Seebeck effect from Drude model

A temperature gradient in a long, thin bar should be accompanied by an electric field directed opposite to the thermal gradient. This effect is known as thermoelectric effect

$$\vec{E} = Q\vec{\nabla}T \qquad \text{[Proportionality const. } Q \rightarrow \text{Thermopower]}$$

The mean electronic velocity at a point 'x' due temperature gradient (for a one-dimensional model) –

$$v_Q = \frac{1}{2}\left[v(x - v\tau) - v(x + v\tau)\right] = (-)\tau v \frac{dv}{dx}$$

$$= (-)\tau \frac{d}{dx}\left(\frac{v^2}{2}\right)$$

Generalizing to three dimensions, $v^2 \rightarrow v_x^2$ and noting $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}v^2$ so that;

$$\vec{v}_Q = (-)\frac{\tau}{6}\frac{dv^2}{dT}(\vec{\nabla}T)$$

Seebeck effect from Drude model

The mean velocity due to thermoelectric electric field

$$\vec{v}_E = (-)\frac{e\vec{E}\tau}{m}$$

$$\vec{E} = (-)\frac{m\vec{v}_E}{e\tau} = \frac{m\vec{v}_Q}{e\tau} = \frac{(-)m}{e\tau} \times \frac{\tau}{6}\frac{dv^2}{dT}(\vec{\nabla}T)$$

or, $$\vec{E} = (-)\frac{1}{3e}\frac{d}{dT}\frac{mv^2}{2}\vec{\nabla}T = (-)\frac{c_v}{3ne}\vec{\nabla}T$$

Thus, $$Q = (-)\frac{c_v}{3ne}$$

$$\vec{E} = Q\vec{\nabla}T$$

Drude took $$c_v = \frac{3nk_B}{2}$$

$$Q = (-)\frac{k_B}{2e} = (-)\,0.43 \times 10^{-4}\ \text{volt}/K$$

Typically observed thermopower at RT~ μV/K, which is 100 times smaller!

Summary of Drude Theory

- Based on kinetic theory of gas
- Assumes some scattering time τ

Successes

- Wiedemann-Franz ratio $\frac{k}{\sigma T}$ comes out close to right
- Many transport properties predicted correctly
- Hall coefficient measurement of carrier density seems reasonable for many materials

Failures

- Hall coefficient is often measured to have opposite sign indicating a change in carrier opposite to that of electron
- Themopower comes out wrong by a factor of 100

Estimate of radius per electron

A metallic element contains 0.6022×10^{24} atoms per mole.

" contains $\frac{\rho_m}{A}$ moles per cm^3

(ρ_m is the mass density, A is the atomic mass of element)

Since each atom contains Z electrons, the no. of electrons/cm^3

$$n = \frac{N}{V} = \left[0.6022 \times 10^{24} \times \frac{\rho_m}{A}\right] \times Z$$

$$\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3}$$

$r_s \rightarrow$ radius of sphere whose volume is equal to the volume per conduction electron

$$\therefore r_s = \left(\frac{3}{4\pi n}\right)^{1/3}$$

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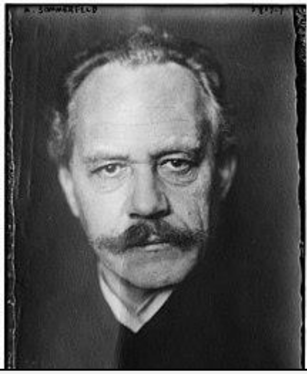
Element	Z	n ($10^{22}/cm^3$)	r_s (Å)
Li	1	4.70	1.72
Na	1	2.65	2.08

Sommerfeld theory of metals (Quantum theory)



Arnold Sommerfeld (Wikipedia)

In 1925 Wolfgang Pauli (Ph.D student of Arnold Sommerfeld) discovered the exclusion principle that no two electrons can be in the exact same state.

In 1926, Pauli and Dirac separately derived what we now call Fermi Dirac statistics.

Upon learining stay about Fermi statistics, in 1927 Sommerfeld applied Fermi-Dirac statistics to Drude model of metals which solved many problems of the original model

Classical statistics can be applied when the average interparticle separation is greater than de-Broglie wavelength

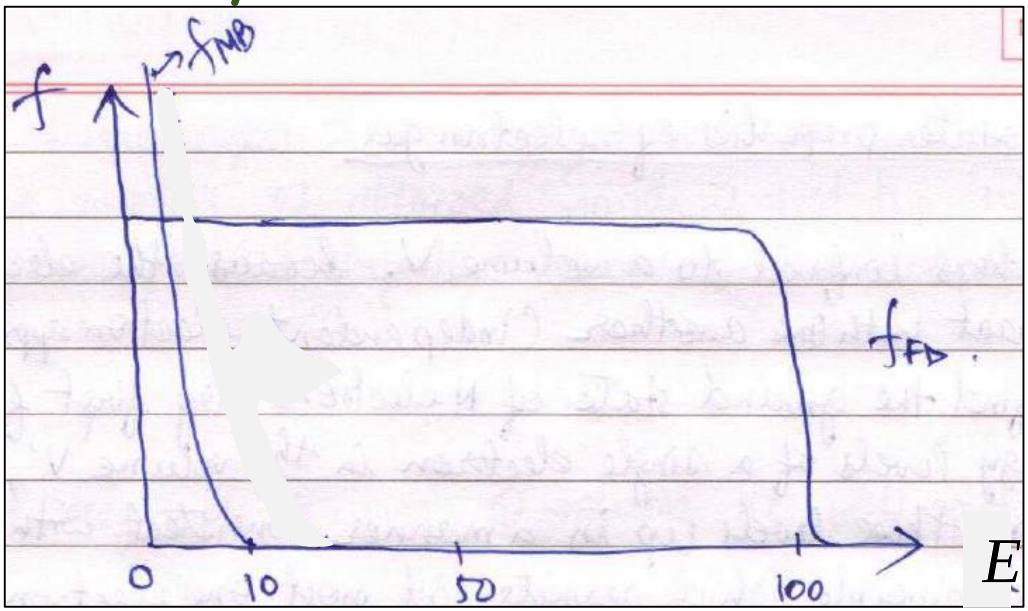
$$\bar{R} \gg \bar{\lambda} \approx \frac{h}{\sqrt{3mkT}}$$ ('m' is the mass of particle)

For conduction electrons in a typical metal at RT (300 K), the system is far from classical regime as λ ~ 62 Å

$$\bar{R} \approx \frac{\lambda}{25}$$

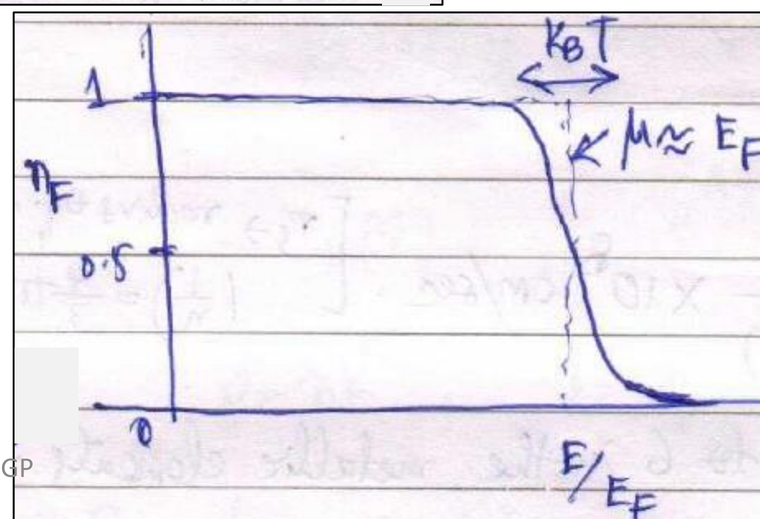
Sommerfeld theory of metals (Quantum theory)

Necessity of Fermi-Dirac (Quantum) statistics for conduction electrons in a metal instead of the Maxwell-Boltzman distribution as used by Drude -



Probability of an eigenstate of energy (E) being occupied is given by Fermi factor-

$$n_F = \frac{1}{e^{\beta(E-E_F)} + 1}$$



Sommerfeld theory of metals (contd.)

N electrons confined to a volume V. Due to independent electron approximation, the ground state of N electrons can be found by first finding the energy levels of a single electron in volume V, and then filling them as per Pauli-exclusion principle

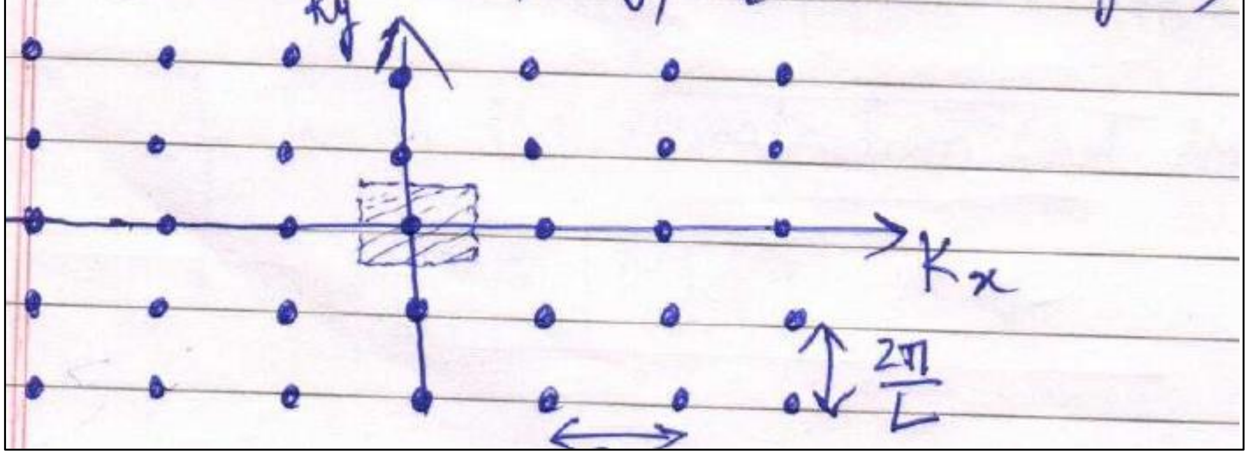
For single electron $$\psi_k(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$$ $$\varepsilon(k) = \frac{\hbar^2 k^2}{2m}$$

Imposition of periodic boundary condition restricts allowed k's -

For example along z-axis (similarly for x and y axes) $$\psi(x,y,z+L) = \psi(x,y,z)$$ $$k_z = \frac{2\pi n_z}{L}$$

(n_x, n_y, n_z → are integers)

Quantizaton of allowed k values (shown in the k_x- k_y plane)



Sommerfeld theory of metals (contd.)

For large number of electrons N-

A region of k-space of volume Ω will contain

$$\frac{\Omega}{\left(\frac{2\pi}{L}\right)^3} = \frac{\Omega V}{8\pi^3} \text{ allowed values of } k.$$

$$N = 2 \times \left(\frac{4}{3}\pi k_F^3\right) \times \frac{V}{8\pi^3} = \frac{k_F^3 V}{3\pi^2}$$

$$\boxed{n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}}$$

$$v_F = \frac{\hbar k_F}{m} = \frac{4.20}{(r_s/a_0)} \times 10^8 \text{ cm/sec.}$$

[$r_s \rightarrow$ radius of a sphere $\left(\frac{1}{n}\right) = \frac{4}{3}\pi r_s^3$]

Typically $(r_s/a_0) = 2$ to 6 in the metallic elements

[Note :- $v_T \sim 10^7$ cm/sec] $\rightarrow$ an order of magnitude smaller than v_F.

Sommerfeld theory of metals (contd.)

$$\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} = \frac{50.1\ \text{eV}}{(r_s/a_0)^2}$$

$$T_F = \frac{\varepsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4\ \text{K}.$$

- With a Fermi energy so large, any temperature (not insanely large) can only make excitations of electrons that are very close to the Fermi surface
- The electrons deep within the Fermi sea (near $k = 0$) cannot be moved by any low energy perturbation as there are no available states there

$$E_{total} = \frac{2V}{(2\pi)^3}\int_0^\infty 4\pi k^2 dk\, n_F\, \epsilon(k)$$

$$k = \sqrt{\frac{2\epsilon m}{\hbar^2}}, \text{ so, } dk = \sqrt{\frac{m}{2\epsilon\hbar^2}}\, d\epsilon$$

Sommerfeld theory of metals (contd.)

Introducing density of states $g(\epsilon)$-

$$E_{total} = V\int_0^{\infty} d\epsilon\,(\epsilon)\,g(\epsilon)\,n_F$$

where, $g(\epsilon)d\epsilon = \frac{2}{(2\pi)^3}4\pi k^2 dk = \frac{2}{(2\pi)^3}4\pi\left(\frac{2\epsilon m}{\hbar^2}\right)\sqrt{\frac{m}{2\epsilon\hbar^2}}\,d\epsilon$

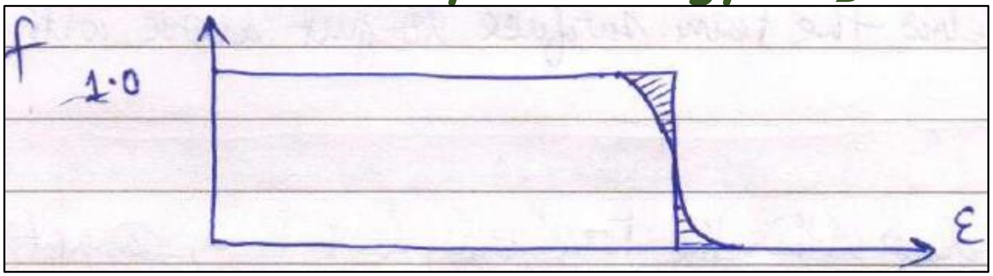
So, $$\boxed{g(\epsilon)d\epsilon = \frac{(2m)^{3/2}}{(2\pi^2)\hbar^3}\epsilon^{1/2}\,d\epsilon.}$$ → No. of eigenstates with energies between ϵ and $\epsilon+d\epsilon$.

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3},\ \text{so,}\ \frac{(2m)^{3/2}}{\hbar^3} = \frac{3\pi^2 n}{E_F^{3/2}}$$

$$g(\epsilon) = \frac{3n}{2E_F}\left(\frac{\epsilon}{E_F}\right)^{1/2}$$

Sommerfeld theory of metals (contd.)

Only electrons with an energy range of roughly 'k_BT' from the Fermi surface can be excited by an energy $\sim k_BT$



$$E(T) = E(T=0) + \left(\frac{\pi^2}{6}\right)\left[V\, g(E_F)(k_BT)\right](k_BT) + \cdots$$

density of states per unit volume $g(\epsilon_F)$

$$C = \frac{\pi^2}{3} k_B\, g(\epsilon_F)\, V (k_BT)$$

The heat capacity

$$\boxed{C = \frac{\partial E}{\partial T} = \left(\frac{\pi^2}{3}\right)\underbrace{\left(\frac{3Nk_B}{2}\right)}_{\text{Classical result of heat capacity}}\left(\frac{T}{T_F}\right)}$$

$\left(\frac{T}{T_F}\right)$ is tiny $\sim$ (0.01 or smaller)

Sommerfeld theory of metals (contd.)

- Drude's theory predicted thermopower $\boxed{Q = (-)\frac{C_v}{3ne}}$ to be 100 times larger. Using Sommerfeld's theory it is clear that the reason was over-estimation of electronic specific heat
- Also -

$$\frac{K}{\sigma} = \frac{1}{3} C_v \frac{m\langle v^2 \rangle}{ne^2}$$

C_v in Drude's theory was over-estimated by $\left(\frac{T_F}{T}\right)$

(Classically $\frac{mv^2}{2} = K_B T$, whereas Sommerfeld's model, one should use Fermi velocity $\frac{mv_F^2}{2} = K_B T_F$)

Then, $\langle v^2 \rangle$ in Drude's theory was underestimated by $\left(\frac{T}{T_F}\right)$

Thus, these two errors cancel out, giving roughly similar value for $\left(\frac{K}{\sigma}\right)$.

Some of the shortcomings of free-electron model

- $\lambda = v_F \tau$ may be 100 Å or more. But there are atoms every few Å in a metal, why do electrons not scatter from these atoms ? (Resolution – Blöch theorem)

- Why core electrons do not count for calculating Fermi energy?

- Why Hall-effect sometimes comes with an opposite sign?

- For some metals, the specific heat is off by factors as large as 10

- Mass of the electron in a metal often varies from the actual rest mass of an electron

Sommerfeld theory of metals (summary)

- Treats properly the fact that electrons are fermions
- High density of electrons results in extremely high Fermi energy and Fermi velocity. Thermal and electric excitations are small redistributions of electrons around the Fermi surface
- Compared to Drude theory, obtains electron velocities ~ 100 times larger, but heat capacity per electron ~ 100 times smaller. Leaves Wiedemann-Franz ratio roughly unchanged from Drude, but fixes problems in prediction of thermal properties
- Drude transport equations make sense if one considers velocities to be drift velocities