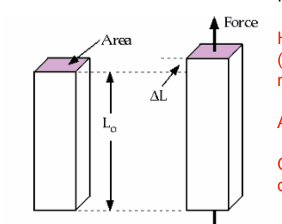
$$\%IC = 1 - e^{-\frac{(X_A - X_B)^2}{4}}$$



%IC=1 %IC=0

Macroscopic Properties: Force vs Extension

Force vs. extension



Strain = ε = $\Delta L/L_o$

Stress = σ = Force/Area

Issues to be addressed:

How are macroscopic properties (mechanical, structural, thermal, electrical, ...) most simply related to bonding?

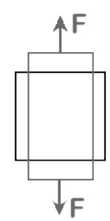
Are there directionality dependencies?

Can point defects (i.e., vacancies or impurities) change such bonding related properties?

For linear-elastic strain, not plastic!
Slope is Young's Modulus.

Macroscopic Properties: Stress-Strain Curves

linear-elastic strain only – not plastic!
Normalized forces (F/A_0) versus normalized strain (dl/l_0)



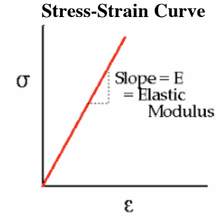
simple tension test

Hooke's Law

$$\sigma = E\,\varepsilon$$

Units:
E: [GPa] or [psi]

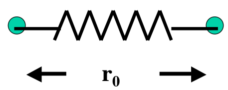
Stress-Strain Curve



Slope is Young's (Elastic) Modulus, E

Macroscopic Properties Inferred from Bonding

• Bond Length, r_0



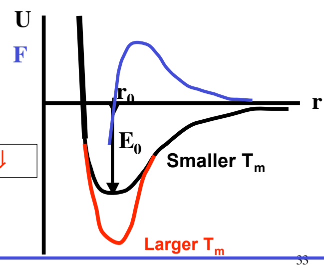
• Binding Energy, U_0
• Melting Temperature, T_m
(really $T_{sublimation}$)

T_m goes ⇑ as U_0 goes ⇓

$$equil.\,bond\ r_0 : F = -\left.\frac{dU}{dr}\right|_{r_0} = 0$$

$$min.\,energy\ E_0 : U(r_0)$$

Stored energy goes ⇑ as U_0 goes ⇓



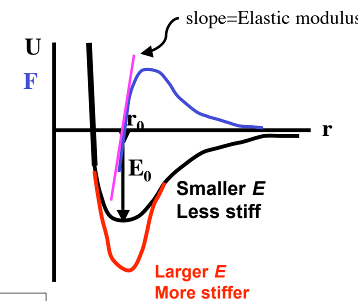
Elastic Moduli, *E* (Young's Modulus)

$E \propto$ curvature at r_0
$\propto d^2U/dr^2(r_0)$

like "spring constant"
F= k(r-r_0)
and linear near equilibrium.

Negative F - compression
Positive F - tension

E modulus ⇑ as E_0 ⇓ (deeper)



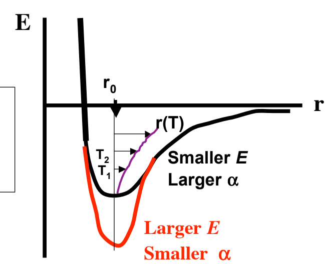
How does a vacancy (missing atom) change Elastic Moduli?

Coefficient of Thermal Expansion, α, or dL/dT

Linear Thermal Strain
$\Delta L(T)/L_0 = \alpha_L\ (T - T_0)$

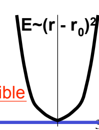
$\alpha \propto$ asymmetry at r_0
No asymmetry at r_0
No affect on r(T) or V(T)

α ⇑ as E_0 ⇑ (less negative)



Volume Thermal Strain
$\Delta V/V_0 = \alpha_V\ (T - T_0)$

Parabolic E vs. r shape

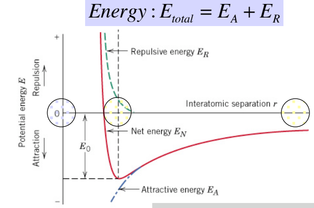


Symmetric well r(T)=r_0: No expansion possible
Atoms just vibrate back and forth!

Origin of Bonding Curve

arises from attractive plus repulsive interactions between atoms(ions)

$$Energy : E_{total} = E_A + E_R$$



Particular forms if E_A and E_R depends upon atoms and quantum mechanics, but often described by simple forms.

$$E_A = \frac{A}{r} \quad and \quad E_R = \frac{B}{r^n}$$

$$(e.g., Coulombic, A = \frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_0})$$

For NaCl, Z_1=Z_{Ca}=+2 and Z_2=Z_O= −2

Macroscopic consequences of generic E_{total} shown in previous slides

$$Force : F = -\left.\frac{dE}{dr}\right|_{r_0} = -\left.\frac{dE_A}{dr}\right|_{r_0} - \left.\frac{dE_R}{dr}\right|_{r_0}$$

Attractive force
Repulsive force

Minus sign in force makes sure that, by definition, repulsive force is "+"

Bond Energy and Melting Temperature

Callister

Table 2.3 Bonding Energies and Melting Temperatures for Various Substances

		Bonding Energy		
Bonding Type	*Substance*	*kJ/mol (kcal/mol)*	*eV/Atom, Ion, Molecule*	*Melting Temperature (°C)*
Ionic	NaCl	640 (153)	3.3	801
	MgO	1000 (239)	5.2	2800
Covalent	Si	450 (108)	4.7	1410
	C (diamond)	713 (170)	7.4	>3550
Metallic	Hg	68 (16)	0.7	−39
	Al	324 (77)	3.4	660
	Fe	406 (97)	4.2	1538
	W	849 (203)	8.8	3410
van der Waals	Ar	7.7 (1.8)	0.08	−189
	Cl_2	31 (7.4)	0.32	−101
Hydrogen	NH_3	35 (8.4)	0.36	−78
	H_2O	51 (12.2)	0.52	0

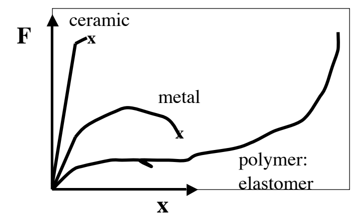
$Z_{Na}=+1$ $Z_{Cl}=-1$

$Z_{Mg}=+2$ $Z_O=-2$

What is relationship between Bonding Energy and T_{melt}?

What can you now say about ...

- **What is T_{melt} of ceramic, metal, polymer? Why?**
- **What is *E* of ceramic, metal, polymer? Why?**
- **What do force-extension or stress-strain curves look like?**



What is stress-strain curve of human tissue?

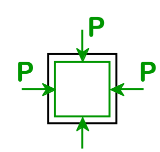
Summary: Bonding, Structure, Properties

Ceramics	Large bond energies
Ionic and Covalent bonds	large T_m, E Small α
Metals	Varying bond energy
Metallic bonding	intermediate T_m, E, α
Polymers	directional properties
Covalent and Secondary	secondary dominates outcome
	small T_m, E large α

Energy vs Volume : Bulk Modulus

- **Elastic Bulk modulus, K:** $P = -K \dfrac{\Delta V}{V_o}$

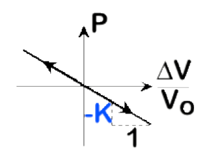
Units:
E: [GPa] or [psi]



Pressure test:

Init. vol = V_o.

Vol chg. = ΔV



How is bulk modulus related to atomic interaction energy?

Repulsive + Attractive Energy $U = U_A + U_R = -\dfrac{A}{r} + \dfrac{B}{r^n} = -Ar^{-1}\left(1 + \dfrac{B}{A} r^{n-1}\right)$

Energy vs Volume : Bulk Modulus

Total Force: equilibrium r_0 when F=0

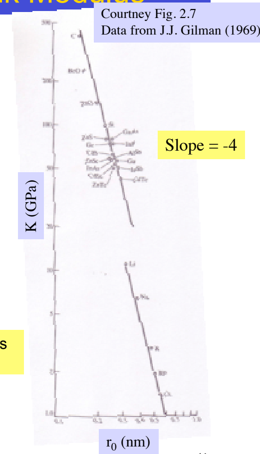
$$F = F_A + F_R = -\frac{d}{dr}(U_A + U_R) \sim r^{-2}$$

Bulk Modulus: volume deformation under hydrostatic Pressure

$$K = -V_0 \left.\frac{dP}{dV}\right|_{V_0} = +V_0 \left.\frac{d^2U}{dV^2}\right|_{V_0} \sim (V_0)^{-4/3} \boxed{\sim r^{-4}}$$

since $V_0 \sim r^3$

Surprisingly this represents alkali, covalent and compounds having diamond cubic structures (but not TiC, TaC, etc.)



Courtney Fig. 2.7
Data from J.J. Gilman (1969)

Simple analysis gives trends in simple systems!

Example Test Question

Why are covalently bonded materials generally less dense than ionically bonded or metallically bonded ones?

Hint: Consider what is distinctive about covalent bonds.

What does this tell you about the density of bonds (bonds per unit volume)?

If I suddenly changes Na^+ to Ca^{2+} and Cl^- to S^{2-} what would happen to the equilibrium bond distance, the melting temperature, etc?

Hint: There are multiple effects due to change in charge.

Synopsis

- Bonding between atoms dictates macroscale properties in solids, e.g. mechanical and electrical, as well as molecules.
  - Binding energies related to sublimation (loosely melting) temperature.
  - In molecules, it determines also the solid/liquid/gas behavior (relative evaporation temperatures), dependent on type of bonds (metallic, ionic, covalent, and secondary).
  - Thermal expansion related to curvature of binding curve.
  - Initial stress-strain behavior (elastic moduli) dictated by binding curve. (NOT TRUE for plasticity, which is controlled by line defects - later!)

- Point defects do not affect mechanical properties to a large extent, but could affect electrical properties (resistivity).