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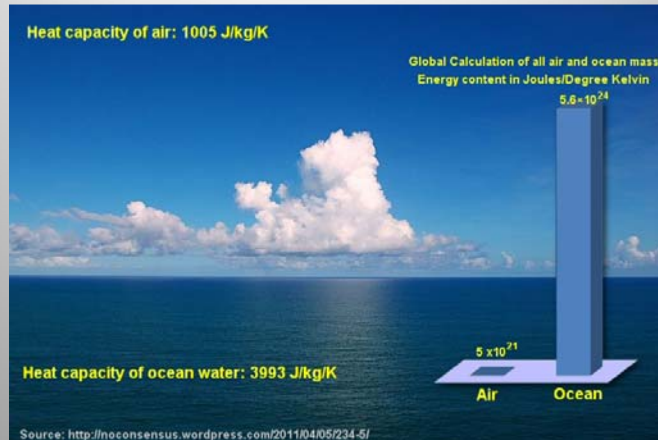
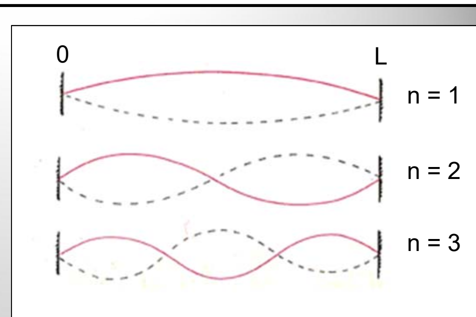


PHYS432
Materials Physics

Heat Capacity

- Debye model:

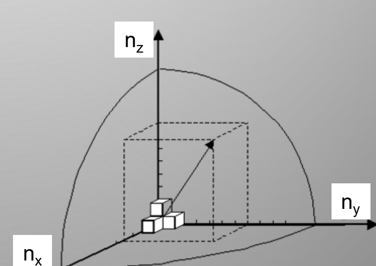
Now, include strong interactions between atoms.



Consider a cubic solid of dimension, L (V = L^3)

$$k^2 = k_x^2 + k_y^2 + k_z^2 = (\pi / L)^2 (n_x^2 + n_y^2 + n_z^2) = (n\pi / L)^2$$

Need number of states below some maximum value of *n*, n_{max}.



$$N = \frac{1}{8}\left(\frac{4}{3}\pi n_{\max}^3\right) = \frac{k^3 V}{6\pi^2}$$

$$N \to \frac{\omega^3 V}{6\pi^2 v^3} \quad \text{in limit of small } k$$

(model: monatomic, so ∃ only acoustic modes)

Heat Capacity

- Debye model:

Density of states, $g(\omega)$: $N = \int g(\omega)d\omega = \int dN \Rightarrow g(\omega) = dN/d\omega$

$$\Rightarrow g(\omega) = \frac{\omega^2 V}{2\pi^2 v^3}$$

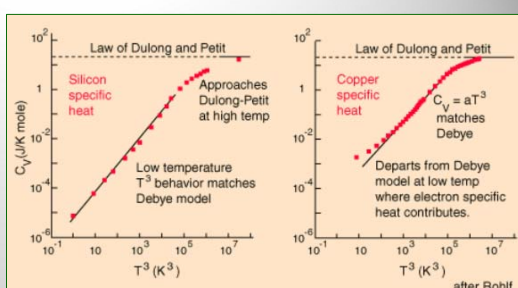
Combine Einstein's result for <E> of quantum oscillators with concept of density of states, *g(ω)*, to get (with introduction of factor of three to allow for longitudinal & transverse modes of oscillation):

$$U = 3\int_0^{\omega_{\max}} \frac{g(\omega)\hbar\omega}{e^{\hbar\omega/k_B T} - 1} d\omega$$

Compute heat capacity from this:

$$C = \frac{\partial U}{\partial T}$$

Heat Capacity



- Debye model:

Now, include strong interactions between atoms.

At low T Debye gives

$$C = \frac{12R\pi}{5}\left(\frac{T}{\theta_D}\right)^3$$

$$\text{where } \theta_D \equiv \frac{\hbar\omega_{\max}}{k_B} = \text{ the Debye temperature}$$

- But, for conductors, it's not quite right at really low T (several K)! Need electronic contribution:

A relatively simple model gives

$$C = C_{electronic} + C_{vibrational}$$

$$C_{metal} = \frac{\pi^2 N_A k^2}{2E_F}T + \frac{12\pi^4 N_A k}{5T_D^3}T^3$$

Electronic specific heat proportional to temperature T — *Vibrational specific heat proportional to cube of temperature T*

Thermal conductivity

	K ($Wm^{-1}K^{-1}$)
Diamond	~2000
Cu	400
Au	310
Al	230
Si	160
Na	140
Glass	~1.0
Polystyrene	

- The thermal conductivity relates to heat flow:

$$\frac{dQ}{dt} = \frac{K\ A\ \Delta T}{L} \quad \text{or} \quad \vec{J}_{th} = K\ \vec{\nabla} T$$

- *Wiedeman-Franz law* relates thermal and electrical conductivities (reasonably accurate for some materials):

$$K / \sigma = \Gamma\ T, \quad where\ \Gamma = const.$$

- Both phonons and electrons contribute

$$K = K_e + K_{ph}$$

impurities & imperfections play a role

phonon contribution dominates

R = L/K = "R-value"

Quantum Mechanics

- Schrödinger's Equation $-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} + U\psi = i\hbar\frac{\partial \psi}{\partial t}$

- Wave functions $\psi(x,t) = Ae^{ikx - i\omega t}$
  (Solutions)

- Wave packets $\psi(x,t) = A\int_{k_1}^{k_2} e^{ikx - i\omega t}\,dk$
  (Also solutions)

Let $\begin{cases} \bar{k} \equiv \frac{1}{2}(k_1 + k_2) \\ \bar{\omega} \equiv \omega(\bar{k}) \\ v_g = \left.\frac{d\omega}{dk}\right|_{k=\bar{k}} \end{cases}$ in $\omega(k) \approx \omega(\bar{k}) + (k - \bar{k})\left.\frac{d\omega}{dk}\right|_{k=\bar{k}}$

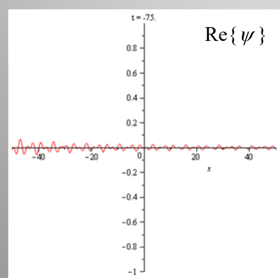
Results in

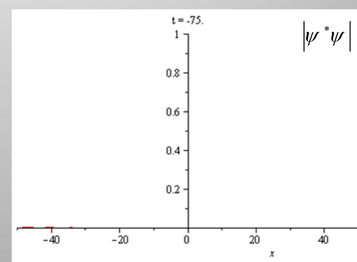
$$\psi(x,t) = 2A\frac{\sin[(x - v_g t)(k_2 - k_1)/2]}{x - v_g t} e^{i\bar{k}x - i\omega t}$$

Quantum Mechanics

- Probability function is then

$$\left|\psi^{*}\psi\right| \equiv \left|\psi\right|^{2} = 4A^{2}\,\frac{\sin^{2}[(x - v_{g}t)\Delta k/2]}{(x - v_{g}t)^{2}}$$





- EX: Particle-in-a-box & Tunneling

Heisenberg Uncertainty Principle

- Cannot know position and momentum simultaneously

$$\Delta x\,\Delta p \approx \hbar$$

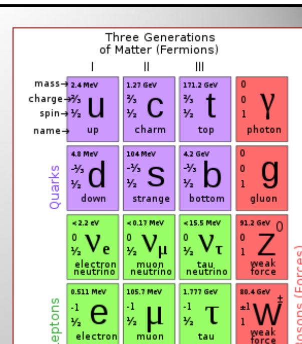
The more precisely the position is determined,
the less precisely the momentum is known in this instant,
and vice versa.
--Heisenberg, uncertainty paper, 1925; 1932 Nobel Prize

Pauli Exclusion Principle

Pauli, 1927 – 1945 Nobel Prize – *explains structure of atoms.*

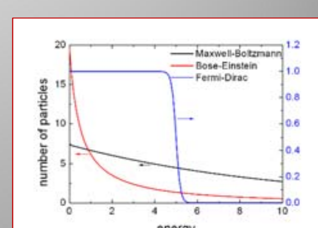
- No more than one quantum particle can be in the same state at the same time
- Applies to **fermions** (particles with half-integer "spin;" *e.g.*, protons, electrons, neutrons)
- For e^-, can have two different "spin" states
- Does not apply to **bosons** (particles with integer "spin;" *e.g.,* photons, mesons, gluons)

What's a Fermion?



- FERMIONS: Particles with half-integer spin obey Fermi-Dirac statistics
  - e.g., quarks (and thus protons, neutrons) and leptons (electrons, muons, taus, neutrinos)

$$\overline{n}_i = 1/(e^{(E_i-\mu)/k_BT} + 1)$$



- BOSONS: Particles with integer spin obey Bose-Einstein statistics
  - e.g., photons, gluons, Zs, and Ws

$$\overline{n}_i = g_i/(e^{(E_i-\mu)/k_BT} - 1)$$

n_i = # particles in state i

Particle in a Box (infinite well)

- Two waves traveling in opposite directions:

$$\psi(x,t) = Ae^{ikx - i\omega t} - Ae^{-ikx - i\omega t}$$

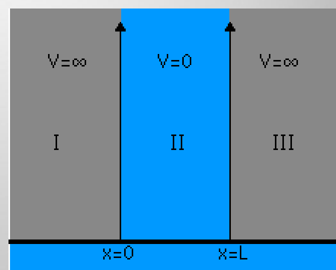
satisfy $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t}$

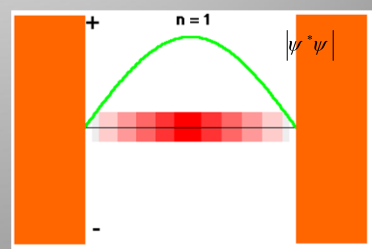
and the BC

$$\psi(0,t) = 0 \text{ and } \psi(L,t) = 0$$

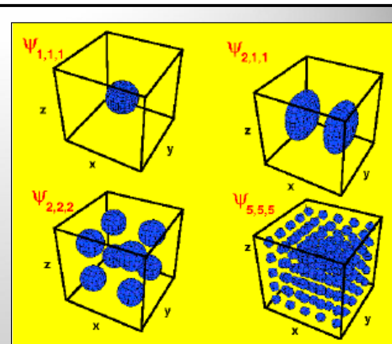
if $k = n(\pi / L)$

so that $|\psi|^2 = 4A^2 \sin^2(n\pi x / L)$





3D Particle in a Box



- Similar idea to 1D
- Restrictions on k

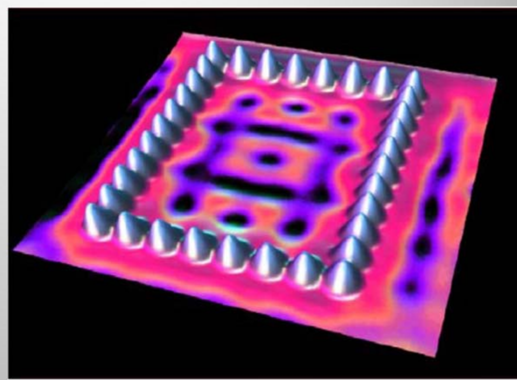
- Periodic (Born Von Karman) BC:

$$\vec{k} = n_x \frac{2\pi}{L}\hat{i} + n_y \frac{2\pi}{L}\hat{j} + n_z \frac{2\pi}{L}\hat{k}$$

www.chem.ufl.edu/~itl/4412_aa/Gifs/box3_00.gif

2D Particle in a Box?

- Similar idea to 1D
- Restrictions on k?



STM image of Fe atoms on Cu(111) surface

Schrodinger's equation?

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}\right)=i\hbar\frac{\partial\psi}{\partial t}$$

Solutions?

$$\psi(x,y)=A\sin(k_x x)\sin(k_y y)$$

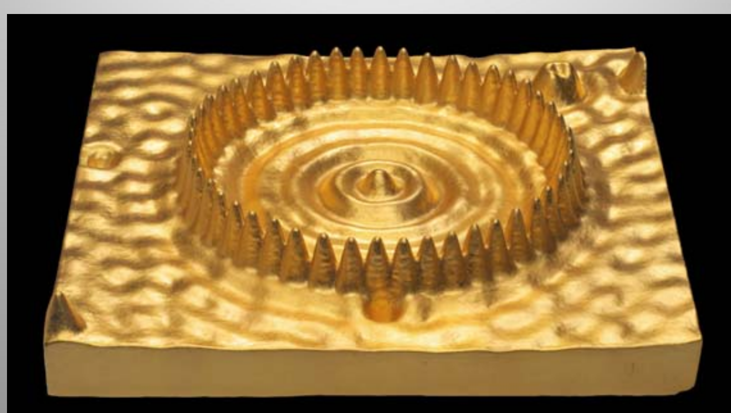
Apply boundary conditions?

$$\vec{k}=n_x\frac{\pi}{L}\hat{i}+n_y\frac{\pi}{L}\hat{j}$$

Remember: $\lambda=\frac{2\pi}{k}=\frac{L}{n}$

2D Particle in Circular Box

Quantum corral:1993 by Lutz, Eigler, and Crommie



STM image of 48 Fe atoms on Cu(111) surface

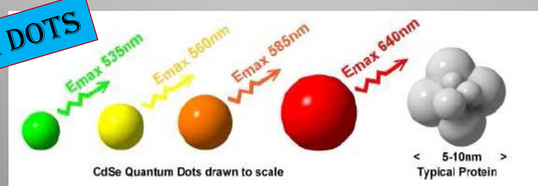
3D Particle in a Box

- In spherical coordinates …

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\delta}{\delta r}\right)\psi(r,\theta,\phi)+\frac{1}{2mr^2}\hat{L}^2\psi(r,\theta,\phi)=E\psi(x)$$

$$E = E_{bulk} + \frac{\hbar^2\pi^2}{2a^2}\left(\frac{1}{m_e^*}+\frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 a}$$

QUANTUM DOTS

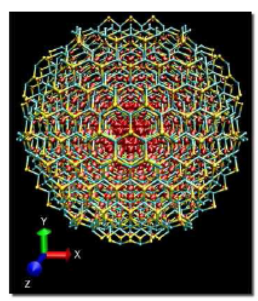


http://courses.washington.edu/overney/NME498_Material/NME498_Lectures/Lecture12_Reid_Quantum_Confinement.pdf

Application: Quantum Dots

Quantum dots are semiconducting materials (CdS, CdSe, etc.) with dimension on the nanometer scale.

The optical properties of the quantum dots are highly dependent on the size of the particle.



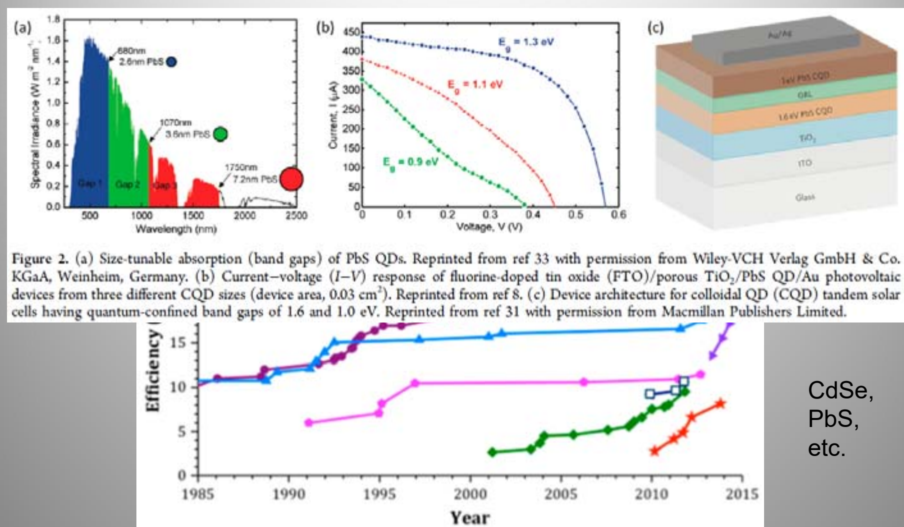
CdSe quantum dots

As diameter decreases, energy gap between ground and excited state increases.

21

http://sitemason.vanderbilt.edu/files/ioOfKM/cdse4.jpg

Q Dot Photovoltaics!



CdSe, PbS, etc.

Quantum-Dot-Based Solar Cells: Recent Advances, Strategies, and Challenges, Mee Rahn Kim and Dongling Ma, J. Phys. Chem. Letters, 2015, 6, 85−99

Electrical conductivity

- Wide range of values!
- Early attempts to model:
  - Drude: free electron gas
  - Sommerfeld: quantum free electron gas