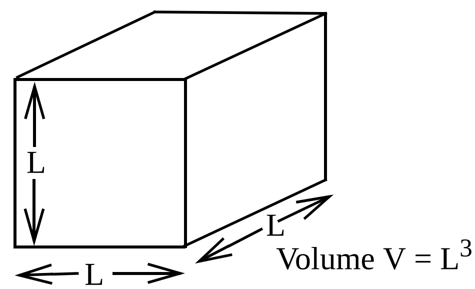
Free Electron Gas

(Read Kittel Ch. 6)

Assume non-interacting particles, mass m, spin 1/2, in a 3-D box

periodic boundary conditions:

etc. for y,z.



→ plane wave solutions. $\psi(\vec{r}) = Ae^{i\vec{k}\cdot\vec{r}}$

energy (dispersion relation)

momentum

velocity

Mode counting

Each state (mode) occupies volume in k-space.

Total # of states N, with wavevector ≤ k :

$$N = 2 \cdot \frac{\frac{4\pi}{3}k^3}{\left(\frac{2\pi}{L}\right)^3} = \frac{V}{3\pi^2}k^3$$

spin (→ 2)

⟹ total # states N, with energy $\leq E$ is:

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2}$$

Density of states

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}E^{1/2}$$

<u>Occupation of states</u>

We have to do quantum statistical mechanics.

<u>Classical</u>, distinguishable particles can have any # of particles in any state. Classical physics has no restrictions. Classical particles can be shown to satisfy a Maxwell-Boltzman distribution - probability of occupation of state at energy, E:

<u>Quantum mechanics</u> - identical particles are indistinguishable. $\longrightarrow$ Hamiltonian invariant on interchange of any two particles

$\longrightarrow$ wave function symmetric or antisymmetric on particle interchange.

Quantum field theory result:
bosons: integer spin particles have a symmetric w.f. on particle interchange.
fermions: half integer spin particles have an antisymmetric w.f.

Consider a collection of particles. The coordinates of particle *i* are represented by Q_i, and the quantum #s (state) of particle *i* are represented by s_i . Then the total wavefunction is:

$$\Psi_{\{s_1, s_2, \ldots, s_n\}}(Q_1, Q_2, \ldots, Q_N)$$

Boson wavefuntions are symmetric:

$$\Psi_{\{\ldots s_j, \ldots, s_i, \ldots\}}(\ldots Q_i, \ldots Q_j, \ldots) = \Psi_{\{\ldots s_i, \ldots, s_j, \ldots\}}(\ldots Q_i, \ldots Q_j, \ldots)$$

Fermion wavefuntions are antisymmetric:

$$\Psi_{\{\ldots s_j, \ldots, s_i, \ldots\}}(\ldots Q_i, \ldots Q_j, \ldots) = -\Psi_{\{\ldots s_i, \ldots, s_j, \ldots\}}(\ldots Q_i, \ldots Q_j, \ldots)$$

Consider fermions: suppose particles i and j, both have same quantum no's. (s). Then:

$$\Psi_{\{\ldots s \ldots s \ldots\}}(\ldots Q_j \ldots Q_i \ldots) = -\Psi_{\{\ldots s \ldots s \ldots\}}(\ldots Q_i \ldots Q_j \ldots)$$

so $\Psi = 0$ when particles j and i are in same state.
The "Pauli exclusion principle" follows from the antisymmetry of the w.f. Two Fermi particles cannot occupy the same state.

Bose-Einstein distribution:

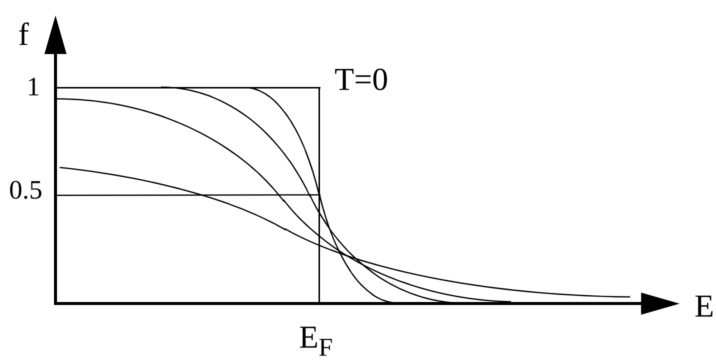
Fermi-Dirac distribution:

$\mu \equiv$ chemical potential

defined by

at T=0 $E_F \equiv \mu$ is the energy of the highest occupied state.

at finite T, $f(E = \mu) = \frac{1}{2}$; $\mu \le E_F$



μ can be negative!

Rigorously, E_F is defined as the highest occupied level at T=0.

for 3D free-electrons:

$$E_F = \mu(T=0) = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

Some other parameters:

Fermi wave vector:

Fermi velocity:

$$v_F = \frac{\hbar k_F}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

Fermi temperature:

some numbers:

Metal	electron density (N/V)cm^{-3}	E_F (eV)	v_F (cm/s)	T_F (K)
Na	2.65×10^{22}	3.23	1.07×10^{8}	3.75×10^{4}
Ag	5.85	5.48	1.39	6.36
Au	5.90	5.51	1.39	6.39
Al	18.06	11.63	2.02	13.49

Classical limit

If the mean interparticle separation, $\bar{R}$ » mean DeBroglie wavelength, $\bar{\lambda}$, then the particles are distinguishable, and Maxwell-Boltzman statistics apply

Interparticle spacing is just given by the particle density:

The quantum mechanical de Broglie wavelength of a particle is related to the particle momentum:

$\bar{p}$ is the average thermal momentum. Classically, we have:

Why is it $\frac{3}{2}kT$ this time? Solving for momentum:

So the wavelength is:

The classical limit can then be expressed as the following inequality, relating the particle density to the temperature:

$$\left(\frac{V}{N}\right)^{1/3} \gg \frac{h}{\sqrt{3mkT}}$$

or

$$T \gg \frac{h^2}{3mk}\left(\frac{N}{V}\right)^{2/3}$$

but:

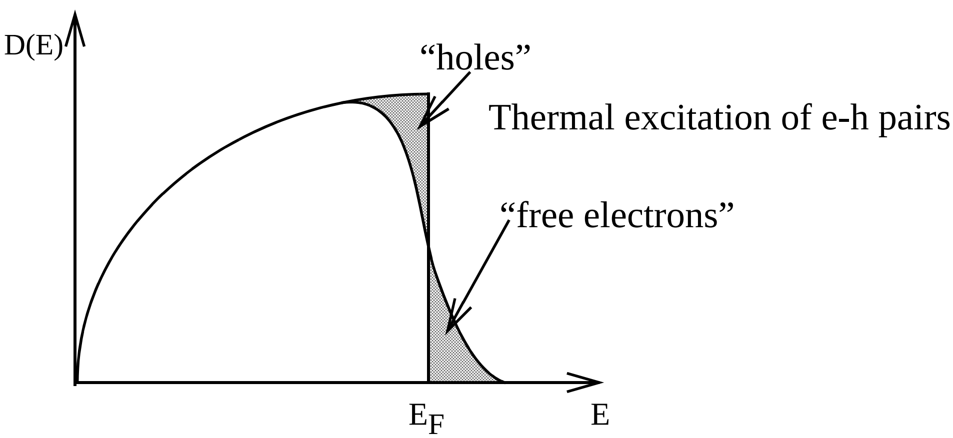
$$T_F = \frac{\hbar^2}{2mk}\left(\frac{3\pi^2 N}{V}\right)^{2/3}$$

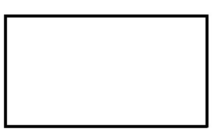
so within factor order unity, $T \gg T_F$ is formally equivalent to the classical limit, which corresponds to either high T <u>or</u> low density N/V.

<u>quantum limit</u>: $T \ll T_F$. This case is also often referred to as “degenerate”

<u>classical limit</u>: $T \gg T_F$ “non-degenerate”. In other words, the system is hotter than kT_F. The classical limit also applies when $|E - \mu| \gg kT$. That is for states far away from μ compared to kT.

<u>Electronic Heat Capacity of Fermi Gas</u>



Classically,  again wrong. Why? This time it’s due to the Pauli principle.

Roughly, only fraction T/T_F of electrons can be thermally excited, so as a rough estimate:

$$U \approx \frac{3}{2}N\left(\frac{T}{T_F}\right)kT$$

This gives:

full calculation gives (see Kittel)