Consequence of Electrons as Waves on Free Electron Model

- Boundary conditions will produce quantized energies for all free electrons in the material
- Two electrons with same spin can not occupy same electron energy (Pauli exclusion principle)

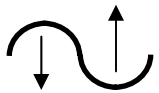
Imagine 1-D crystal for now

Traveling wave picture

$e^{i(kx-\omega t)}$

$e^{-i(kx+\omega t)}$

Standing wave picture

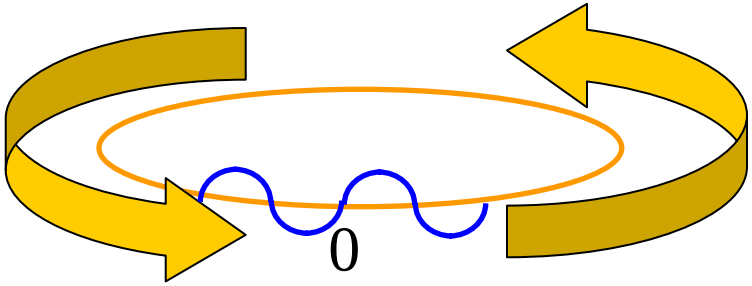


$$e^{i(kx-\omega t)} + e^{-i(kx+\omega t)} = e^{-i\omega t}(e^{ikx} + e^{-ikx})$$
$$= e^{-i\omega t}(2\cos kx)$$

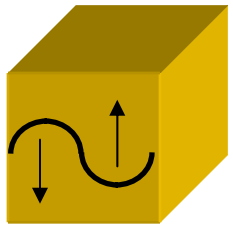
Since material is usually big and electron small, traveling wave picture used

Consequence of Electrons as Waves on Free Electron Model

Traveling wave picture



Standing wave picture



$$\Psi(x) = \Psi(x+L)$$

$$e^{ikx} = e^{ik(x+L)}$$

$$1 = e^{ikL}$$

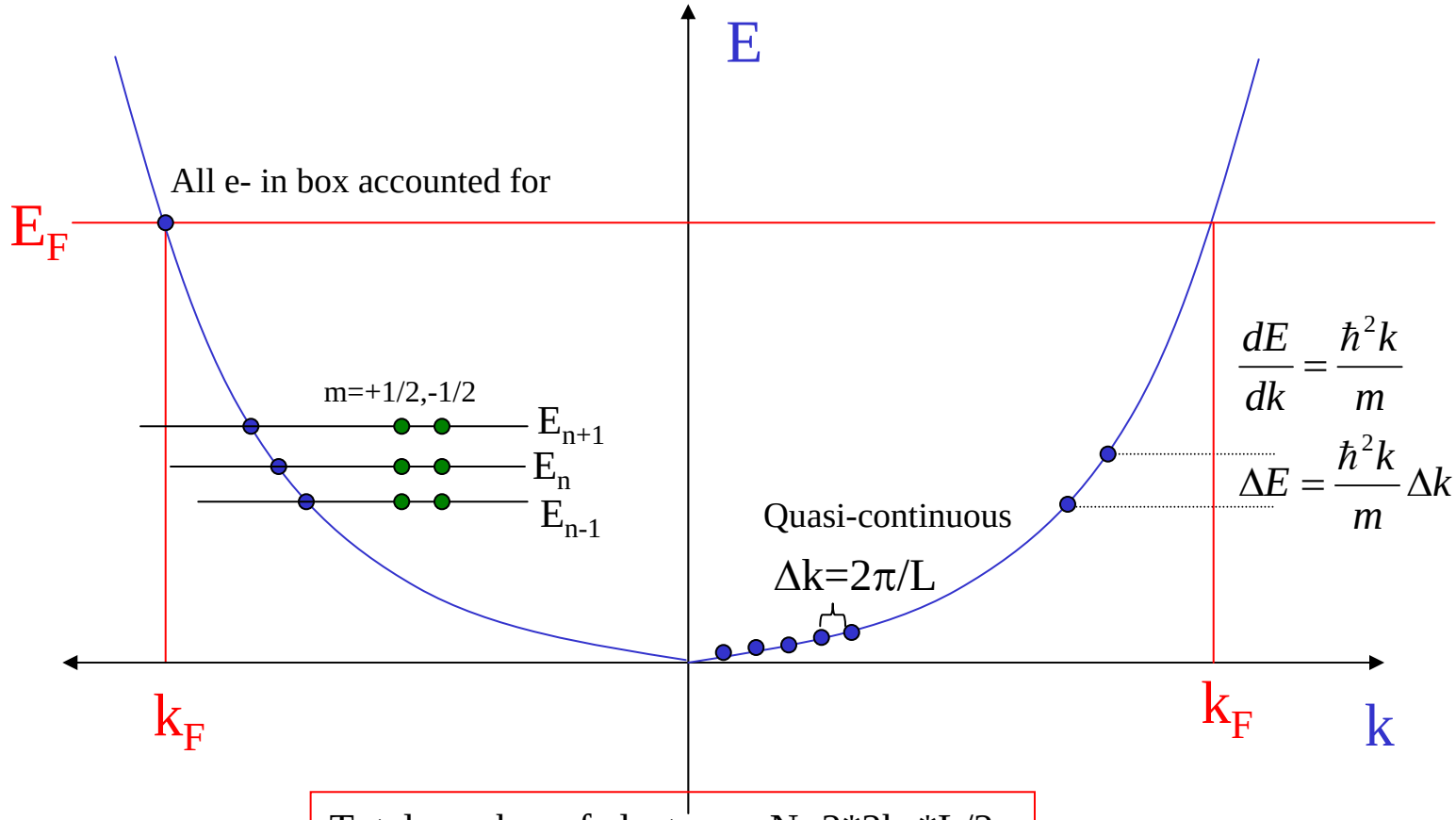
$$k = \frac{2\pi n}{L}$$

Just having a boundary condition means that k and E are quasi-continuous, i.e. for large L, they appear continuous but are discrete

Representation of E,k for 1-D Material

- states
- electrons

$$E = \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$



Total number of electrons=N=2*2k_F*L/2π

Representation of E,k for 1-D Material

$$E = \frac{\hbar^2 k^2}{2m}; k = \frac{\sqrt{2mE}}{\hbar}$$

$$N = \frac{2k_F L}{\pi}$$

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$g(E) = \frac{dN}{dk}\frac{dk}{dE}\frac{1}{L} = \frac{2}{\pi}\frac{m}{\hbar^2 k} = \frac{\sqrt{2m}}{\pi\hbar}E^{-\frac{1}{2}}$$

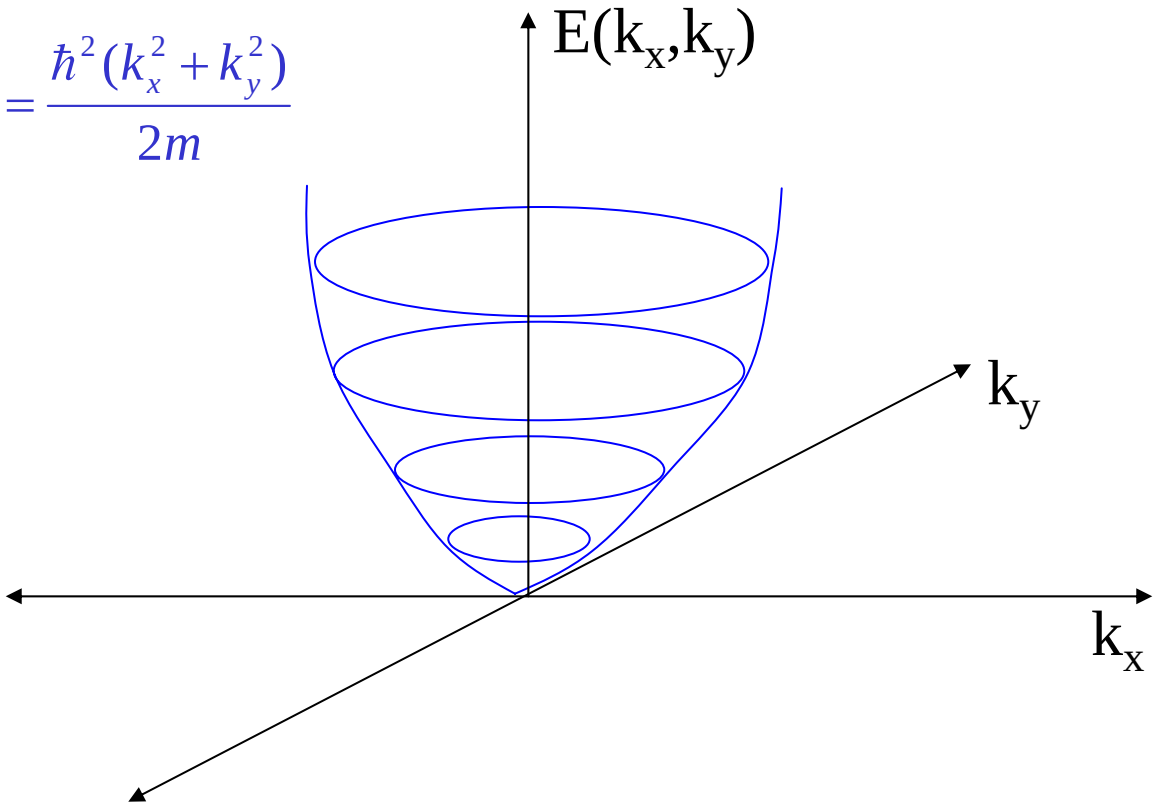
g(E)=density of states=number of electrons per energy per length

$$n = \frac{N}{L} = \frac{2k_F}{\pi} = \frac{2\sqrt{2mE_F}}{\hbar\pi} \text{ or } k_F = \frac{n\pi}{2}$$

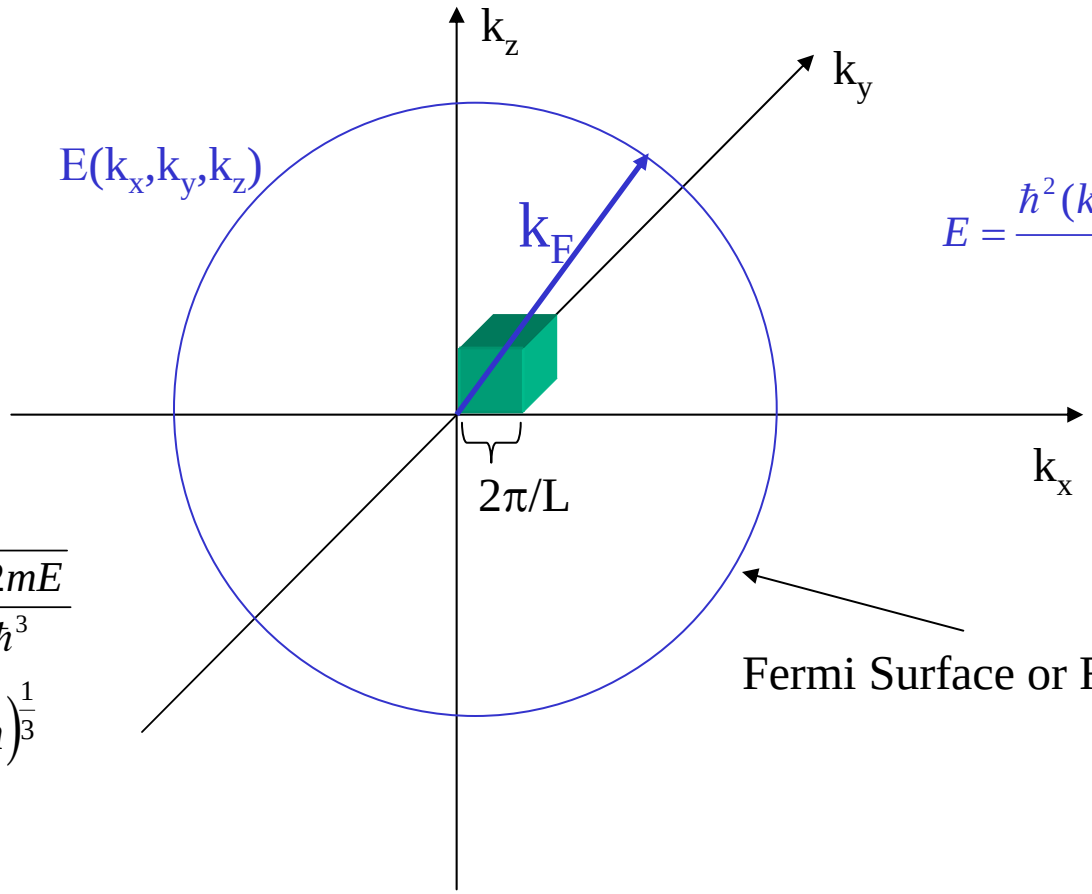
- n=is the number of electrons per unit length, and is determined by the crystal structure and valence
- The electron density, n, determines the energy and velocity of the highest occupied electron state at T=0

Representation of E,k for 2-D Material

$$E = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m}$$



Representation of E,k for 3-D Material



$$E = \frac{\hbar^2(k_x^2 + k_y^2 + k_z^2)}{2m}$$

$$g(E) = \frac{m}{\pi^2}\frac{\sqrt{2mE}}{\hbar^3}$$

$$k_F = \left(3\pi^2 n\right)^{\frac{1}{3}}$$

Fermi Surface or Fermi Sphere

$$v_F = \frac{\hbar k_F}{m} \qquad E_F = \frac{\hbar^2 k_F^2}{2m} \qquad T_F = \frac{E_F}{k_B}$$

So how have material properties changed?

- The Fermi velocity is much higher than kT even at T=0! Pauli Exclusion raises the energy of the electrons since only 2 e- allowed in each level
- Only electrons near Fermi surface can interact, i.e. absorb energy and contribute to properties

$T_F \sim 10^4 K$ ($T_{room} \sim 10^2 K$),
$E_F \sim 100 E_{class}$, $v_F^2 \sim 100 v_{class}^2$

Element	r_s / a_o	ε_F	T_F	k_F	v_F
Li	3.25	4.74 eV	5.51 x 10^4 K	1.12 x 10^8 cm^{-1}	1.29 x 10^8 cm/sec
Na	3.93	3.24	3.77	0.92	1.07
K	4.86	2.12	2.46	0.75	0.86
Rb	5.20	1.85	2.15	0.70	0.81
Cs	5.62	1.59	1.84	0.65	0.75
Cu	2.67	7.00	8.16	1.36	1.57
Ag	3.02	5.49	6.38	1.20	1.39
Au	3.01	5.53	6.42	1.21	1.40
Be	1.87	14.3	16.6	1.94	2.25
Mg	2.66	7.08	8.23	1.36	1.58
Ca	3.27	4.69	5.44	1.11	1.28
Sr	3.57	3.93	4.57	1.02	1.18
Ba	3.71	3.64	4.23	0.98	1.13
Nb	3.07	5.32	6.18	1.18	1.37
Fe	2.12	11.1	13.0	1.71	1.98
Mn	2.14	10.9	12.7	1.70	1.96
Zn	2.30	9.47	11.0	1.58	1.83
Cd	2.59	7.47	8.68	1.40	1.62
Hg	2.65	7.13	8.29	1.37	1.58
Al	2.07	11.7	13.6	1.75	2.03
Ga	2.19	10.4	12.1	1.66	1.92
In	2.41	8.63	10.0	1.51	1.74
Tl	2.48	8.15	9.46	1.46	1.69
Sn	2.22	10.2	11.8	1.64	1.90
Pb	2.30	9.47	11.0	1.58	1.83
Bi	2.25	9.90	11.5	1.61	1.87
Sb	2.14	10.9	12.7	1.70	1.96

*Fermi energies, fermi temperatures, fermi waves vectors, and fermi velocities for representative metals**

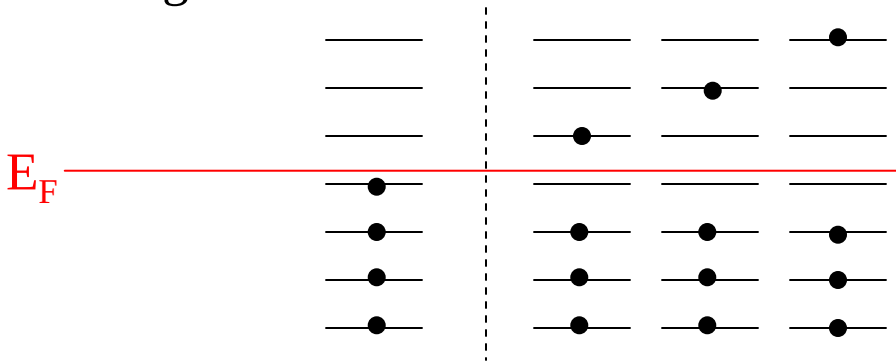
** The table entries are calculated from the values of r_s / a_0 given in Table 1.1 using m = 9.11 x 10^{-28} grams.*

Table by MIT OpenCourseWare.

Effect of Temperature (T>0): Coupled electronic-thermal properties in conductors (i.e. c_v)

- Electrons at the Fermi surface are able to increase energy: responsible for properties
- Fermi-Dirac distribution
- NOT Bolltzmann distribution, in which any number of particles can occupy each energy state/level

Originates from:



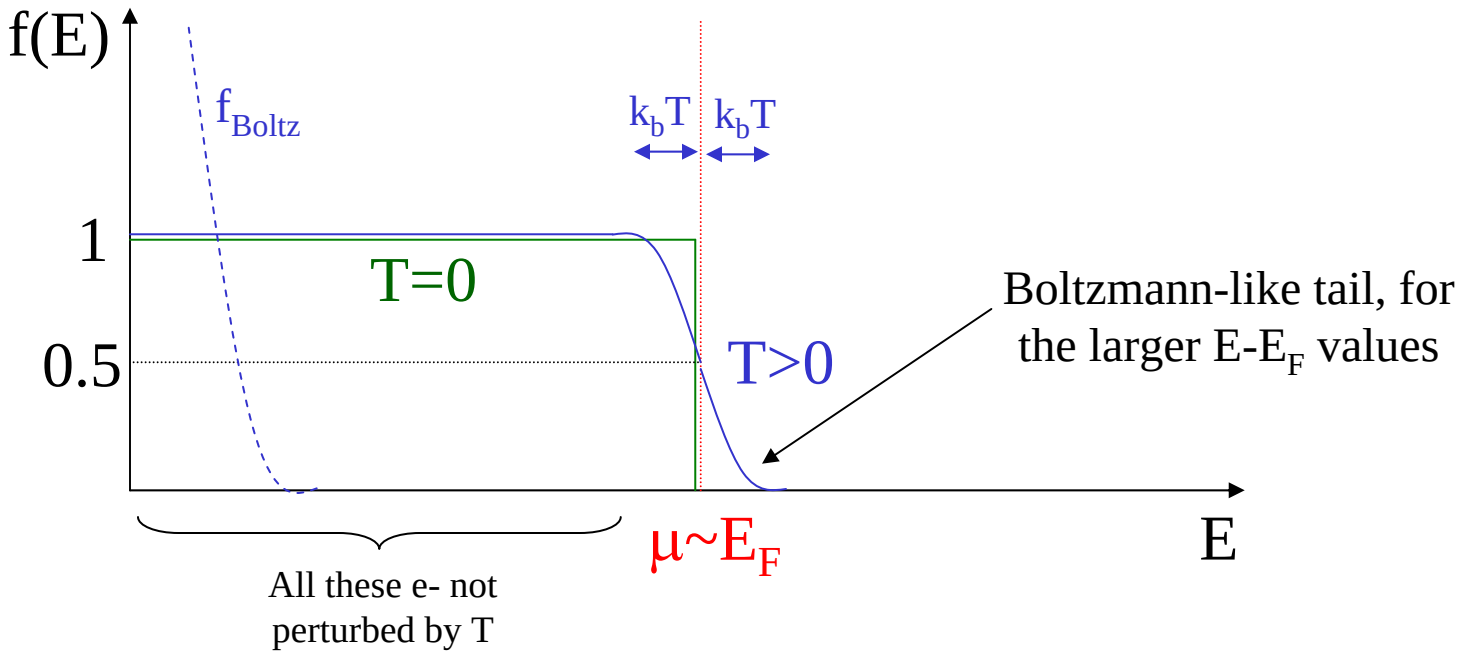
...N possible configurations

$$f = \frac{1}{e^{\frac{(E-E_F)}{k_bT}} + 1}$$

If $E-E_F/k_bT$ is large (i.e. far from E_F) than

$$f = e^{\frac{-(E-E_F)}{k_bT}}$$

Fermi-Dirac Distribution: the Fermi Surface when T>0



Heat capacity of metal (which is ~ heat capacity of free e- in a metal):

U=total energy of electrons in system

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad U \sim \Delta E \cdot \Delta N \sim k_b T \cdot \left[g(E_F)\cdot k_b T\right] \sim g(E_F)\cdot (k_b T)^2$$

$$c_v = \left(\frac{\partial U}{\partial T}\right)_v = 2 \cdot g(E_F) \cdot k_b^2 T$$

Right dependence, very close to exact derivation

Heat Capacity (c_v) of electrons in Metal

- Rough derivation shows c_v~const. x T , thereby giving correct dependence
- New heat capacity is about 100 times less than the classical expectation

Exact derivation:

$$c_v = \frac{\pi^2}{3} \cdot k_b^2 T \cdot g(E_F)$$

$$\frac{c_{vclass}}{c_{vquant}} = \frac{\frac{3}{2} n k_b}{\frac{\pi^2}{2}\left(\frac{k_b T}{E_F}\right) n k_b} = \frac{3}{\pi^2}\frac{E_F}{k_b T} \sim 100 @ RT$$