Free Electron Model

- As we mentioned previously, the Pauli exclusion principle plays an important role in the behavior of solids
- The first quantum model we'll look at is called the free electron model or the Fermi gas model
- It's simple but provides a reasonable description of the properties of the alkalai metals (Li, Na, …) and the nobel metals (Cu, Ag, Au)

Free Electron Model

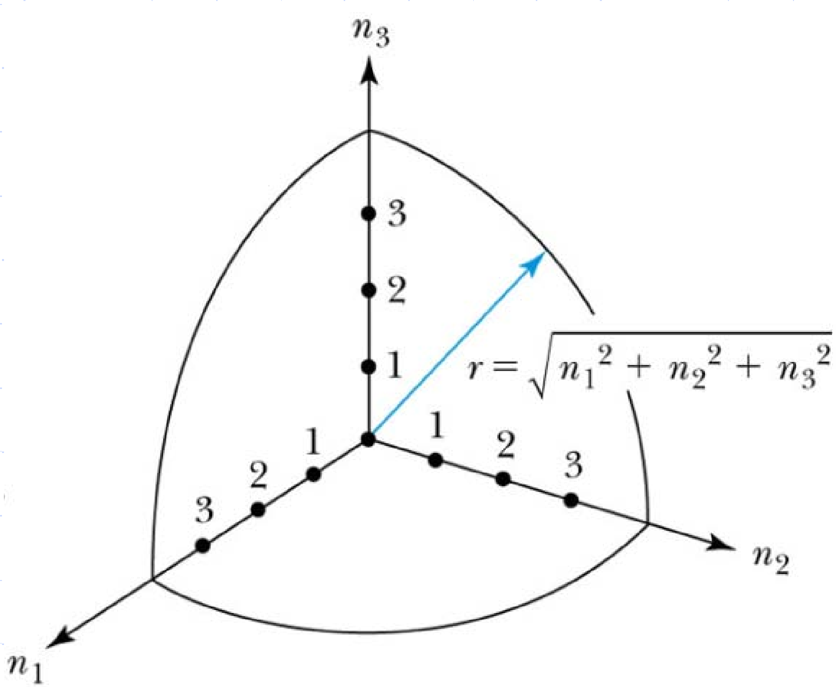
- Assume N electrons that are non-interacting (identical) fermions
- Assume they are confined to a box of $V=L^3$
  - Hopefully you recall the energy levels of the 3D infinite potential well

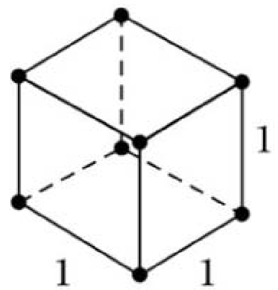
$$E_{n_x n_y n_z} = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

  - Note as L grows large the discrete energy spectrum becomes continuous
  - What is the ground state when N is large?
- Assume T=0 to start with

Free Electron Model

- Consider a number space to help count the number of states





Cube of unit "volume"

Free Electron Model

- Then we can write

$$E = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \equiv E_1 r^2$$

The number of states up to radius r is just

$$N_r = (2)\left(\frac{1}{8}\right)\left(\frac{4}{3}\pi r^3\right)$$

We can rewrite this in terms of energy

$$N_r = \frac{1}{3}\pi\left(\frac{E}{E_1}\right)^{3/2}$$

And at $T = 0$ the Fermi energy is the highest occupied energy state

$$N_r = \frac{1}{3}\pi\left(\frac{E_F}{E_1}\right)^{3/2}$$

Free Electron Model

- We can then solve for the Fermi energy

$$E_F = E_1\left(\frac{3N}{\pi}\right)^{3/2} = \frac{\hbar^2\pi^2}{2m}\left(\frac{3N}{\pi L^3}\right)^{2/3}$$

- Many metals have ~1 free electron/ion or $n=N/L^3 \sim 10^{29}$ e/m^3
- Thus the Fermi energy E_F for most metals is ~ 10 eV
- And the Fermi temperature $T_F=E_F/k_B$ is ~ 10^5 K
  - Extremely high and much greater than T for room temperature ~ 300 K
  - But this is not the temperature of the electron gas, rather it is a measure of where the Fermi energy is at

Free Electron Model

- N/L^3

Table 9.3 Free-Electron Number Densities for Selected Elements at $T = 300$ K

Element	N/V ($\times 10^{28}$ m^{-3})	Element	N/V ($\times 10^{28}$ m^{-3})
Cu	8.47	Mn (α)	16.5
Ag	5.86	Zn	13.2
Au	5.90	Cd	9.27
Be	24.7	Hg (78 K)	8.65
Mg	8.61	Al	18.1
Ca	4.61	Ga	15.4
Sr	3.55	In	11.5
Ba	3.15	Sn	14.8
Nb	5.56	Pb	13.2
Fe	17.0		

Free Electron Model

- E_F and T_F

Table 9.4 Fermi Energies (T = 300 K), Fermi Temperatures, and Fermi Velocities for Selected Metals

Element	E_F (eV)	T_F ($\times 10^4$ K)	u_F ($\times 10^6$ m/s)
Li	4.74	5.51	1.29
Na	3.24	3.77	1.07
K	2.12	2.46	0.86
Rb	1.85	2.15	0.81
Cs	1.59	1.84	0.75
Cu	7.00	8.16	1.57
Ag	5.49	6.38	1.39
Au	5.53	6.42	1.40
Be	14.3	16.6	2.25
Mg	7.08	8.23	1.58
Ca	4.69	5.44	1.28
Sr	3.93	4.57	1.18
Ba	3.64	4.23	1.13
Nb	5.32	6.18	1.37
Fe	11.1	13.0	1.98
Mn	10.9	12.7	1.96
Zn	9.47	11.0	1.83
Cd	7.17	8.68	1.62
Hg	7.13	8.29	1.58
Al	11.7	13.6	2.03
Ga	10.4	12.1	1.92
In	8.63	10.0	1.74
Tl	8.15	9.46	1.69
Sn	10.2	11.8	1.90
Pb	9.47	11.0	1.83
Bi	9.90	11.5	1.87
Sb	10.9	12.7	1.96

Free Electron Model

- Comment
  - Once you know the Fermi energy you can also calculate the Fermi momentum and the Fermi velocity

$$p_F = \sqrt{2mE_F}$$

$$v_F = \frac{p_F}{m} = \sqrt{\frac{2E_F}{m}}$$

  - The Fermi velocity is the same order of magnitude as the orbital velocity of the outer electrons in an atom and ~10 times the mean thermal velocity of a non-degenerate electron gas
  - It's still non-relativistic however

Free Electron Model

- The density of states g(E) is defined as

$$g(E) = \frac{dN}{dE} = \frac{\pi}{2} E_1^{-3/2} E^{1/2}$$

It can also be written in terms of E_F

$$g(E) = \frac{3N}{2} E_F^{-3/2} E^{1/2}$$

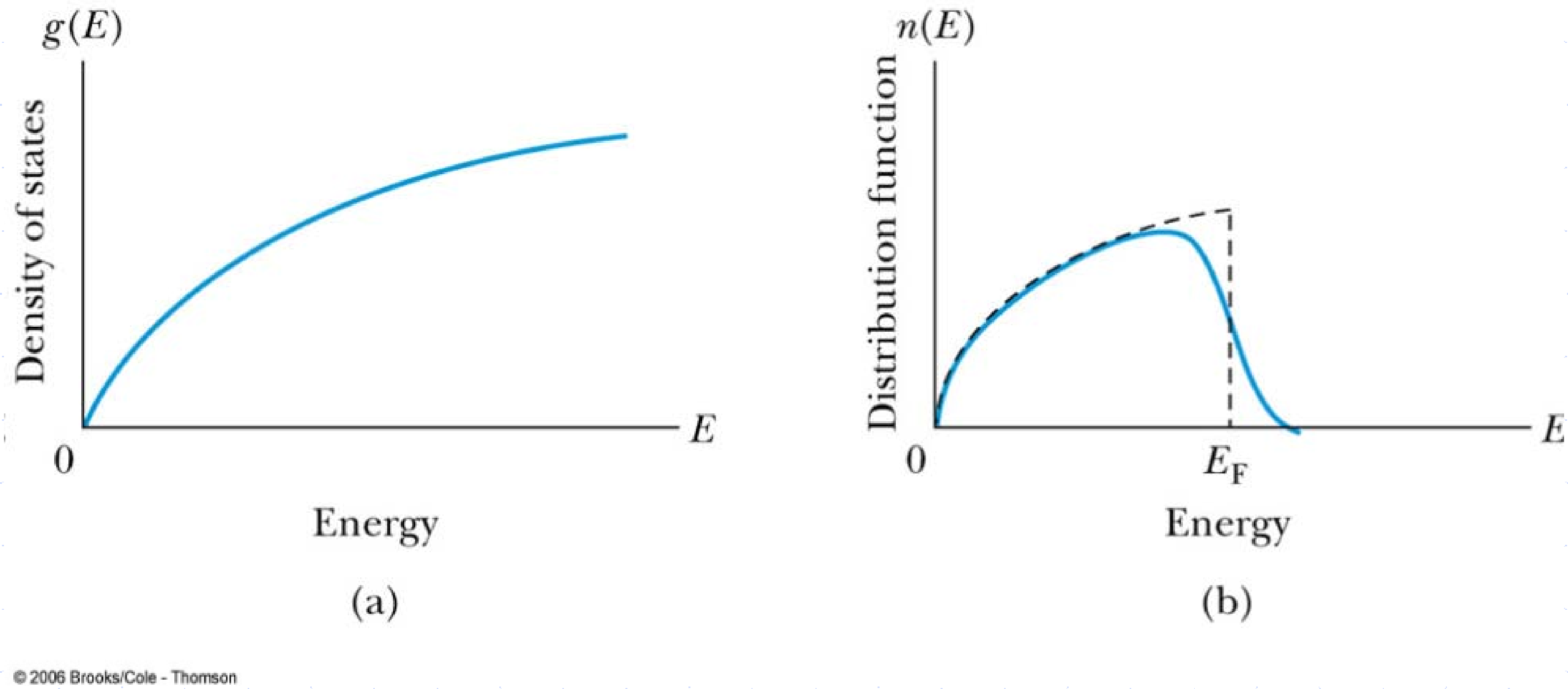
- Thus we can calculate $n(E)=g(E)F_{FD}$

Recall $F_{FD} = 1$ for $E < E_F$ and 0 for $E > E_F$

Then $n(E) = g(E)$ for $E < E_F$ and 0 for $E > E_F$

Free Electron Model

- g(E) and n(E)



Free Electron Model

- As we learned earlier, once you know n(E) you can calculate many thermodynamic quantities
  - Sanity check

$$N = \int_0^\infty n(E)dE = \int_o^{E_F} g(E)dE$$

$$N = \frac{3}{2} N E_F^{-3/2} \frac{2}{3} E_F^{3/2} = N$$

Free Electron Model

- Total energy

$$U = \int_0^{\infty} E n(E) dE = \int_0^{E_F} E g(E) dE$$

$$U = \frac{3}{2} N E_F^{-3/2} \frac{2}{5} E_F^{5/2} = \frac{3}{5} N E_F$$

- I used U here to indicate the total energy

Free Electron Model

- Recall our discussion earlier in the semester on the molar heat capacity of solids

$$E = \frac{f}{2} N k_B T = \frac{f}{2} nRT$$

$$C_V = \frac{1}{n}\frac{dE}{dT} = \frac{f}{2} R$$

$$\text{For solids } C_V = 3R \approx 25 \text{ J/molK}$$

This is called the DuLong - Petit law

- But conduction electrons in a metal should contribute an additional (3/2)R
  - The observed electronic contribution is only ~0.02R

Free Electron Model

- We can calculate the electronic contribution in the free electron model

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

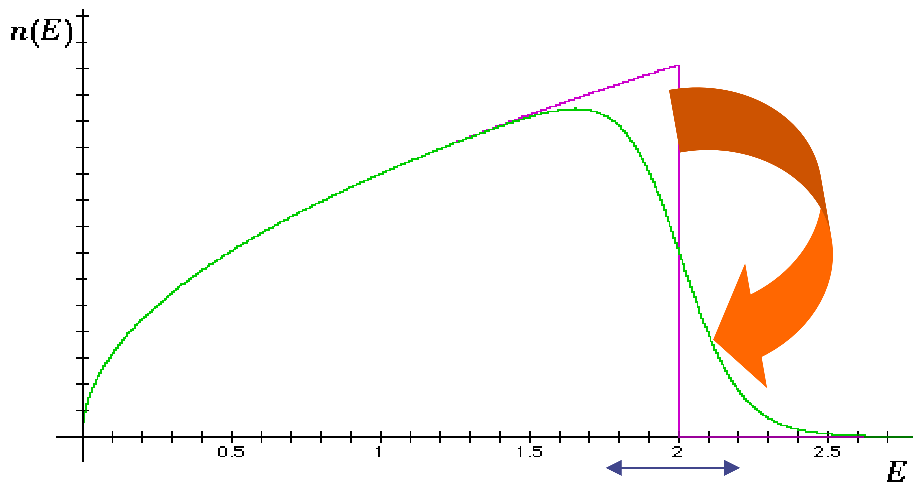
- However up to this point we have been working at T=0 in order to calculate C_V so we have to calculate U(T) for T>0

$$U(T) = \int_0^\infty E n(E) dE = \int_0^\infty E g(E) F_{FD} dE$$

$$U(T) = \int_0^\infty E g(E) \frac{1}{e^{\beta(E-E_F)}+1}$$

Free Electron Model

- We could do the integral but it's more important to notice that in heating a Fermi gas, we populate some states above E_F and deplete some states below E_F
- This modification is only important in a narrow energy range k_BT around E_F



k_BT

Free Electron Model

- The fraction of electrons transferred to higher energy is $k_B T / E_F$
- The energy increase of these electrons is $k_B T$
- So the increase in internal energy is $N\left(k_B T\right)^2 / E_F$
- Making the molar heat capacity

$$C_V = \frac{\partial U}{\partial T} \propto N \frac{k_B^2 T}{E_F} = R \frac{T}{T_F}$$

$$(\text{for 1 mole, N} = \text{N}_{\text{Av}})$$

Free Electron Model

- The correct proportionality constant is found doing the integral

$$C_V = \frac{\pi^2}{2} N_{Av} k_B \frac{k_B T}{E_F} = \frac{\pi^2}{2} R \frac{T}{T_F}$$

- The point is, that at room temperature, $T \ll T_F$ and the electronic contribution to the heat capacity is small
- This is because only a small fraction of electrons around E_F can be thermally excited because of the Pauli exclusion principle
  - This was one of the big successes of the free electron model and not predicted classically

Free Electron Model

- The free electron model for metals can also be used to calculate
  - Electrical conductivity
    - Although to get agreement with experiment, long collision lengths (mean free paths) were required
    - The source of how electrons can move ~ 1 centimeter (for a pure metal at low T) without scattering was unknown
  - Thermal conductivity
    - Although the classical calculation of thermal conductivity (fortuitously) gave good agreement with experiment also