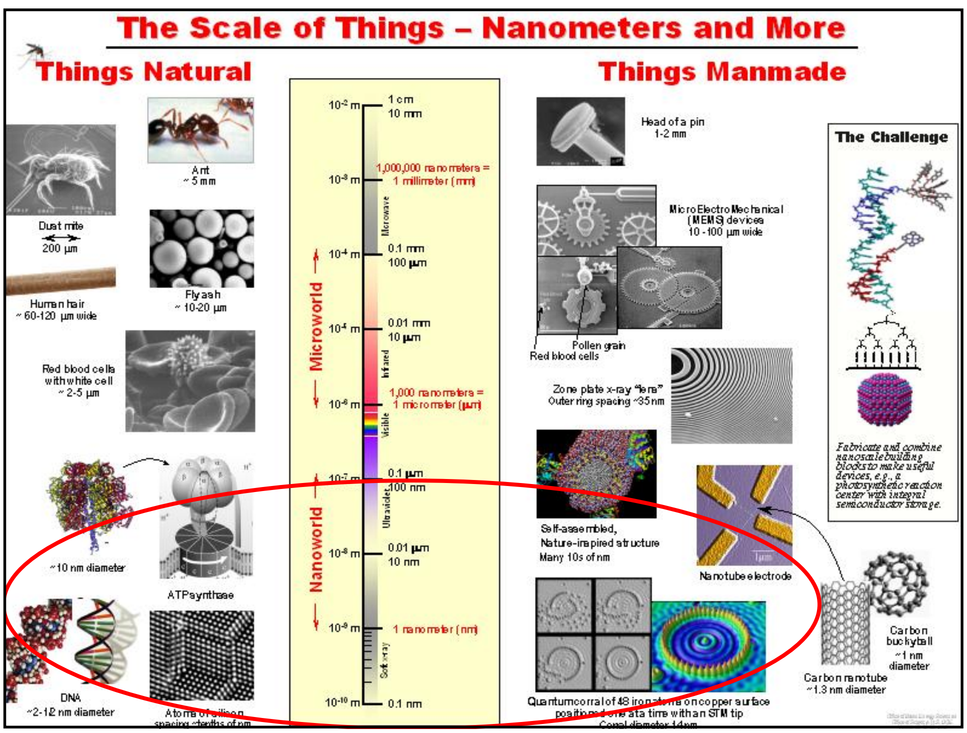
Introduction of Nano Science and Tech

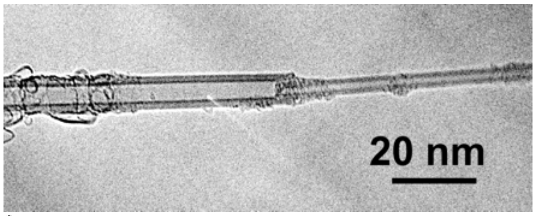
Thinking at the Nanoscale
-Departure from the continuum

Nick Fang

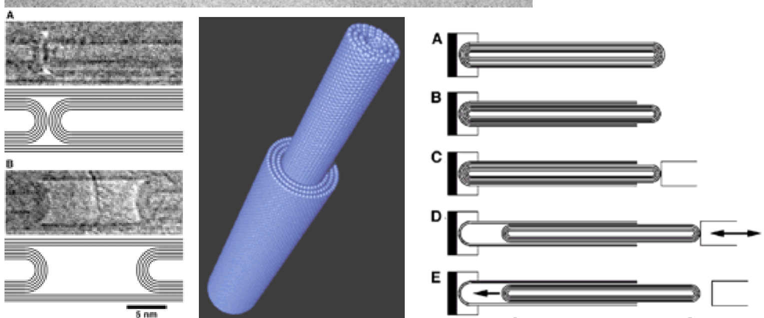
Course Website: **nanoHUB.org**
Compass.illinois.edu



Nanoscale Friction



- •Telescoping nanotube segments
- •No wear or fatigue
- •van der Waals energy-based retraction force



John Cumings, A. Zettl, *Science* 2000

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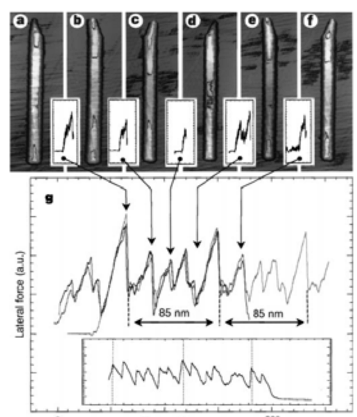
Nanoscale Friction

- Macroscale friction assumes

$$F = \mu N$$

- The static friction force not explained
- Molecular scale: breaking contacts, sliding and slipping (e.g. rolling nanotubes on graphites)



http://www.3rdtech.com/carbon_nanotubes.htm

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Departure from continuum

- **Quantum Effects (Two Lectures)**
  - **Atomic bonding**
  - **Confinement**
  - **Coherence**
- **Basics of Kinetics and Statistical Thermodynamics (Two Lectures)**
  - **Microscopic Origin of Macroscopic Laws**
  - **Transport properties**

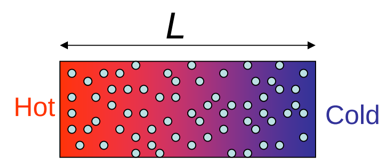
Constitutive Equations Revisited

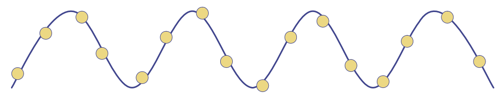
- Hooke's Law $\sigma = E\varepsilon$
- Fourier's Law $\mathbf{q} = -k\nabla T$
- Fick's Law of Diffusion $\mathbf{J} = -D\nabla C$
- Newton's law on shear stress $\tau = -\mu\,(du/dy)$
- Ohm's Law $J = \sigma E$

? Are they still valid in the nanoscale?

Microscopic Origins of Physical Laws --The Particle Nature

Materials	Dominant energy carriers
Gases:	Molecules
Metals:	Electrons
Insulators:	Phonons (crystal vibration)



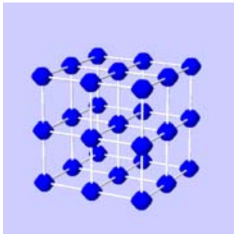


Constructionist Approach

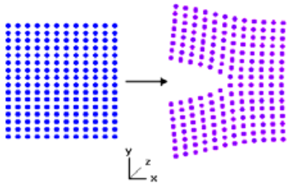
- Look at most basic level to begin our understanding
- Today we'll look at:
  - How atoms bond together
  - Energy quantization
  - Energy propagation in materials
    - Lattice vibration, phonons
    - Electron bands

Mechanics at Atomic Scale

- Microscopically, we are viewing the dynamics at atomic lattices; the restoring forces are provided by the chemical bonds



- The elastic modulus, strength and flipping conditions are well captured by the spring lattice models, e.g.:

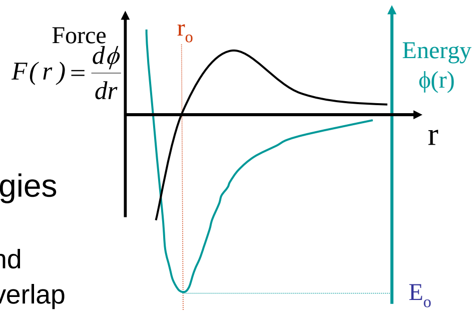


Bulk modulus

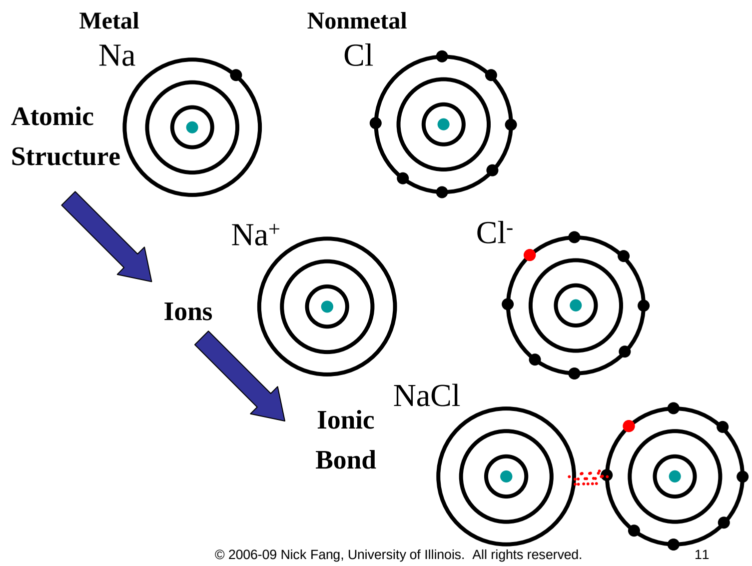
$$B = \frac{a_0^2}{9V}\frac{d^2E}{da^2}$$

Atomic Bonding in Solids

- Primary
  - Ionic
  - Covalent
  - Metallic
- Secondary
  - Van der Waals
  - Hydrogen
- Interatomic potential energies
  - Function of separation, r
  - *Attractive* - depends on bond
  - *Repulsive* - atomic scale overlap
- Bonding energy (E_o) is strongly dependent on bond type
  - Effect on modulus ???
  - Effect on thermal expansion ???



Ionic Bonding



Notes on Ionic Bonding

- To be stable, all positive ions must be near negative ions
- Bond strength is equal in all directions (nondirectional)
- Energy considerations
  - *Columbic* attractive force

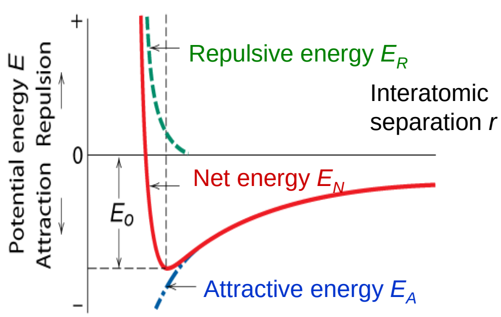
$$\phi_A \propto -\frac{1}{r}$$

  - Repulsive force:

$$\phi_R \propto \frac{1}{r^n} \quad (n \approx 8)$$

- Generally, very high bonding energies
- Typically hard, brittle, thermally and electrically insulative
- ***Ceramics***

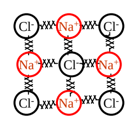
Adapted from Fig. 2.8(b), *Callister 7e.*



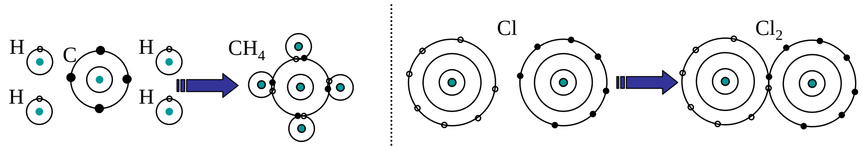
r

"Stable"

$$\phi = -\frac{\alpha}{r} + \frac{\beta}{r^8}$$



Covalent Bonding



- Two atoms share electrons - extra electron belongs to both
- Bonding is directional - between atoms being bonded
- Many interatomic bonds are partially ionic *and* covalent
  - Wider separation in periodic table ⇒ more ionic
- ***Ceramics, Metals, Polymer backbones***

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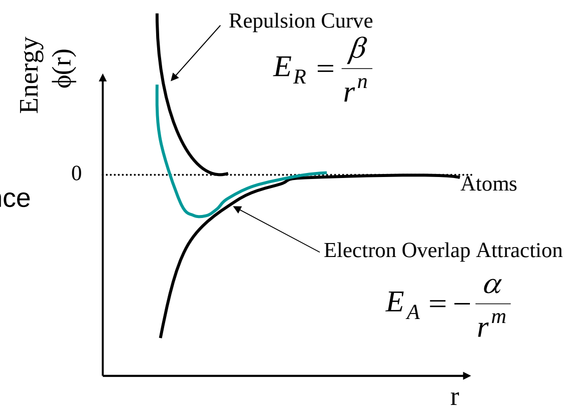
Covalent Potential

- Widely variable properties
  - Diamond
    - Hardest substance known
    - Very stiff, strong
    - T_{melt} = 3550 ºC
  - Bismuth
    - Very soft
    - Weak
    - T_{melt} = 270 ºC
  - Based on ***m*** & ***n***



$$\phi = -\frac{\alpha}{r^m} + \frac{\beta}{r^n} \quad (m < n)$$

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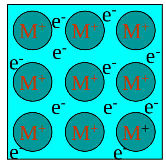
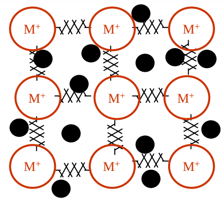
Metallic Bonding





- Ion Cores (M^+)- net positive charge equal to total valence
- Valence electrons (e^-) drift through metal in "electron cloud"
  – Electrically shield ion cores
  – Physically hold cores together
- Nondirectional bond
- Metallic bonding potential similar to covalent (use same eqn.)
- Wide variety of bonding energies and hence properties
- Excellent conductors due to mobility of electron cloud
- ***Metals and metallic alloys***

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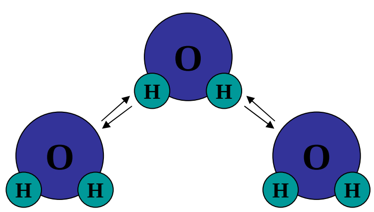
Van der Waals Bonding



$$\phi = -\frac{\alpha}{r^6} + \frac{\beta}{r^n} \quad (n \approx 12)$$

- Sometimes called *physical* bonds to contrast with *chemical* (primary)
- Much lower energy than primary bonds
- Arise from electric dipoles -
  – Separation of + and - portions of atom - much weaker than ions
  – Bonding from attraction of + from one dipole to - of other dipole
- Hydrogen bonding is special case when hydrogen is present
  – Strongest secondary bonding type
- ***Polymeric interchain bonds***

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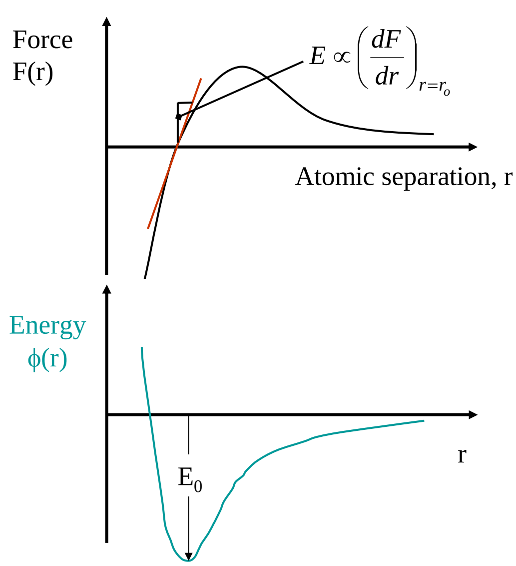
Summary: Bonding

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

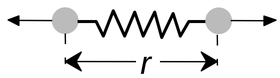
Atomistic Origins of Properties



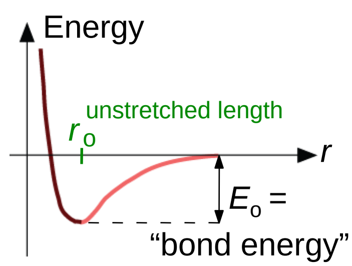
- ***Modulus***
  - Proportional to slope of force-separation curve at equilibrium separation distance
- *Thermal properties*
  - Melting point Tm
  - Coefficient of Thermal Expansion α

Properties From Bonding: T_m

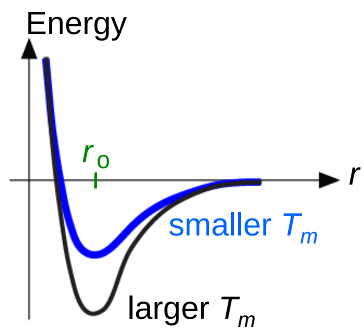
- Bond length, r



- Bond energy, E_o



- Melting Temperature, T_m



T_m is larger if E_o is larger.

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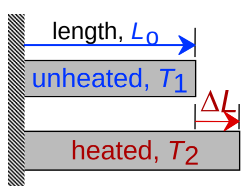
Properties From Bonding : α

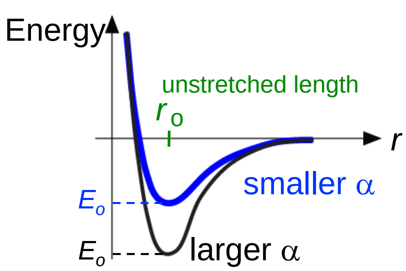
- Coefficient of thermal expansion, α



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.

Polymers: ~100-200 x 10^{-6} C^{-1}
Metals: ~10-20 x 10^{-6} C^{-1}
Ceramics: ~1-10 x 10^{-6} C^{-1}

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Material Waves & Energy Quantization

De Broglie proposed that the energy and wavelength of particles can be described by the following relationship

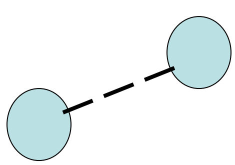
$$E = \frac{p^2}{2m}; p = \frac{h}{\lambda}; \lambda = \frac{h}{\sqrt{2mE}}$$

Schrodinger further postulate that the wavefunction of any matter obeys the equation

$$-\frac{\hbar^2}{2m}\nabla^2\Psi_t + U\Psi_t = i\hbar\frac{\partial\Psi_t}{\partial t},$$

How Much Energy Per Particle?

- Classical Rigid body:



$$E_{translation} = \frac{1}{2}mv^2$$

$$E_{vibration} = \frac{1}{2}kx^2$$

$$E_{rotation} = \frac{1}{2}I\omega^2$$

Quantum Effects

- How the energy are presented in discrete levels?

$$E_{translation} = \frac{\hbar^2 k^2}{2m}$$

$$E_{\text{Vibration}} = h\nu(n+\frac{1}{2}); \nu = \frac{1}{2\pi}\sqrt{\frac{K}{m}}$$

$$(n{=}0,1,2\cdots)$$

$$E_{\text{Rotation}} = hBl(l+1) \quad (l{=}0,1\cdots)$$

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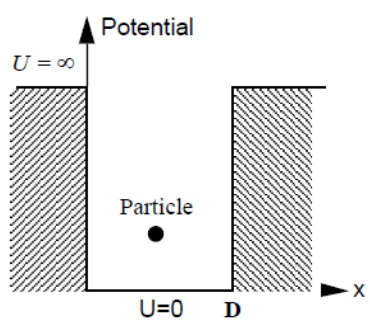
Effect of Confinement



Wave equation of this particle
By Quantum Mechanics

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - E\Psi = 0 \quad (0<x<D);$$

$$-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} - E\Psi = 0 \quad (0<x<D);$$

We can try a tentative solution:

$$\Psi = Ae^{-ikx} + Be^{ikx},$$

$$k = \frac{\sqrt{2mE}}{\hbar}$$

Note: the particle cannot escape from the potential well (Boundary Conditions)

$$\begin{cases} x=0 & A+B=0 \\ x=D & A\exp[-ikD] + B\exp[ikD] = 0 \end{cases}$$

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Solution of a Confined 1D system

- From the above boundary conditions, we obtain:

$$\sin(kD) = 0; \qquad k_n D = n\pi$$

(n=0, ±1, ± 2, …) the probability of the particles can only take standing wave forms!

Recall:

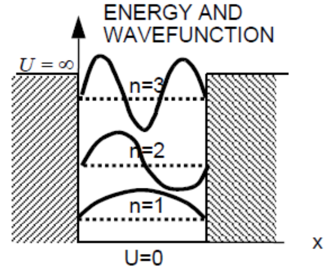
$$k = \frac{\sqrt{2mE}}{\hbar}$$

Finite Energy steps:

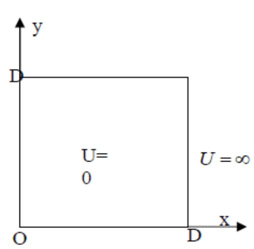
$$E_n = \frac{n^2\hbar^2\pi^2}{2mD^2}$$

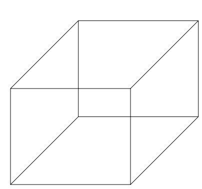
When D=1nm, m_e=9.1x10^{-31}kg

E_2-E_1=1.13eV!



Extension to 2D and 3D systems





Schrodinger equation in 2D system:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2}\right) - E\Psi = 0$$

$$\Psi_{\ell n} = C_{\ell n}\sin\left(\frac{n\pi x}{D}\right)\sin\left(\frac{\ell\pi y}{D}\right).$$

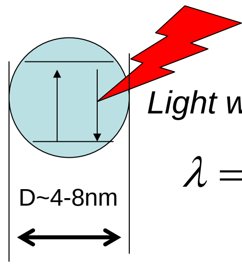
$$E_{\ell n} = \frac{(\ell^2 + n^2)\pi^2\hbar^2}{2mD^2} \quad (\ell, n = 1, 2, \ldots)$$

Likewise in 3D confinement:

$$E_{jln} = \frac{(j^2 + l^2 + n^2)\hbar^2\pi^2}{2mD^2}$$

Example: Quantum Dots

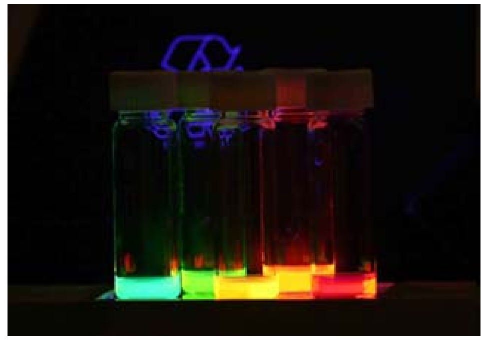
Quantum dots of the same material, but with different sizes, can emit light of different colors.



Light wavelength

$$\lambda = \frac{hc}{\Delta E}$$

$$\frac{\partial \lambda}{\partial D} \propto \frac{16 m_e^* c}{h} D$$



http://en.wikipedia.org/wiki/Quantum_dots

Additional Reading

- William D.Callister, "Materials Science and Engineering", 7th Edition, Chapter 2, Wiley
- Tien, Majumdar, Gerner, "Microscale Energy Transport", Chapter 1, Taylor&Francis (pdf online)
- Introduction to Quantum Dots Lab on nanoHUB: http://nanohub.org/resources/2846

