

## Sommerfeld-Drude model

### Recap of Drude model:

1. Treated electrons as free particles moving in a constant potential background.
2. Treated electrons as *identical* and *distinguishable*.
3. Applied classical (Maxwell-Boltzmann) statistics on them.

### Drawbacks of this approach:

1. electrons cannot be treated classically – they are Fermions
2. They are *identical* and *indistinguishable*.
3. They obey Pauli exclusion principle

These observations imply that electrons obey Fermi-Dirac (FD) statistics.

Sommerfeld Drude model: - Retains almost all aspects of Drude model with the following modifications:

1. Treats electrons using FD 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.

### Ground state of ideal electron gas

Electron confined in a cube of sides  $L$  at  $T=0$ , potential inside the cube is constant (take it to be zero) – potential at boundaries  $\infty$ . Assume non-interacting electrons i.e.

$$\psi(r_1, r_2, \dots, r_N) = \psi(r_1)\psi(r_2) \dots \dots \psi(r_N)$$

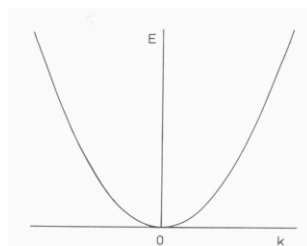
Hamiltonian is:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi = \epsilon \psi$$

Using the periodic boundary condition  $\psi(x + L, y, z) = \psi(x, y, z)$  and so on,

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

with the energy eigenvalues  $\epsilon(k) = \frac{\hbar^2 k^2}{2m}$  - this is the dispersion relation for free electrons.



**Figure 1: Dispersion relation for free electrons**

$\mathbf{k}$  is a position independent wave vector, each value of  $\mathbf{k}$  label a distinct state.

$$\mathbf{p}\psi = \hbar\mathbf{k}\psi$$

implying that  $\mathbf{k}$  plays the role of wave-vector for the free electrons

Allowed values of  $k$  are given by the quantization condition  $\psi(x + L, y, z) = \psi(x, y, z)$  to be

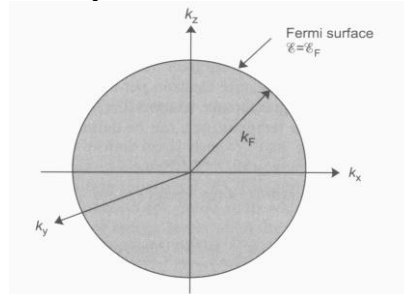
$$k_x = \frac{2\pi}{L} n_x \text{ where } n_x \text{ is an integer}$$

Now we have levels – put electrons in them following Pauli exclusion principle (Pauli exclusion principle is a manifestation of e-e interaction although we did not put it in explicitly in the Hamiltonian) – can do this as electrons are treated to be independent - each level denoted by a particular value of  $k$  can accommodate two electrons (for two values of the spin projection).

For large  $N$  the filled states form a sphere in  $k$ -space (remember  $(k) \propto k^2$ ) – 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*.  $k_F$  is given by:

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

$$k_F = (3\pi^2 n)^{\frac{1}{3}} \text{--- (1)}$$



**Figure 2: Fermi sphere at T=0**

The highest occupied energy level in the ground state is called the *Fermi energy*. This separates the completely filled states from the completely empty ones in the ground state. For free electrons  $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$ . For metallic systems *Fermi energy*  $\epsilon_F \sim eV$  and *Fermi velocity*  $v_F = \frac{\hbar k_F}{m} \sim 10^6$  m/s.

Total ground state energy is

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

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

$$\sum_K \rightarrow \frac{V}{8\pi^3} \int d\mathbf{k}$$

thus the total energy of the electronic system is

$$E = 2 \frac{V}{8\pi^3} \int \frac{\hbar^2 k^2}{2m} d\mathbf{k} = 2 \frac{V}{8\pi^3} \int \frac{\hbar^2 k^2}{2m} 4\pi k^2 dk = \frac{1}{10} \frac{\hbar^2}{\pi^2 m} k_F^5$$

Average energy per particle is

$$\frac{E}{N} = \frac{E/N}{V/V} = \left( \frac{1}{10} \frac{\hbar^2}{\pi^2 m} k_F^5 \right) / (k_F^3 / 3\pi^2) = \frac{3}{5} \varepsilon_F = \frac{3}{5} k_B T_F$$

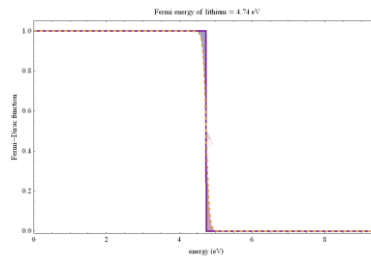
In contrast to a classical gas, the degenerate quantum mechanical electron gas has appreciable ground-state energy. The Fermi temperature  $T_F \sim 10^5$  K; hence compared to classical gas at room temperature the average energy of electrons is about 100 times more.

### Ideal electron gas at finite temperatures

Probability that a state with energy  $\varepsilon$  is occupied at temperature  $T$  is

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

where  $\mu$  is the chemical potential and equals  $\varepsilon_F$  at  $T=0$ . Nominally it is the value of energy at which the probability of occupation is  $1/2$ .



**Figure 3: Fermi function at zero temperature and at a finite temperature**

The total energy of the electron gas at a finite temperature is:

$$E = 2 \frac{V}{8\pi^3} \int f(\varepsilon) \varepsilon(k) d\mathbf{k}$$

Or the energy density  $u=E/V$  is

$$u = \frac{1}{4\pi^3} \int f(\varepsilon) \varepsilon(k) d\mathbf{k}$$

Similarly number density  $n$  is:

$$n = \frac{1}{4\pi^3} \int f(\varepsilon) d\mathbf{k}$$

Change the integral form from over  $k$  to over energy:

$$\frac{d\mathbf{k}}{4\pi^3} = \frac{1}{4\pi^3} 4\pi k^2 dk = \frac{1}{\pi^2} k^2 dk = \frac{1}{\pi^2} \frac{2m\varepsilon}{\hbar^2} \sqrt{\frac{m}{2\hbar^2}} \frac{d\varepsilon}{\sqrt{\varepsilon}}$$

or

$$n = \frac{1}{4\pi^3} \int f(\varepsilon) d\mathbf{k} = \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon$$

where

$$g(\varepsilon) = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \sqrt{\varepsilon} = \frac{3}{2} \frac{n}{\varepsilon_F} \sqrt{\frac{\varepsilon}{\varepsilon_F}}$$

is the density of states,  $g(\varepsilon)d\varepsilon = \#$  states per unit volume in the energy interval  $\varepsilon$  and  $d\varepsilon$ .

Similarly,

$$u = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon$$

This is a general form independent of any approximations regarding the interaction of the electrons (which enters only through the specific form of  $g(\varepsilon)$  used).

The number density in Sommerfeld model is given by:

$$n = \int_0^\infty f(\varepsilon) g(\varepsilon) d\varepsilon = \frac{1}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \sqrt{\varepsilon} f(\varepsilon) d\varepsilon$$

or,

$$n = 2 \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2} \left( \frac{\mu}{k_B T} \right)$$

where  $F_{1/2}(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{y^{1/2}}{e^{(y-x)} + 1} dy$  is Fermi integral of order  $1/2$  - can be solved exactly only in two extreme limits.

1.  $\frac{\mu}{k_B T} \ll 1$  (valid for low-density systems like semiconductors):

$$n = 2 \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} e^{\frac{\mu}{k_B T}}$$

2.  $\frac{\mu}{k_B T} \gg 1$  (valid for high-density systems like metals):

$$F_{1/2}(x) \approx \frac{4}{3\sqrt{\pi}} x^{3/2} \left[ 1 + \frac{\pi^2}{8} \frac{1}{x^2} + \dots \right]$$

$$n = \frac{1}{3\pi^2} \left( \frac{2m\mu}{\hbar^2} \right)^{3/2} \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 + \dots \right] \text{---(2)}$$

Also, from equation (1) we have

$$n = \frac{1}{3\pi^2} k_F^3 = \frac{1}{3\pi^2} \left( \frac{2m\varepsilon_F}{\hbar^2} \right)^{3/2} \text{----(3)}$$

Combining eqns. 2 and 3 we get,

$$\varepsilon_F = \mu \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 + \dots \right]^{2/3}$$

This gives the expression for  $\mu$  in terms of  $\varepsilon_F$  (in the limit  $\frac{k_B T}{\mu} \ll 1$ ):

$$\mu = \varepsilon_F \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\varepsilon_F} \right)^2 + \dots \right]$$

Even near the melting point of metals,  $k_B T / \varepsilon_F \ll 1$ , hence for metals at all temperatures  $\mu \sim \varepsilon_F$ .

The energy density in Sommerfeld mode can be similarly calculated:

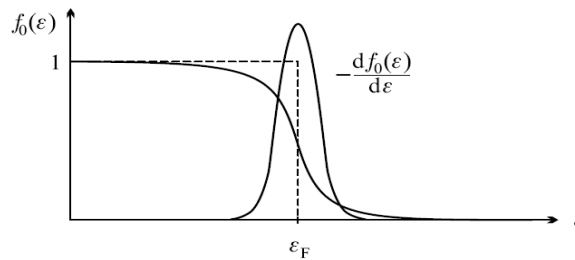
$$u = \int_0^\infty \varepsilon f(\varepsilon) g(\varepsilon) d\varepsilon = u_0 + \frac{\pi^2}{6} (k_B T)^2 g(\varepsilon_F)$$

The specific heat then becomes:

$$c_V = \frac{\partial u}{\partial T} = \frac{\pi^2}{3} k_B^2 T g(\varepsilon_F) = \frac{\pi^2}{2} \frac{k_B T}{\varepsilon_F} n k_B$$

Compared to classical value  $\sim n k_B$  the Sommerfeld electronic contribution is  $\sim \frac{k_B T}{\varepsilon_F} \sim 100$  times smaller.

Physically  $c_V \sim T$  easy to understand – at any finite temperature the Fermi distribution changes appreciably from its zero temperature value only in a narrow region of width few  $k_B T$  around  $\mu$ . The Fermi edge is smeared out over this narrow energy range by the thermally created electron–hole pairs. The states are neither fully occupied nor completely empty here. At energies that are farther than a few times  $k_B T$  from the chemical potential  $\mu$ , states within the Fermi sphere continue to be completely filled, as if they were frozen in, while states outside the Fermi sphere remain empty. Thus, the majority of the electrons are frozen in states well below the Fermi energy: only electrons in a region of a few times  $k_B T$  in width around  $\varepsilon_F$  – i.e., about a fraction  $k_B T / \varepsilon_F$  of all electrons – can be excited thermally, giving finite contributions to the specific heat.



**Figure 4: Derivative of Fermi function at a finite temperature**

Number of electrons excited at any temperature  $T$  is  $\propto g(\varepsilon_F) k_B T$ . Each of them gains energy  $\sim k_B T$ . Total energy gain  $\sim (k_B T)^2 g(\varepsilon_F)$ . So

$$c_V = \frac{\partial u}{\partial T} \sim k_B^2 T g(\varepsilon_F)$$

$c_V \propto T$  is not seen at room temperature, rather the specific heat over any extended temperature range goes as  $c_V = \gamma T + AT^3$ .

The values of  $\gamma$  measured for Alkali metals match quite well with the experimental values. The difference in the calculated and experimental values can be attributed to an apparent change in the mass of the electrons in response to the periodic potential due to the ions in the crystal. For certain compounds (called *Heavy Fermions*) like  $\text{CeAl}_3$  and  $\text{CeCu}_6$   $\gamma_{\text{ex}}$  can be hundreds of times larger than  $\gamma_{\text{th}}$  – to account for these we need strong e-e interactions.

Other properties of electron gas from Sommerfeld model:  $\tau$  does not depend on the distribution function – only properties that explicitly depend on  $v$  or  $l$  will change from the Drude value.

- Thermal conductivity  $\kappa = \frac{1}{3} v l C_v$  remains unchanged.
- Thermo power  $Q = -\frac{1}{3ne} c_v = -\frac{\pi^2}{6} \left(\frac{k_B}{e}\right) \left(\frac{k_B T}{\epsilon_F}\right) \sim \frac{k_B T}{\epsilon_F} \times 10^{-4} \text{V/K}$  - 100 times smaller than Drude value, closer to measured values of  $Q$ .
- Electrical properties remain unchanged.
- Wiedemann-Franz law still remains theoretically valid (experimentally valid only at very low  $T$  and at high  $T$ ).

How can we use quantum statistics in a classical dynamical theory? – Why does Sommerfeld model work?

We can use classical description if uncertainty principle is not violated. For typical electron  $p \sim \hbar k_F$  so maximum  $\Delta p \sim \hbar k_F$ ; implying the uncertainty in its position is  $\Delta x \sim \frac{\hbar}{\Delta p} \sim \frac{1}{k_F}$  which is of the order of the lattice spacing. If we do not want to probe electron dynamics in the scale of lattice spacings classical description is OK. Conduction electrons are delocalized – need not probe them on atomic scale – mean free path  $\sim 100$  Angstroms. Probing with visible light (wavelength  $\sim 1000$  Angstroms) also poses no problems. Cannot study electron dynamics under X-ray excitation ( $\lambda \sim 1$  Angstrom) by using this model.