The Sommerfeld Theory of Metals

In the Drude model it is implicitly assumed that the electronic velocity distribution is given by the Maxwell-Boltzmann's:

$$f(\vec{v}) = n\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{\frac{1}{2}mv^2}{k_B T}}$$

1. The Maxwell-Boltzmann velocity distribution:

Consider a classical gas with total energy $K(\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$

The kinetic part is a quadratic function of the momenta, while the potential part depends only on the particle positions. The probability of occurrence of a microstate at equilibrium at T is given by the canonical distribution:

$$p(\vec{r}_1, \dots, \vec{r}_N, \vec{p}_1, \dots, \vec{p}_N) = A\, e^{-[K+U]/kT} = A\, e^{-\frac{K}{kT}} e^{-\frac{U}{kT}}$$

This factorization implies that the probabilities of position and momenta are independent. The probability for the momenta are:

$$f(\vec{p}_1, \dots \vec{p}_N)\, d^N\vec{p} = C\, e^{-\frac{K}{kT}} d^N\vec{p}$$

Because K is the sum of the energy of each particle, this probability is still factorized: the momenta distribution of the various particles are independent (and do not depend on the interactions)

For a single particle:

$$f(p_x\, p_y\, p_z)\, dp_x\, dp_y\, dp_z = C\, e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT}\, dp_x\, dp_y\, dp_z$$

$$C = \frac{1}{\int_{-\infty}^{+\infty} e^{-(p_x^2+p_y^2+p_z^2)/2mKT} dp_x\, dp_y\, dp_z} = \frac{1}{\left[\int_{-\infty}^{+\infty} e^{-p^2/2mKT} dp\right]^3} =$$

$$= \left(2\pi m KT\right)^{-3/2}$$

Hence:

$$d^3p \quad f(p_x, p_y, p_z) = \left(\frac{1}{2\pi m KT}\right)^{3/2} e^{-\frac{(p_x^2+p_y^2+p_z^2)}{2mKT}} dp_x\, dp_y\, dp_z$$

$$f(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{v_x^2+v_y^2+v_z^2}{2KT}} dv_x\, dv_y\, dv_z$$

□

2. The Fermi-Dirac distribution

Occupation numbers: we divide the system into sub-systems, each of which is the set of all particles that are in a given single particle microstate. Then, the number of the particles in a sub-systems can vary ⇒ the use of the grand-canonical ensemble: (Move to the next page)

$$Z_G = \sum_S e^{-\beta(E_S - \mu N_S)} \quad ; \quad \Omega = -KT \ln Z_G$$

S ≡ runs over the micro-states; The mean number of particles is then

$$\bar{N} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}$$

The probability of occupation of a particular microstate is:

$$p_S = \frac{1}{Z_G} e^{-\beta(E_S - \mu N_S)}$$

For a single particle microstate k (a sub-system), the grand-partition function is

$$Z_{G,k} = \sum_{n_k} e^{-\beta\, n_k (\varepsilon_k - \mu)}$$

For fermions, $n_k = 0$, or 1: $\rightarrow$ $Z_{G,k} = 1 + e^{-\beta(\varepsilon_k - \mu)}$

Then, the Landau potential becomes:

$$\Omega_k = -kT \ln Z_{G,k} = -kT \ln\left[1 + e^{-\beta(\varepsilon_k - \mu)}\right]$$

Then,

$$\bar{n}_k = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{-\beta(\mu - \varepsilon_k)}}{1 + e^{-\beta(\mu - \varepsilon_k)}} = \frac{1}{e^{\beta(\varepsilon_k - \mu)} + 1}$$

$\square$

For an ideal Fermi gas: $\varepsilon_k = \frac{1}{2} m v^2$

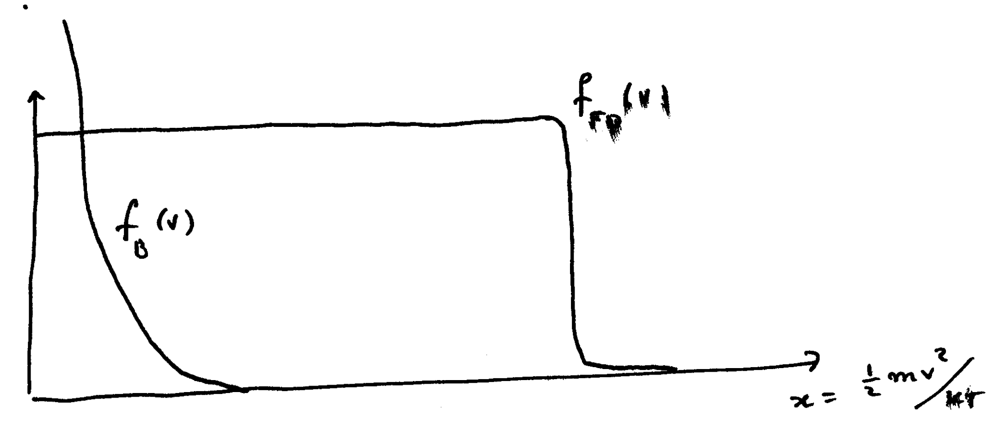
$$v = \frac{\hbar k}{m} \qquad \frac{d^3 k}{(2\pi)^3} = \left(\frac{m}{\hbar}\right)^3 \frac{1}{(2\pi)^3}\, d^3 v$$

OR:

$$d^3 v\, f(\vec{v}) = \left(\frac{m}{\hbar}\right)^3 \frac{1}{4\pi^3}\, \frac{1}{e^{\beta(\frac{1}{2}mv^2 - \mu)} + 1}\, d^3 v$$

(including spin) $\square$

What are the consequences of this dramatic change in terms of the electron gas?



3. The ground-state of N electrons confined to a volume V:

(ideal gas: electrons do not interact with each other)

$$-\frac{\hbar^2}{2m}\nabla^2\psi = \varepsilon\,\psi \qquad (1)$$

Boundary conditions (Periodic) $\quad \psi(x,y,z+L) = \psi(x,y,z)$ etc

$\qquad\qquad\qquad\qquad\qquad\qquad\quad\; \psi(x,y+L,z) = \psi(x,y,z)$ etc

The general solution of (1) is $\psi_k = \frac{1}{\sqrt{V}}\, e^{i\vec{k}\cdot\vec{r}}$, with $\varepsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$

$\hat{p} = -i\hbar\partial_{\vec{r}} \Rightarrow \hat{p}\,\psi = \hbar\vec{k}\,\psi$ (each eigenstate has a well defined momentum $\vec{p} = \hbar\vec{k}$, and hence $\vec{v} = \frac{\vec{p}}{m} = \frac{\hbar\vec{k}}{m}$ $\quad \left(\varepsilon(\vec{k}) = \frac{p^2}{2m}\right)$

We now invoke the boundary conditions:

$$e^{ik_xL} = e^{ik_yL} = e^{ik_zL} = 1 \quad \Rightarrow \quad k_i = \frac{2\pi m_i}{L}$$

Each allowed k-point occupies a volume $\left(\frac{2\pi}{L}\right)^3$ in k-space

Therefore, a volume Ω of the k-space will contain $\frac{\Omega}{(2\pi/L)^3}$ points, or the number of allowed k-points per unit volume is:

$$\frac{V}{(2\pi)^3}$$

The ground state, will then correspond to occupy all the k-states within a sphere of radius k_F: Hence:

$$\frac{4}{3}\pi k_F^3 \,\frac{V}{(2\pi)^3} = \frac{N}{2} \text{ electrons}$$

$\qquad\qquad\qquad\qquad\qquad\qquad\quad \mapsto$ (spin)

$$\frac{N}{V} = \frac{k_F^3}{3\pi^2} = n \quad ; \quad E_F = \frac{\hbar^2 k_F^2}{2m}$$

That means that at $T = 0\,K$, all states up to E_F are occupied and all states above E_F are empty.

Let us express these quantities in terms of the electron density

$$k_F = (3\pi^2 n)^{1/3} \qquad E_F = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m} ,$$

or in terms of a dimensionless parameter $\frac{r_s}{a_0}$

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \equiv \text{Radius of the "free space" sphere per electron}$$

$$r_s^3 = \frac{3}{4\pi n} \rightarrow n = \frac{3}{4\pi r_s^3} \rightarrow k_F = \left(\frac{3\pi^{\cancel{2}}\, 3}{4\cancel{\pi} r_s^3}\right)^{1/3} = \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s}$$

$$k_F \sim \frac{3{,}63}{r_s/a_0} \; \mathring{A}^{-1} \Rightarrow \text{de Broglie wavelength} \sim \mathring{A}$$

As a result, the velocity $v_F = \frac{\hbar k_F}{m} = 10^8 \text{ cm} \cdot s^{-1}$ (1% c)

(Note that this is at $T = 0\,K$)

$$E_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right) (k_F a_0)^2$$

$\downarrow$

R_y (rydberg) $\equiv$ ground state binding energy of the hidrogen atom $\sim 13{,}6$ eV

$$E_F = (13{,}6\,\text{eV})(k_F a_0)^2 =$$

$$= \frac{50{,}1\,\text{eV}}{(r_s/a_0)^2}$$

(something in the range of 1,5 — 15 eV)

Because the k-volume per point is $\frac{8\pi^3}{V}$

$$\sum_{\vec{k}} F(\vec{k}) = \frac{V}{8\pi^3} \sum_{\vec{k}} F(\vec{k})\, \Delta\vec{k}$$

In the limit $V \to \infty$ ($\Delta\vec{k} \to 0$) this goes to:

$$\int \frac{d\vec{k}}{8\pi^3} f(\vec{k}) = \lim_{V\to\infty} \frac{1}{V} \sum_{\vec{k}} f(\vec{k})$$

- $$\frac{E}{V} = \frac{1}{4\pi^3} \int_0^{k_F} d\vec{k}\, \frac{\hbar^2 k^2}{2m} = \frac{4\pi}{4\pi^3} \frac{\hbar^2}{2m} \int_0^{k_F} k^4\, dk = \frac{1}{\pi^2} \frac{\hbar^2}{10m} k_F^5$$

- $$\frac{N}{V} = \frac{4\pi}{4\pi^3} \int_0^{k_F} k^2\, dk = \frac{1}{\pi^2} \frac{1}{3} k_F^3$$

Hence $\frac{E}{N} = \frac{3}{5} E_F = \frac{3}{5} k_B T_F \quad \to T_F \sim 10^4\,\mathrm{K}\,!$

$$P = -\left(\frac{\partial E}{\partial V}\right)_N = \left[\frac{\partial}{\partial V}\left(\frac{3}{5} N E_F\right)\right]_N = \frac{\partial}{\partial V}\left(\frac{3}{5} N \cdot \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m}\right)$$

$$n^{2/3} = \left(\frac{N}{V}\right)^{2/3} \to \quad P = \frac{2}{3}\frac{E}{V}$$

$$B = -V \frac{\partial P}{\partial V} \text{ (bulk modulus)} = \frac{2}{3} n E_F$$

□

4. Thermal properties of the free electron gas:

$$\frac{E}{V} = u = \int \frac{d\vec{k}}{4\pi^3}\, \varepsilon(\vec{k})\, f_{FD}(\varepsilon(\vec{k}))$$

$$\frac{N}{V} = n = \int \frac{d\vec{k}}{4\pi^3}\, f(\varepsilon)$$

$$d\vec{k} = k^2 4\pi\, dk \qquad \frac{\hbar^2 k^2}{2m} = E \qquad dE = \frac{2\hbar^2 k}{2m}\, dk$$

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

$$= \sqrt{\frac{2mE}{\hbar^2}}\, \frac{m}{\hbar^2}\, dE$$

$$u = \int \frac{d\vec{k}}{4\pi^3}\, \varepsilon(\vec{k})\, f_{FD}(\varepsilon) =$$

$$= \int \underbrace{\frac{1}{\pi^2}\, \frac{m}{\hbar^2} \sqrt{\frac{2mE}{\hbar^2}}}_{g(\varepsilon)\ \equiv\ \text{density of states}}\, \varepsilon\, f(\varepsilon)\, d\varepsilon = \int g(\varepsilon)\, f(\varepsilon)\, \varepsilon\, d\varepsilon$$

$$n = \int g(\varepsilon)\, f(\varepsilon)\, d\varepsilon \qquad \underline{\text{etc}}.$$

The Sommerfeld expansion:

The above integrals have a general form of

$$\int_{-\infty}^{+\infty} H(\varepsilon)\, f(\varepsilon)\, d\varepsilon\,, \quad \text{where} \quad f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}$$

$H(\varepsilon) \to 0$ as $\varepsilon \to -\infty$, and diverges at most as a power law as $\varepsilon \to \infty$.

Define: $$K(\varepsilon) = \int_{-\infty}^{\varepsilon} H(\varepsilon')\, d\varepsilon' \quad ; \quad \frac{dK}{d\varepsilon} = H(\varepsilon)$$

Then,
$$\int_{-\infty}^{+\infty} H(\varepsilon)\, f(\varepsilon)\, d\varepsilon = \underbrace{K(\varepsilon)\, f(\varepsilon)\Big|_{-\infty}^{+\infty}}_{0} - \int K(\varepsilon) \left(+\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon$$

Consider $$K(\varepsilon) = K(\mu) + \sum_{n=1}^{\infty} \frac{(\varepsilon-\mu)^n}{n!} \left(\frac{d^n K}{d\varepsilon^n}\right)_{\varepsilon=\mu}$$ **(Taylor's series)**

So: $$\int_{-\infty}^{+\infty} H(\varepsilon)\, f(\varepsilon)\, d\varepsilon = \int_{-\infty}^{+\infty} \left[K(\mu) + \sum_{n=1}^{\infty} \frac{(\varepsilon-\mu)^n}{n!} \frac{d^n K}{d\varepsilon^n} \right] \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon$$

$\frac{\partial f}{\partial \varepsilon}$ is even in $(\varepsilon-\mu)$ $\Rightarrow$ only $n =$ even contribute to the above series].

$$\int_{-\infty}^{+\infty} H(\varepsilon)\, f(\varepsilon)\, d\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon)\, d\varepsilon + \sum_{n=1}^{\infty} \int \frac{(\varepsilon-\mu)^{2n}}{2n!} \left(\frac{d^{2n-1} H}{d\varepsilon^{2n-1}}\right)_{\varepsilon=\mu} \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon$$

$$\sum_{n=1}^{\infty} \int \frac{(\varepsilon-\mu)^{2n}}{2n!} \left(\frac{d^{2n-1} H}{d\varepsilon^{2n-1}}\right)_{\varepsilon=\mu} \left(-\frac{\partial f}{\partial \varepsilon}\right) d\varepsilon = \sum_n \left(\frac{d^{2n-1} H}{d\varepsilon^{2n-1}}\right)_{\varepsilon=\mu} \int_{-\infty}^{+\infty} \left(\frac{\varepsilon-\mu}{KT}\right)^{2m} (KT)^{2m} \left(-\frac{\partial f}{\partial \varepsilon}\right) \frac{d\varepsilon}{2n!}$$

$$= \sum_{n=1}^{\infty} \left(\frac{d^{2n-1} H}{d\varepsilon^{2n-1}}\right)_{\varepsilon=\mu} a_n\, (KT)^{2n}$$

with
$$a_n = \int \frac{x^{2n}}{2n!} \left(-\frac{d}{dx} \frac{1}{e^x+1}\right) dx$$

Hence: $$\int_{-\infty}^{+\infty} H(\varepsilon)\, f(\varepsilon)\, d\varepsilon = \sum_{n=1}^{\infty} a_n \left(\frac{d^{2n-1} H}{d\varepsilon^{2n-1}}\right)_{\varepsilon=\mu} (kT)^{2n} + \int_{-\infty}^{\mu} H(\varepsilon)\, d\varepsilon$$

(Sommerfeld expansion)

$$\longrightarrow \int_{-\infty}^{+\infty} H(\varepsilon) f(\varepsilon)\, d\varepsilon = \int_{-\infty}^{\mu} H(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(k_B T)^2 H'(\mu) + \frac{7\pi^4}{360}(k_B T)^4 H'''(\mu) + \theta\left(\frac{k_B T}{\mu}\right)$$

- $$u = \int_{-\infty}^{+\infty} d\varepsilon\, \underbrace{g(\varepsilon)\, \varepsilon\, f(\varepsilon)}_{H(\varepsilon)} = \int_{-\infty}^{\mu} g(\varepsilon)\cdot\varepsilon\, d\varepsilon + \frac{\pi^2}{6}(kT)^2 \left[g(\mu) + \mu\, g'(\mu)\right] + \theta($$

- $$n = \int_{-\infty}^{+\infty} d\varepsilon\, g(\varepsilon)\, f(\varepsilon) = \int_{-\infty}^{\mu} g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(kT)^2 g'(\mu) + \theta(T^4)$$

Let us consider first this second term; Take $g(\varepsilon) = 0$ if $\varepsilon < 0$:
then

$$n = \int_0^{E_F} d\varepsilon\, g(\varepsilon) = \int_0^{\mu(T)} g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(kT)^2 g'(\mu) + \cdots$$

$$= \int_0^{E_F} g(\varepsilon)\, d\varepsilon + g(E_F)(\mu - E_F) + \frac{\pi^2}{6}(kT)^2 g'(E_F) + \cdots$$

Hence

$$g(E_F)(\mu - E_F) = -\frac{\pi^2}{6}(kT)^2 g'(E_F)$$

$$\mu(T) \sim E_F - \frac{\pi^2}{6}(kT)^2 \left(\frac{g'}{g}\right)_{E_F}$$

$$\left(g \propto \varepsilon^{1/2} \quad g' \propto \frac{1}{2}\varepsilon^{-1/2} \quad g \propto \varepsilon^{1/2} \right)$$

$$\mu(T) \sim E_F - \frac{\pi^2}{6}(kT)^2 \frac{1}{2E_F}$$

$$\sim E_F\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_F}\right)^2 + \cdots\right]$$

Now, u:

$$u = \int_{-\infty}^{\mu} g(\varepsilon)\,\varepsilon\, d\varepsilon + \frac{\pi^2}{6}(kT)^2\left[g(\mu) + \mu\, g'(\mu)\right] + \cdots$$

$$= \int_0^{E_F} \varepsilon\, g(\varepsilon)\, d\varepsilon + \overbrace{(\mu - E_F)\, E_F\, g(E_F) + \frac{\pi^2}{6}(kT)^2 E_F\, g'(E_F)}^{0} +$$

$$+ \frac{\pi^2}{6}(kT)^2 g(E_F) + \cdots$$

$$= \int_0^{E_F} \varepsilon\, g(\varepsilon)\, d\varepsilon + \frac{\pi^2}{6}(kT)^2 g(E_F) + \cdots \; O(T^4)$$

$$u(T) = u_0 + \frac{\pi^2}{6}(kT)^2 g(E_F) + \cdots$$

$$c_v = \frac{du}{dT} = \underbrace{\frac{\pi^2}{3} k_B^2\, g(E_F)}_{\gamma}\, T$$

For free electrons: $g(E_F) = \frac{3}{2}\frac{n}{E_F}$

$$c_v = \frac{\pi^2}{2} k_B \cancel{T} \cdot \frac{k_B n T}{E_F}$$ → becomes a function of T

$$= \frac{3}{2} n k_B \cdot \frac{\cancel{\ } kT}{3 E_F}\pi^2$$

$$\frac{3}{2} n k_B \cdot \frac{\pi^2}{2}\frac{k_B T}{E_F}$$