

PYL 102

Monday, Sept. 23, 2024

Sommerfeld model

Basic assumption of Drude model

1. Between collisions electrons move in straight line - effect of electron-electron interaction is ignored (reasonably valid) – effect of electron-ion is ignored (completely invalid).
2. Mean free time between collisions is τ (probability of collision per unit time is $1/\tau$; probability of having a collision in infinitesimal time interval dt is dt/τ)
3. Relaxation time is independent of position and velocity of electron.
4. Electrons achieve thermal equilibrium by collisions with lattice – they emerge after collision at a random direction with speed appropriate to the temperature of the region where collision happened – the hotter the region; the higher the speed of the emerging electrons.

Note: electrons (unlike gas molecules) are charged and are moving in the background of other charged entities; electron densities also large ($\sim 10^{28}/\text{cm}^3$); still Drude applied kinetic theory (valid for neutral dilute classical gas) to metals.

Ohm's Law

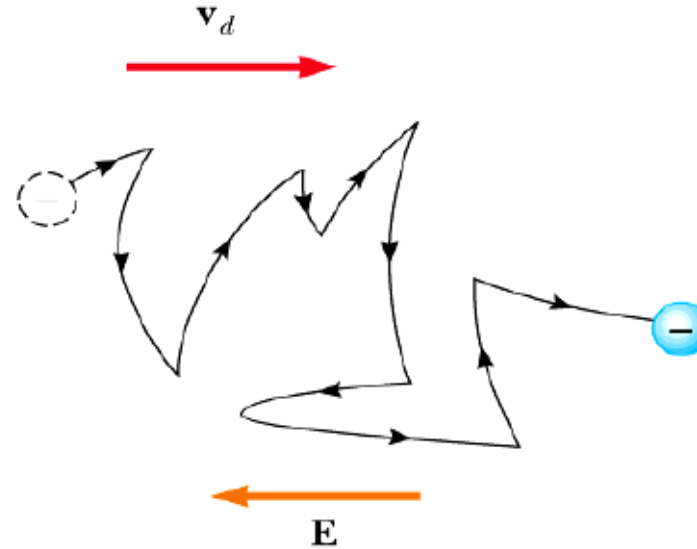
Collisions between electrons and atoms in a conductor determines the conductivity

$$\sigma = \frac{n\lambda e^2}{m_e \bar{v}}$$

λ : mean free path of an electron in the conductor, i.e., the average traveling distance of an electron that will not collide with an atom or other electron.

n : bulk electron density in a conductor

\bar{v} : average speed of an electron



Electronic heat capacity

The Drude model predicts the electronic heat capacity to be the classical “equipartition of energy” $C_{el} = 3/2 nk_B$ This is independent of temperature.

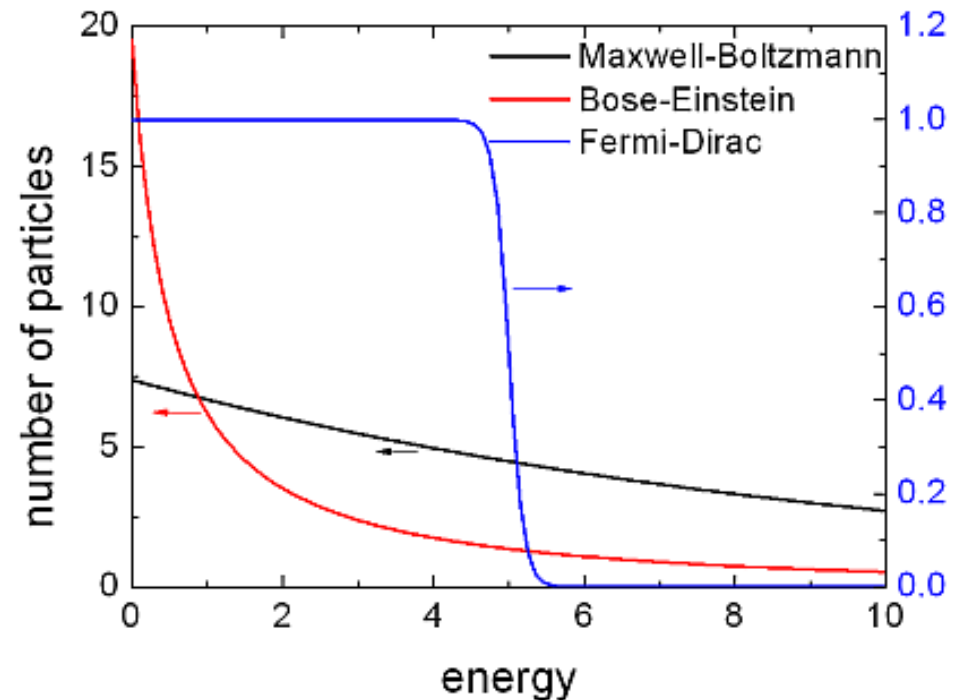
Experimentally, the low-temperature heat capacity of metals follows the relationship $C_V = \gamma T + AT^3$. The second term is obviously the phonon (Debye) component, leading us to suspect that $C_{el} = \gamma T$. Even at room temperature, the electronic component of the heat capacity of metals is much smaller than the Drude prediction. This is a severe failing of the model.

Sommerfeld Model

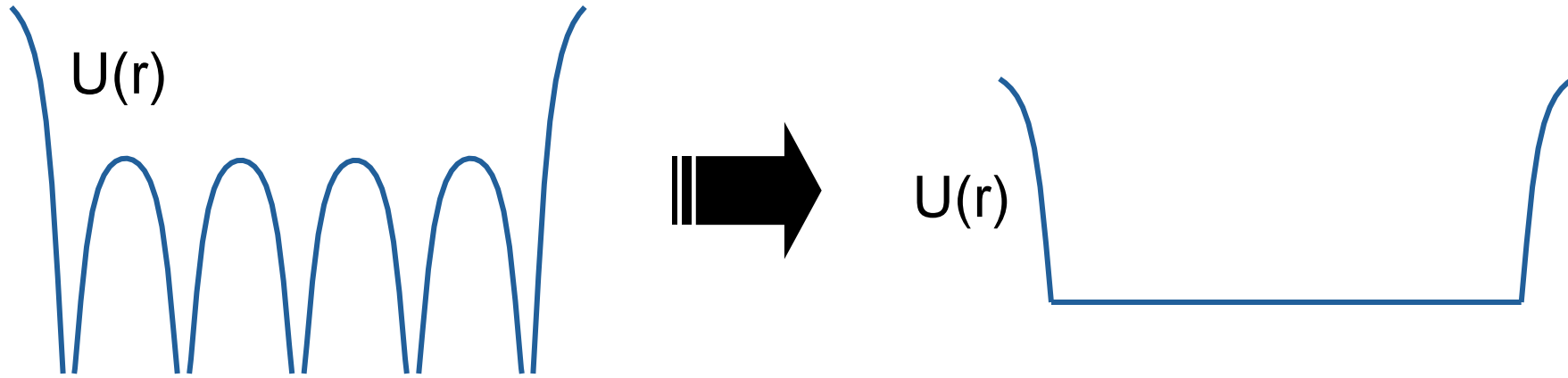
1. Treats electrons using Fermi Dirac statistics.
2. Recognizes that their energies are discrete – treats them like a particle in a box of constant energy.
3. Uses Pauli principle to distribute them in the available energy states.

Improvement to the Drude Model

- Sommerfeld recognized we needed to utilize Pauli's exclusion principle. Electrons cannot all be in the lowest energy state, since this would violate the Pauli Principle.



Sommerfeld still assumes the free electron approximation

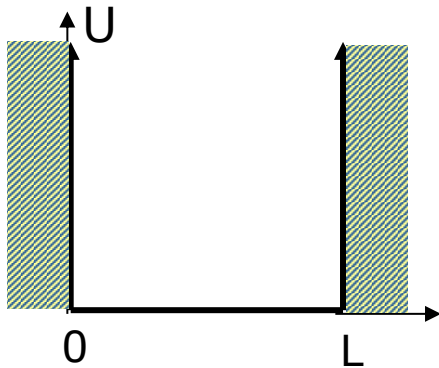


Neglect periodic potential & scattering

Reasonable for “simple metals” (Alkali Li,Na,K,Cs,Rb)

Ground state of ideal electron gas

- These conduction electrons can be considered as moving independently in a square well and the edges of well corresponds to the edges of the sample. (ignores periodic potential from atoms)
- Electron confined in a cube of sides L , potential inside the cube is constant (take it to be zero) – potential at boundaries. Assume non-interacting electrons $\Psi(r_1, r_2, \dots, r_N) = \Psi(r_1)\Psi(r_2) \dots \dots \Psi(r_N)$

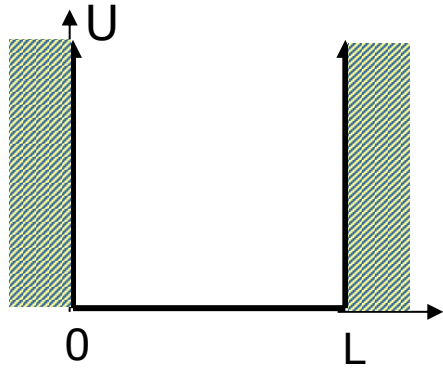


Cube $V=L^3$

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi = \varepsilon \psi$$

ε is the total energy of the system. The square of the wave function ($\psi \psi^*$) is equal to the probability of finding the particle at a particular region of space.

Electrons in crystals are moving through atomic potentials. Sommerfield/Drude models ignore those; use flat average.



$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r})$$

Eigenstates $\psi(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k} \cdot \vec{r}}$

with eigenvalues $\varepsilon = \frac{\hbar^2 k^2}{2m}$
Dispersion relation for e's

Possible Boundary conditions

1. $\Psi(0)=0$ and $\Psi(L)=0$
2. $\Psi(x,y,z) = \Psi(x+L,y,z)$

where $k = \frac{n\pi}{L}$ in 3D:

$$k_x = \frac{n_x \pi}{L}, k_y = \frac{n_y \pi}{L}, k_z = \frac{n_z \pi}{L}$$

Where n_x, n_y and n_z are integers

$$e^{i\vec{k}_x L} = 1 = e^{i\vec{k}_y L} = e^{i\vec{k}_z L}$$

For large N the filled states form a sphere in k-space – its radius is k_F (this is called the Fermi wave-vector) and volume $\frac{4}{3}\pi k_F^3$. This is the Fermi sphere. At $T = 0$

$$N = 2 \times \frac{4}{3}\pi k_F^3 \times \frac{1}{\left(\frac{2\pi}{L}\right)^3}$$

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

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

Total energy of the electronic system is

$$E = 2 \times \sum_{k < k_F} \frac{\hbar^2 k^2}{2m}$$

For large N; the values of k are arbitrarily close to each other – can treat as continuum:

$$E = 2 \frac{V}{8\pi^3} \int \frac{\hbar^2 k^2 dk}{2m} = \frac{1}{10} \frac{\hbar^2 k_F^5}{\pi^2 m}$$

Average energy per particle is

$$\frac{E}{N} = \frac{3}{5} \varepsilon_F$$

In contrast to a classical gas, the degenerate quantum mechanical electron gas has appreciable ground-state energy.

$$g(k)_{3D} dk = 2 \times \frac{4\pi k^2 dk L^3}{8\pi^3} = \frac{k^2 dk L^3}{\pi^2}$$

2 is introduced for spin up and spin down conditions for a given k value.

$$k = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow dk = \left(\frac{2mE}{\hbar^2} \right)^{-1/2} \frac{m}{\hbar^2} dE$$

$$g(E_F) dE = \frac{2mE}{\pi^2 \hbar^2} \left(\frac{2mE}{\hbar^2} \right)^{-1/2} \frac{m}{\hbar^2} dE = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

The electronic density of states at $E \approx E_F$ As only the electrons within $\sim kT$ of E_F are able to take part in thermal processes, only the density of electron states at the Fermi energy, $g(E_F)$, will be particularly important in many calculations.

In the free-electron approximation, the Fermi energy is given by $E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

$$g(E_F) \equiv dn/dE_F$$

$$\ln(E_F) = 2/3 \ln(n) + \text{constant}$$

$$g(E_F) = 3/2 (n/E_F)$$

Fermi Energy for Sodium

Density=0.971 g/cc

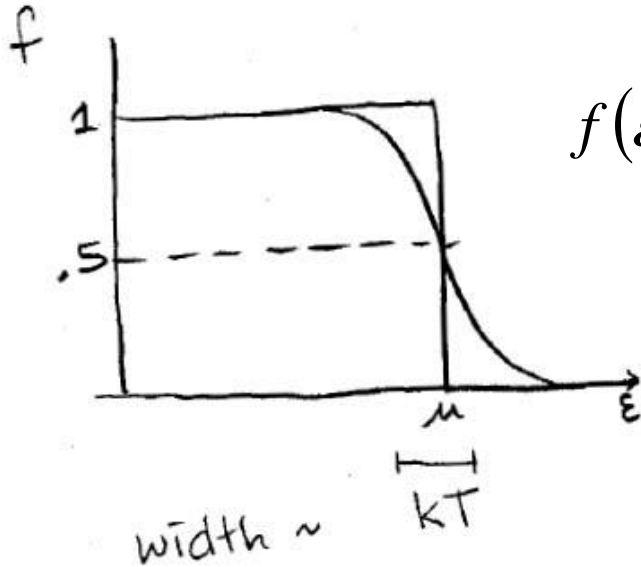
Atomic Weight=22.99

$$\frac{N}{V} = \frac{6.02 \times 10^{23} \times 0.971}{22.99} \times 10^6$$
$$= 2.543 \times 10^{28}$$

Substituting we get $E_F = \frac{\hbar^2}{2m} (3\pi^2 n)^{2/3}$

$E_F = 3.16 \text{ eV}$

Fermi-Dirac Distribution Function



$$f(\varepsilon, T) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$$

Becomes a step function at $T = 0$.

Low E : $f \sim 1$.

High E : $f \sim 0$.

μ = chemical potential gives the probability of occupation of a state of energy E

$\mu(T=0) = \varepsilon_F$ Fermi energy

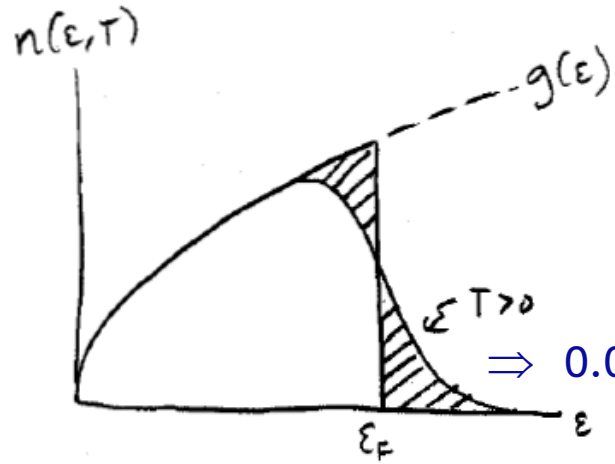
$$f(\varepsilon = \mu) = \frac{1}{1 + 1}$$

Right at the Fermi level: $f = 1/2$.

Turning to the finite T figure, f only varies significantly within $k_B T$ of μ . This has two implications.

1. As $kT \ll E_F$, this implies that $\mu \approx E_F$
2. Only electrons with energies within kT of μ , i.e. E_F , will be able to contribute to thermal processes, transport etc.. Electrons further below μ will be unable to acquire sufficient thermal energy to be excited into empty states; states more than $\sim kT$ above μ will be empty

Electronic Heat Capacity



Width of shaded region $\sim kT$

Room temp $T \sim 300\text{K}$, $T_F \sim 10^4\text{K}$

→ Small width

→ Few electrons thermally excited

⇒ 0.01% @ room temp

How many electrons are excited thermally?

Shaded area \approx triangle. Area = (base)(height)/2

Number of excited electrons: $\approx (g(\epsilon_F)/2)(kT)/2 \approx g(\epsilon_F)(kT)/4$

Excitation energy $\approx kT$ (thermal)

Total thermal energy in electrons $U(T)$: $U(T) \propto (kT)^2$

Electronic heat capacity $C_{el} = \frac{dU}{dT}$

DOS $g(E) = \frac{1}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$

At $T=0$

$$U(0) = \int_0^{E_F} E g(E) dE = \int_0^{E_F} E^{3/2} \left(\frac{1}{2\pi^2} \right) \left(\frac{2m}{\hbar^2} \right)^{3/2} dE$$

$$\Rightarrow U(0) = \frac{E_F^{5/2}}{5\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2}$$

At finite temp. e^- s are excited into higher levels.

$$U(T) = \int_0^\infty E g(E) f_D(E, T) dE = \left(\frac{1}{2\pi^2} \right) \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{E^{3/2} dE}{e^{(E-\mu)/kT} + 1}$$

$$U(T) = U(0) + \frac{n\pi^2 k^2 T^2}{4E_F} \quad (\text{for } \mu \approx E_F) \quad kT$$

$$C_{el} = \frac{dU(T)}{dT}$$

$$C_{el} = \frac{1}{2} n k \left(\frac{kT}{E_F} \right)$$

1. C_{el} is proportional to T , as are experimental data
2. C_{el} is a factor $\sim kT/E_F$ smaller than the classical (Drude) value, as are experimental data.